Using peroxides for direct (reactive-extrusion) and indirect (compounding) upcycling of Polypropylene post-consumer waste

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I confirm, that going to press of this thesis needs the confirmation of the examination committee.

Affidavit

I declare in lieu of oath, that I wrote this thesis and performed the associated research myself, using only literature cited in this volume. If text passages from sources are used literally, they are marked as such.

I confirm that this work is original and has not been submitted elsewhere for any examination, nor is it currently under consideration for a thesis elsewhere.

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Danksagung

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Abstract

In 2019, polypropylene (PP) alone accounted for 19.4% of the European market and is one of the leading types of plastic used in various sectors. However, it is mainly used in products that are considered disposable consumer goods or are discarded after a single use. For this reason, topics such as recycling, circular economy or sustainability are present everywhere nowadays and are becoming increasingly important. This thesis aims to contribute and provide options for possible recycling or even upcycling of PP.

In mechanical recycling, PP tends to chain degradation, which can occur through thermo-oxidative processes but also in a shear-induced way. In this process, the molecular weight of PP is drastically deteriorated, which is significantly reflected in the viscosity. To circumvent this negative influence, the introduction of long-chain branching is a well-established method. This allows long side chains to be generated on the PP, thus not only improving the property portfolio, but even expanding it. These increase the melt stiffness and show strain-hardening behavior, which means that PP could be used in new areas of application.

In this thesis, the long-chain branching was carried out using different peroxides, which can be divided into different classes based on their chemical structure (symmetrical and asymmetrical), using a single-screw extruder. The mechanical properties of the individual modifications were analyzed by means of tensile tests (modulus of elasticity, yield strength and elongation at break) but also impact tests (impact tensile strength). In order to investigate the change in the melting properties, rheological measurement methods were used (dynamic rheology and MFR measurements). The final proof of the formation of long-chain branching on the PP and the associated formation/increase in melt stiffness was provided by the use of extensional rheological tests.

In general, the reactive extrusion was carried out at a temperature of 180 °C, slightly above the melting temperature of PP. However, in order to simulate industrial processes, the extrusion temperature was increased to 240 °C and the effect of temperature on the modification was investigated. Single and double extrusions were also carried out to analyses the effect of reprocessing already modified PP. As the choice of peroxides and their concentration play an important role in reactive extrusion, the change in concentration was determined using a concentration series. The direct modification of flakes of yoghurt cups

(post-consumer waste) was successfully carried out using a peroxide concentration of 200 mmol/kg PP. In addition to the direct introduction of long-chain branching, the indirect modification of virgin PP but also post-consumer PP (yoghurt cups, coffee capsules and buckets) was investigated. Already modified PP mixtures served as so-called "masterbatches", which were used as blending materials. An improvement in the mechanical and rheological properties was also achieved with this modification variant.

In addition, it was shown that PPs with different molecular weights, which are used in different areas, can be mixed with each other. For this purpose, blends (binary and quaternary) could be processed at a temperature of 180 °C, 200 °C and 240 °C and modified with Dimistryl peroxydicarbonate (20 mmol/ kg PP). By introducing the long-chain branching in the different blends, the mechanical properties could at least be kept constant or even increased compared to the non-modified blend mixtures. Furthermore, the melt strength of the modified blends could be clearly increased by the modification with peroxide. With regard to the recycling of different PP streams, these results facilitate the separation and further processing.

Besides the homopolymers, block copolymers of PP and filled PP systems (talc and glass fiber reinforced PP) were also investigated. Here, direct modification with Dimistryl peroxydicarbonate did not achieve the desired improvement in properties. In particular, the strain hardening could not be increased compared to the starting material. However, this limitation could be partially circumvented for the filled systems by using the "masterbatches" based on Dimistryl peroxydicarbonate and Dilauroyl peroxide. Further test series should follow in this regard by using the indirect method.

Kurzfassung

2019 hatte allein Polypropylen (PP) einen Anteil von 19.4 % am europäischen Markt und gehört zu den führenden Kunststoffsorten die in den verschiedenen Bereichen eingesetzt werden. Jedoch wird es vorwiegend in Produkten eingesetzt, welche als Wegwerf-Konsumgüter gelten oder nach dem einmaligen Gebrauch entsorgt werden. Aus diesem Grund sind heutzutage Themen wie Recycling, Kreislaufwirtschaft oder Nachhaltigkeit überall präsent und werden immer wichtiger. Diese Arbeit soll einen Teil dazu beitragen und Möglichkeiten für ein eventuelles Recycling oder sogar Upcycling von PP liefern.

Beim werkstofflichen Recycling neigt PP zum Kettenabbau, welche durch thermo-oxidative Prozesse aber auch in scherinduzierter Art auftreten können. Dabei wird das Molekulargewicht von PP drastisch reduziert, was sich in der signifikanten Abnahme der Viskosität zeigt. Um diese negative Beeinflussung zu umgehen ist die Einführung von Langkettenverzweigungen eine gut etablierte Methode. Dadurch können lange Seitenketten am PP generiert werden und somit das Eigenschaftsportfolio nicht nur verbessert, sondern sogar erweitert werden. Diese erhöhen nämlich die Schmelzsteifigkeit und zeigen ein dehnverfestigendes Verhalten wodurch PP in neuen Anwendungsgebieten eingesetzt werden könnte.

Die Langkettenverzweigungen wurden mittels verschiedenen Peroxiden, die sich in unterschiedliche Klassen an Hand ihrer chemischen Struktur (symmetrisch und unsymmetrisch) unterteilen lassen, unter der Verwendung eines Einschneckenextruders durchgeführt. Die mechanischen Eigenschaften der einzelnen Modifizierungen sind mittels Zugversuch (E-Modul, Streckgrenze und Bruchdehnung) aber auch Schlagzugversuchen (Schlagzugzähigkeit) analysiert worden. Um die Veränderung der Schmelzeeigenschaften zu untersuchen sind rheologische Messverfahren eingesetzt worden (dynamische Rheologie und MFR-Messungen). Der schlussendliche Nachweis zur Bildung von Langkettenverzweigungen am PP und der damit verbundenen Bildung/Erhöhung der Schmelzsteifigkeit lieferte der Einsatz der dehnrheologischen Untersuchungen.

Generell wurde die Reaktivextrusion bei einer Temperatur von 180 °C, wenig oberhalb der Schmelztemperatur von PP, durchgeführt. Um jedoch industrienahe Prozesse zu simulieren wurde die Extrusionstemperatur auf 240 °C erhöht und die Einwirkung der Temperatur auf die

Modifizierung untersucht. Dazu wurden auch einfach- und zweifach Extrusionen durchgeführt, um den Effekt der Wiederverarbeitung von bereits modifizierten PP zu analysieren. Da bei der Reaktivextrusion neben der Wahl der Peroxide auch die Konzentrationen dieser eine wichtige Rolle spielen, wurde die Veränderung der Konzentrationen an Hand einer Konzentrationsreihe ermittelt. Die direkte Modifizierung von Joghurtbechermaterial (post-consumer waste) konnte mittels einer Peroxidkonzentration von 200 mmol/kg PP erfolgreich vollzogen werden. Zusätzlich zu der direkten Einführung von Langkettenverzweigungen wurde die indirekte Modifizierung von reinem PP aber auch post-consumer PP (Joghurtbecher, Kaffeekapseln und Kübeln) untersucht. Dabei dienten bereits modifizierte PP Mischungen als sogenannte „Masterbatches", welche als Blendmaterialien eingesetzt worden sind. Auch bei dieser Variante der Modifizierung konnte eine Verbesserung der mechanischen als auch rheologischen Eigenschaften erzielt werden.

Zusätzlich konnte gezeigt werden, dass PPs mit unterschiedlichen Molekulargewichten, welche in verschiedenen Bereichen Anwendung finden, sich miteinander mischen lassen. Dazu konnten Blends (binär und quartär) bei einer Temperatur von 180 °C, 200 °C und 240 °C verarbeitet und mit Dimistryl peroxydicarbonat (20 mmol/ kg PP) modifiziert werden. Durch die Einführung der Langkettenverzweigungen in den verschiedenen Blends konnten die mechanischen Eigenschaften zumindest konstant gehalten oder sogar gesteigert werden im Vergleich zu den nicht modifizierten Blendmischungen. Weiterst konnte die Schmelzesteifigkeit der modifizierten Blends eindeutig gesteigert werden durch die Modifizierung mittels des Peroxids. Hinsichtlich Recycling von unterschiedlichen PP-Strömen bringen diese Ergebnisse eine Erleichterung bezüglich der Trennung und der weiteren Verarbeitung mit.

Neben den Homopolymeren sind auch zusätzlich Block-copolymeren von PP und gefüllte PP-Systeme (Talkum und glasfaserverstärktes PP) untersucht worden. Hier konnte durch die direkte Modifizierung mittels Dimistryl peroxydicarbonat nicht die gewünschte Verbesserung der Eigenschaften erreicht werden. Insbesondere die Dehnverfestigung konnte nicht gesteigert werden im Vergleich zum Ausgangsmaterial. Diese Limitierung konnte jedoch durch die Verwendung der „masterbtaches" basierend auf Dimistryl peroxydicarbonat und Dilauroyl peroxid zum Teil für die gefüllten Systeme umgangen werden. Mittels der indirekten Methode sollten diesbezüglich noch weitere Versuchsreihen folgen.

Preface

The work in this thesis is part of larger project, which is being supported by the Austrian Forschungsförderungsgesellschaft (FFG). The project Recycling Healig polyOlefins (RHO) was founded as a network for knowledge exchange and knowledge gain in the field of recycling possibilities of polyolefin.

The doctoral thesis based on the three first author journal articles listed below.

Publication I

Influence of Different Types of Peroxides on the Long-Chain Branching of PP via Reactive Extrusion

S. Stanic, G. Gottlieb, T. Koch, K. Schmid, S. Knaus and V.M. Archodoulaki

Polymers 2020, 12 (10), 886

https://doi.org/10.3390/polym12040886

Publication II

Upcycling of polypropylene with various concentrations of peroxydicarbonate and dilauroyl peroxide and two processing steps

S. Stanic, T. Koch, K. Schmid, S. Knaus and V.M. Archodoulaki

Journal of Applied Polymer Science (2021): 50659

https://doi.org/10.1002/app.50659

Publication III

Improving Rheological and Mechanical Properties of Various Virgin and Recycled Polypropylenes by Blending with Long-Chain Branched Polypropylene

S. Stanic, T. Koch, K. Schmid, S. Knaus and V.M. Archodoulaki

Polymers 2021, 13 (7), 1137

https://doi.org/10.3390/polym13071137

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List of Abbreviations and Symbols

PP	Polypropylene
HMS-PP	High melt strength polypropylene
LCB	Long Chain Branching
LCB-PP	Long Chain Branching polypropylene
PET	polyethylene terephthalate
PE	Polyethylene
NAFTA	North American Free Trade Agreement
OECD	Organization for Economic Co-operation and Development
EU	European Union
CO_2	Carbon dioxide
NO_x	Nitrogen oxides
SO_x	Sulfur oxides
3D	three-dimensional
HP	Homopolymer
ICP	Impact Co-Polymer
RCP	Random Co-Polymer
BOPP	Biaxial oriented polypropylene
HDPE	High density polyethylene
EPR	Ethylene-propylene rubber
SEP	Styrene-ethylene-propylene rubber
HALS	Hindered Amine Light Stabilizers
EP(D)M	Ethylene-propylene-(diene)-rubber

MFR	Melt Flow Ratio
REACH	Registration Evaluation Authorization of Chemicals
PODIC	Peroxydicarbonate
DSC	Differential Scanning Calorimetry
T_m	Melting temperature
Tc	Crystallization Temperature
ΔH_m	Melting enthalpy
M_w	Molecular weight
MMD	Molar mass distribution
NBR	Nitrile butadiene rubber
SBR	Styrene butadiene rubber
EVA	Ethylene vinyl acetate copolymer
E_t	Elasticity modulus
ε_B	Elongation at break
a_{tN}	Tensile impact strength
G´& G´´	Storage and Loss modulus
ω	Angular frequency
SER	Sentmanat Extensional Rheometer
$\dot{\varepsilon}$	Strain rate
LVE	Linear viscoelastic envelope
χ	Strain Hardening Coefficient

1. Introduction

1.1. Aim of this work

In recent years, the topic of recycling plastics has become very important in society as well as in industry and has been promoted by specific regulations or bans (ban on plastic bags or straw helmets). Generally, it seems that plastics suffer from a bad image and the advantages of this material are suppressed, as everyone is confronted with pictures of littered beaches and dead sea animals in the media. The increase in plastic waste due to the rising consumption of plastic goods has also contributed to the creation of topics such as circular economy and sustainability with promising goals.

The aim of this work was to investigate the long-chain branching potential of peroxides in a direct (reactive extrusion) and indirect (compounding) way on virgin polypropylene as well as on recyclates and thus to generate a possibility for potential recycling. Long chain branching by means of reactive extrusion in melt has been established as a suitable method and has shown that slight changes in the chemical structure contribute to changing the rheological, mechanical and thermal properties of PP. In order to investigate these changes in the materials used in this work (virgin PP and recycled PP), they and their modifications will be characterized by the use of rheological (dynamic rheology and extensional rheology), mechanical (tensile testing and impact testing) and thermic (differential scanning calorimetry) measurement methods.

At the beginning of this work, a suitable system for introducing long-chain branching should be found. On the one hand, grafting of monomers in combination with peroxides could be used for this. Through the preliminary work of Kamleitner et al. [1], first successful introductions of long-chain branching had already been carried out by grafting styrene (480 mmol/kg PP) and using 2,5-dimethyl-2,5-di-(tert-butylperoxy)-hexane (20 mmol/kg PP). In a first step, to prevent possible risks (toxicity) from the use of styrene as a monomer, biocompatible monomers such as vinyl compounds or oxazoline should be used as a substitute.

In addition, various peroxides (Di-tert-butyl peroxide; Bis(1-methyl-1-phenylethylene) peroxide; tert-Amyl peroxy-2-ethylhexylcarbonate; tert-Butyl peroxy-2-ethylhexylcarbonate; tert-Butyl peroxyisopropyl-carbonate; Dimistryl peroxydicarbonate; Dilauroyl peroxide) with different properties should be investigated in principle and possibly known peroxides that are toxic, mutagenic or toxic for reproduction should be replaced by peroxides with lower toxicity. Therefore, five peroxides (tert-Amyl peroxy-2-ethylhexylcarbonate; tert-Butyl peroxy-2-ethylhexylcarbonate; tert-Butyl peroxyisopropyl-carbonate; Dimistryl peroxydicarbonate; Dilauroyl peroxide) which differ in their chemical structure (symmetric and asymmetric) but also in their reactivity are investigated. **(Publication I)**

During the modification in the melt by means of reactive extrusion, the temperature and the choice of the peroxides play an important role and can be considered as limiting factors for the long-chain branching behavior. These influencing factors, such as the effect of the temperature on the degradation behavior of PP, should be investigated by varying the temperature from 180 °C, which is known from the literature, and an increased temperature of 240 °C, which simulates process conditions in industry. **(Publication I)**

However, not only the branching behavior depends on the temperature, but also the thermo-oxidative degradation of PP is more advanced at higher temperatures. From the peroxide side, the choice of concentration also plays an important role in reactive extrusion. Since the formation of radicals during the reaction leads to the degradation of the PP through thermal and mechanical loading, the concentration of peroxides is also important. For this reason, the concentrations for the two best possible peroxides and their influence on the degradation behavior as well as their branching behavior should be analyzed on the basis of a concentration series (10, 20, 100 and 200 mmol/kg PP). It is also useful to investigate the multiple processing of these modified materials and to compare the behavior between single and double extrusion, i.e. modification and processing step, in order to achieve potential recycling possibilities. **(Publication II)**

In addition to the homopolymers, the branching behavior of PP block copolymers used in the various pipe applications and the resulting changes in consistency were also to be investigated. Three materials (Eltex Tub350-HM00, Total PPC 16040 and Borealis PP BA 202E) with high molecular weight should be analyzed.

The question arose whether there is another possibility to change the properties of PP not only by direct modification by using peroxides, but also by producing blends that contain long-chain branched material as a second component. For this reason, various blending materials (linear PP, HMS-PP, LCB-PPs) were used in this work and should be characterized for their effects on virgin PP as well as on PP post-consumer waste (flakes of yoghurt cups, flakes of buckets and flakes of coffee caps) and their property changes. **(Publication III)**

In order to simulate recycling of post-consumer waste PP, flakes of yoghurt cups should be used for this purpose. Their properties and the property changes due to the introduction of long-chain branching through the direct use of peroxides during reactive extrusion should be investigated and enable a potential upcycling of PP post-consumer waste by improving the properties. **(Publication II)**

With regard to the recycling of PP and its wide product range (pipes, films and everyday consumer products), the question arose as to how PPs with different molecular weights can be mixed with each other and thus facilitate recycling and further processes. The investigations were to be carried out using blends (binary and quaternary) of different virgin PPs (PP HA104E, PP HC600TF, PP HD601CF and PP HF 700SA) at different extrusion temperatures (180 °C, 200 °C and 240 °C). The introduction of LCB should be done by using Dimistryl peroxydicarbonate (20 mmol/kg PP) and the associated changes in the respective blends should be investigated.

1.2. Plastic – Material of a new era

The global production of plastics has experienced very strong growth in recent decades. The continuous growth could also be observed in recent years. In 2015, the annual production of plastics was 322 million tons/year, in 2017 it was already 348 million tons/year, and in 2019 production has risen to 368 million tons/year. A continuous trend can be seen with an increase of about 10 million tons/year. If this trend continues, global plastic production may reach 500 million tons/year by 2030. For this reason, plastic is already being touted as the material of the 21st century.[2-4]

A wide range of plastics and their products are now everywhere and in every situation for a large number of people. Basically, it is impossible to imagine life today without plastics, even if you take a look at your own everyday life. To name just a few examples, there is the PET water bottle, the yoghurt pot made of polypropylene or polystyrene, the sole of running shoes made of polyurethane and so on. So one could list countless more examples in which plastics play an important role in our lives. But the question arises: How did plastics and their products become so popular?

For more than 100 years' various developments have taken place for the production of polymers and served as substitutes. One example is the celluloid invented in the nineteenth century to artificially replace ivory, which was widely used until then. From today's point of view, the first technically viable plastic was vulcanized natural rubber, which was used as a substitute for ebony.[5] The history goes from the beginning of the 20th century from Bakelite, which was the first fully synthetic plastic produced by Leo Hendrik Baekeland, to polystyrene, polyamide or better known as nylon, to finally the polyolefines of the early 1950s.[5]

During this period, in the 1920s, the groundbreaking work of the later Nobel Prize winner Herman Staudinger laid the foundation for the understanding of these high molecular substances. Since then, polymer science has developed into a highly relevant technical and industrial field of work, which has greatly advanced the history of plastics.[6] From 1950 the production of plastics really took off. While the production volume still amounted to about 2 million tons per year, in 2019 the worldwide production arises to 368 million tons per year. Especially after the second oil crisis in 1979/1980, the production of plastics increased rapidly and thus contributed to the fact that plastics have a higher production volume worldwide than crude steel or aluminum.[4, 7, 8]

Such facts clearly demonstrate the importance of plastics and the important role they play in our society. Although Europe is only in third place in terms of global production with 16 %, behind NAFTA (North American Free Trade Agreement) with 19 % and the sole leader China with 31 %, which has also seen the most growth in recent years.[4] In Figure 1 is the global share of plastic production demonstrated.

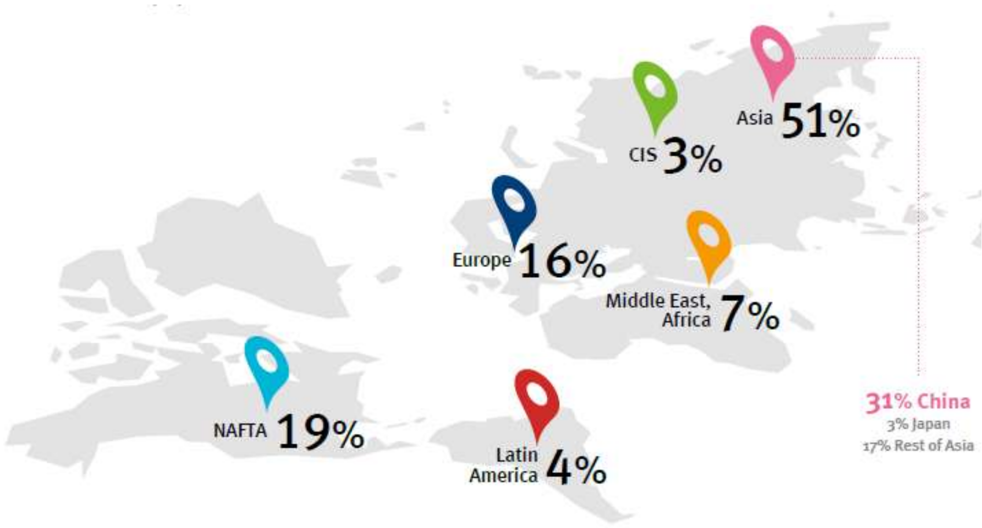


Figure 1: Global share of plastic production [4]

The three largest sectors in Europe where plastics are used are packaging (40%), building and construction (20%) as well as the automotive industry (10%). Smaller applications include electronic, agricultural sector, sports and medical devices. For these different applications and areas, plastics can be divided into different polymers. Seven polymers or plastic types alone represent more than 80 % of the European plastics market, represented in Figure 2.[4]

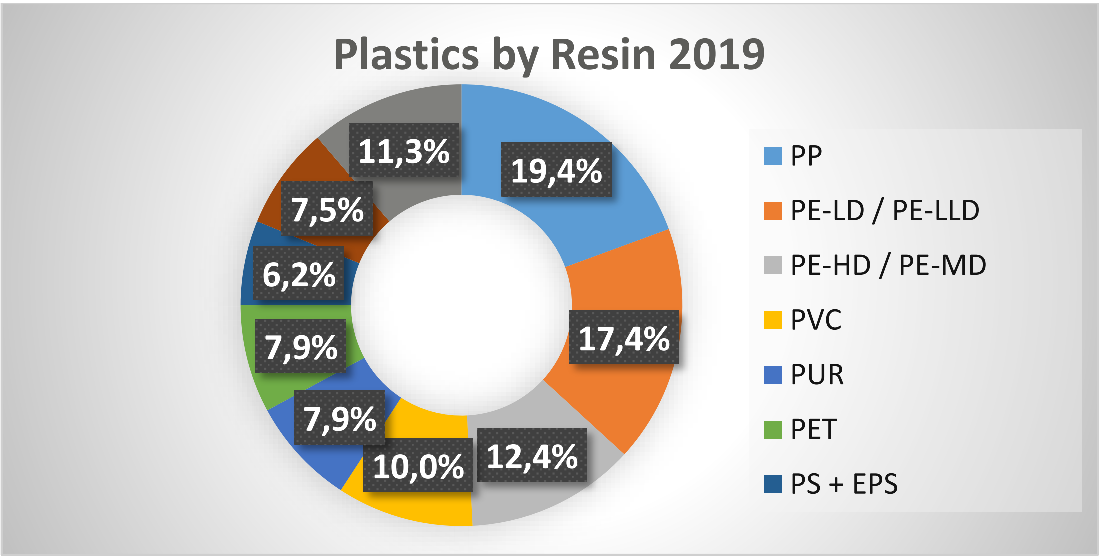


Figure 2: Listing of the different plastics by type of resin in 2019 [4]

Considering all types of PE together, this corresponds to almost 30 % of the European market and thus represents the largest group of plastics. PP follows with 19.4 % and is the second largest group of plastics. These two groups of PP and PE are thus the most important polymers for the production of plastics on the European market.[4]

The production of the various plastics was achieved exclusively with a total proportion of 99 % from fossil fuel-based raw materials.[9] This results in an average annual consumption of about 4-5 % of the global oil and gas production needed for the production of plastics worldwide.[10, 11] For this reason, a small sector of biologically based and biodegradable plastics has been established in recent years, compared to the previous plastics production, with about 4 million tons per year (and rising).[8] However, such "novel" plastics are still niche products and one must continue to work on new solutions to ensure the future of the material of the 21st century. Because bans or the ban on this versatile material will not solve the problems, especially environmental problems which are currently always mentioned in this context.

1.3. Problems and solutions for a sustainable use of plastics

Since the start of mass plastic production in the 1950s and the associated steady growth in the manufacture of a wide variety of plastics, over 8 billion tons of plastics have been produced and 5 billion tons have ended up in landfills or in the environment.[8] In the last few years, various problems have become apparent being caused by the production and use of plastic products. The plastic pollution has quickly gained political attention and is one of the biggest challenges of our time. It is well known that the conventional plastics are not easily degradable or cannot be degraded in the conventional environment and therefore they remain in the landscape for several years.[12] But not only the topic of landscape pollution but also the pollution of the oceans has become very important in the last years.[13] The negative impacts of marine pollution include the pressure on biodiversity and ecosystem functions, impacts on ecosystems such as coral reefs, health effects on various organisms and animals, but also that plastics in general, and micro-plastics in particular, can act as sinks for toxic chemicals.[14-22] However, Asian countries such as China, Indonesia, Vietnam and Sri Lanka are particularly responsible for marine pollution.[23, 24] However, these countries are used by the OECD countries to export their plastic waste to these countries.[25] Meanwhile these importing countries are overstrained and send the plastic waste back or like China they stop the introduction of plastic waste by banning imports.[26, 27] The import ban imposed by China in January 2018 has resulted in a chaos in the global recycling of plastic waste.[28] China is the largest importer up to that date, accounting for 45 % of global plastic waste between 1992 and 2016.[25] As a result of this ban, many regions of the world, including the European Union (EU), have had to consider new strategies for dealing with plastic waste in the future.

To this goal, the EU Commission has launched a voluntary commitment to promote the market for recycled plastics at the end of 2018. This includes the following objectives:[3]

- Recovery and recycling of 60 % of all plastic packaging until 2030
- 100% reuse, recycling or energy recovery all plastic packaging up to 2040
- Collection of more recycling-related data
- Prevent unintentional leakage of plastics into the environment
- Establish eco-design guidelines for packaging by 2020
- Support for the introduction of quality standards for separation of plastics

In 2015 the EU presented for the first time its ambitious Action Plan for Circular Economy, which contains a wide range of measures, including a binding landfill target to reduce landfill to a maximum of 10 % of municipal waste by 2035. This is intended to create a closing loop in which plastic waste is reused, thus creating sustainability for plastic as a material. Since 2014, the recycling rate of post-consumer waste has surpassed the landfilling rate and has doubled in the period from 2006 to 2018. Also the export of plastic waste from the EU decreased by 39 % in two years from 2016 to 2018.[3]

Recycling thus contributes to reducing the landfilling of plastics and the associated environmental problems such as contamination of soil, air and water bodies. In addition, the recycling of plastics helps to reduce oil consumption and CO_2 emissions. In principle, recycling is about completely or partially reusing the actual product after the end of its useful life, regardless of whether it is plastics, paper, metal, and so on.

There are generally four different types of recycling for plastics, which are illustrated in the following Figure 3:

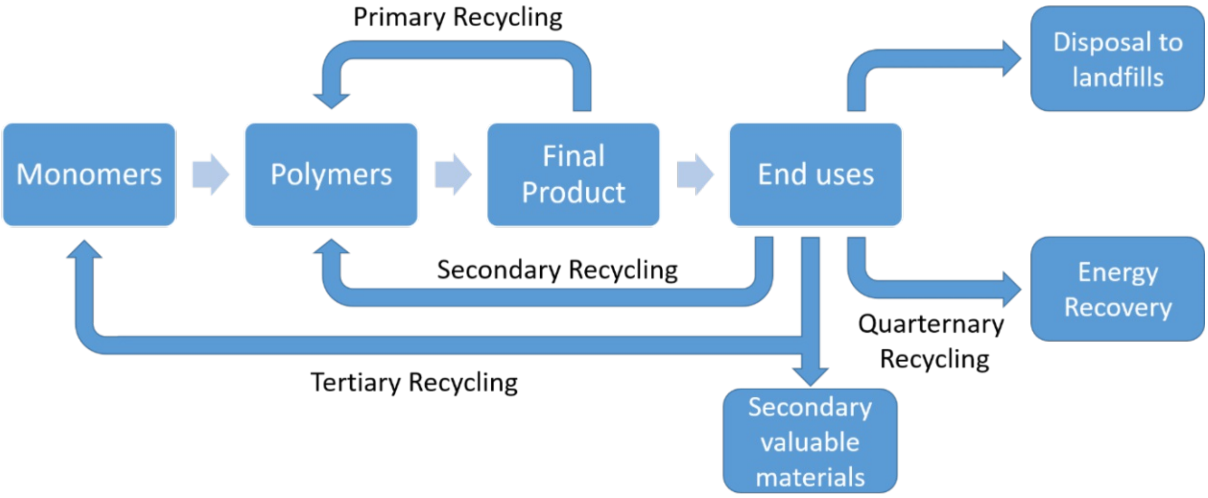


Figure 3: Recycling methodes of plastics [29]

- Primary recycling

This recycling process is a closed-loop process in which the newly produced material has the same or similar properties as the input material.[30, 31] The scrap or waste to be recycled is mixed with virgin material to ensure product quality or it is reused as a second class material (down cycling).[32] The process itself is very simple but the prerequisite is that the waste is sorted by type and that there is no contamination by other materials/plastics.[33]

- Secondary recycling

This is a widespread recycling process and, like primary recycling, belongs to mechanical recycling.[34] Due to the mechanical stress, the starting material is converted into a less demanding product by damage during the recycling process.[32] Two different approaches are described for this process. One is to separate the plastics from their impurities, and the other is to separate them into a generic form and then recycle them into products made from virgin material. The other is to separate the plastic from its impurities but re-melt it without separation.[35] Secondary recycling includes various methods of recycling (such as extrusion, injection molding, blow molding, etc.).[36] In order to carry out this type of recycling, some processing steps must be followed and are usually: cutting or crushing, separation of impurities, floc separation by flotation, granule production, pre-washing followed by drying, collection of the product and storage.[31, 32]

- Tertiary recycling

For the two previous processes, a certain purity is a prerequisite for the respective process to be used. This is sometimes a difficult task as most municipal waste consists of heterogeneous components. Especially in secondary recycling, the inhomogeneity of municipal waste makes it difficult to recycle.[30]

Tertiary recycling contributes to energy sustainability in contrast to primary and secondary recycling. This is because the basic idea here is to recover the raw material from which the plastic was once made. In this case, petroleum-based products.[31] This recovery is called the depolymerisation process, with chemical recycling (solvolysis) and thermal recycling (thermolysis) being the main types of tertiary recycling. In addition, pyrolysis, cracking, gasification and chemolysis are among the most important methods of tertiary recycling.[35]

- Quaternary recycling

Another method of recycling is this variant, which deals with the incineration of material or waste.[37] This recycling method is therefore a final variant like the landfilling of plastic waste. Basically, this variant is not a recycling process in the classical sense, because the material is not processed for reuse but is energetically recycled. This means that quaternary recycling does not result in a closed cycle and is also referred to as a type of waste treatment method.

However, quaternary recycling is the more effective way of waste disposal. As also shown in the figure, the number of this method has increased significantly in recent years, which is connected to the fact that the efficiency of new incineration plants has increased significantly.[38] This is to significantly reduce the volume of waste and to generate energy through the incineration of the waste. Most plastics have a very high calorific value, making this type of recycling very efficient.[39]

However, the incineration of waste creates a number of environmental problems, mainly the emission of certain air pollutants such as CO_2, NO_x and SO_x. It is also known that incineration produces volatile organic compounds (VOCs), smoke (particulate matter), particle-bound heavy metals, polycyclic aromatic hydrocarbons (PAHs), polychlorinated dibenzofurans (PCDFs) and dioxins.[32] These can all be controlled by various filters or by adding activated carbon or ammonia to the combustion chamber.[40] However, emissions are still a major problem with this variant. Furthermore, it only makes sense to choose this variant if the other preceding recycling methods cannot be used.

With these in literature known recycling processes and with the legal requirements of the various governments as well as the EU, plastic waste has emerged as a new resource and has already established itself in many markets like building & construction, packaging, agriculture and many others. In 2018, 5 million tons of plastic recyclates were 80 % recycled within the EU to produce new products.[4] There are numerous innovative approaches on how this "new raw material" can best be used, such as:

- Plastic roads:

To prevent plastic waste from ending up in the oceans or landfills, melted plastic products are used in road construction. MacRebur is a pioneering company that uses only single-use plastics for road construction. They are active in various sectors such as roads, car parks, private driveways and so on. For one ton of their bitumen mix they need 80,000 plastic bottles and for one kilometer of road the equivalent of 740,541 plastic bags are recycled.[41, 42]

- Building blocks from plastic bottles:

The so-called Ecobricks are plastic bottles filled to a certain density with used, clean and dry plastic to make a brick that can be used again and again. They are used to build furniture, garden rooms or even houses with these bricks. Various materials can be filled into the bottles, including non-biological, non-recyclable materials.[43]

- Street furniture from the 3D printer:

At The New Raw, plastic waste is used to make new types of furniture from the 3D printer, which can already be found in a wide range of cities in Europe. The basic idea behind it was to ensure a closed material cycle and to use additive manufacturing processes for a more sustainable future.[44]

- Oil from plastic waste:

With OMV's ReOil project, another idea for using plastic waste has emerged in recent years. Since plastics are made from crude oil, they can also be reused as a source of crude oil. In this process, the plastic waste is melted at 400°C and then vaporized into gas. This leads to depolymerization in which the molecular chains of the polymers are broken up, which are then selectively polymerized again into smaller chains in further chemical processes.

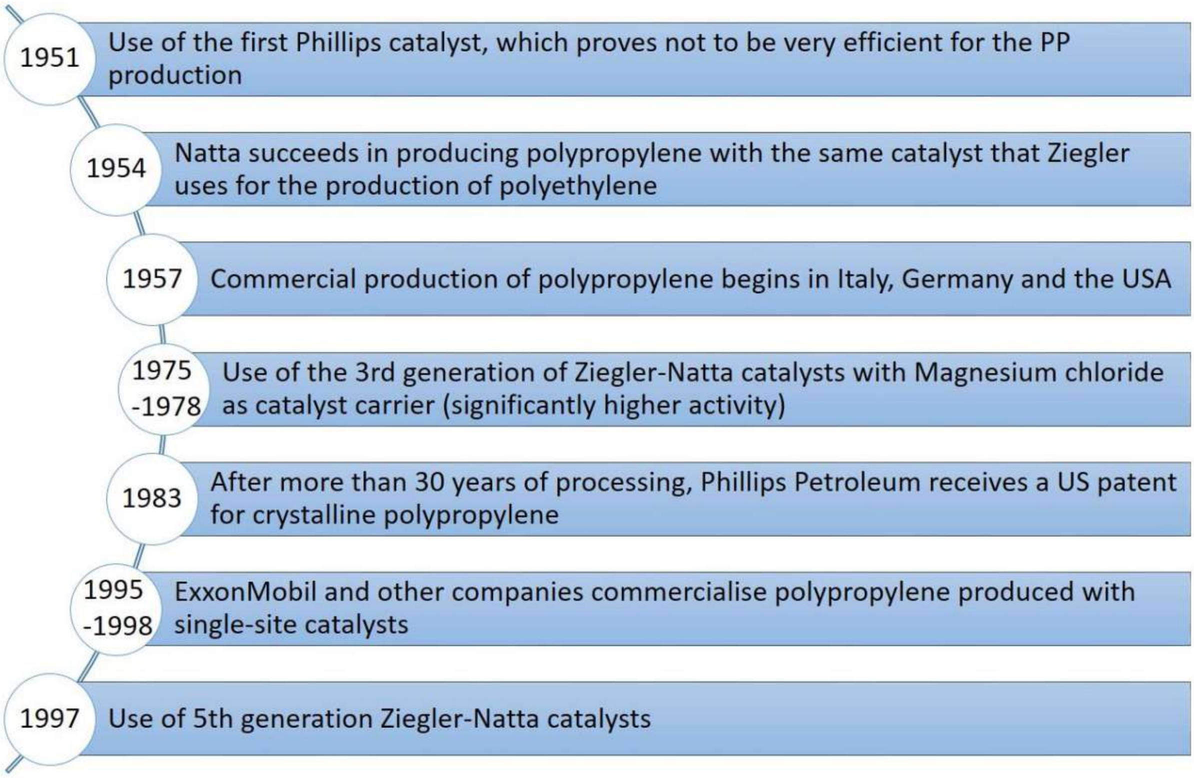
This means that 100 kg of plastic waste can currently be converted into 100 liters of crude oil per hour. In the near future, there will be another plant that will convert up to 2000 kg of waste per hour into valuable crude oil in order to shrink the waste mountains.[45]

2. Material

2.1. Polypropylene in General

Polypropylene is everywhere these days and is used in a wide variety of industries. Next to polyethylene, it is the most widely used plastic of our time and has shown a very high average annual growth rate in recent decades, even during crisis.[46]

Polypropylene was first mentioned in its crystalline form in the 1950s and is no longer comparable with today's production of the plastic granulate. The historical course and the milestones achieved in the production of PP are briefly listed in the following Figure 4 and should give a rough overview of what has happened in this field over the last decades.[47]



1951 Use of the first Phillips catalyst, which proves not to be very efficient for the PP production

1954 Natta succeeds in producing polypropylene with the same catalyst that Ziegler uses for the production of polyethylene

1957 Commercial production of polypropylene begins in Italy, Germany and the USA

1975 -1978 Use of the 3rd generation of Ziegler-Natta catalysts with Magnesium chloride as catalyst carrier (significantly higher activity)

1983 After more than 30 years of processing, Phillips Petroleum receives a US patent for crystalline polypropylene

1995 -1998 ExxonMobil and other companies commercialise polypropylene produced with single-site catalysts

1997 Use of 5th generation Ziegler-Natta catalysts

Figure 4: The historical development for the production of PP [47]

As can be seen from the historical development, the choice or technical development of the catalyst is the decisive criterion for the greatest possible productivity in the production of PP. Today, 40-70 kg of PP can be produced per g of catalyst, whereas in the early days of PP production 1-2 kg per g of catalyst was achieved.[47, 48]

During the production of PP, i.e. the polymerization of propylene, different enantiomers can occur and depending on whether the stereochemistry of the C_2 atom is regularly randomly arranged, different stereoisomers can be produced. These are ultimately referred to as isotactic, sydiotactic or atactic PP. In isotactic PP, the tertiary carbons are all configured in the same way, in syndiotactic PP there is an alternating configuration, while in atactic PP there is no regular arrangement of the methyl group.[49] The schematic structure of these three different variants is shown in the following Figure 5.

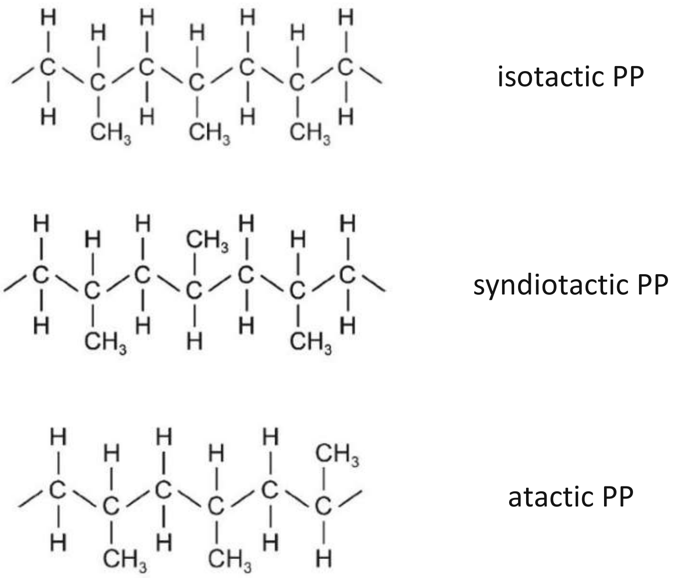


Figure 5: Schematic Structure of the different stereoisomers of PP [48]

The most important types of commercially available and thus most widespread PP on the plastics market are the homopolymer polypropylene (HP) with the largest share of the market, followed by the impact copolymer polypropylene (ICP) and the random copolymer polypropylene (RCP).[47]

- Homopolymer Polypropylene (HP)

Homopolymer is produced in a wide variety of reactors using catalysts, in which the monomers polymerize stereo specifically to form polymer chains that can be crystallized. The extent to which crystallization takes place depends on various conditions. HP has both crystalline and non-crystalline regions and is therefore also considered a two-phase system. The non-crystalline or amorphous areas consist of isotactic and atactic PP, whereby the isotactic PP is crystallizable and gradually crystallizes until the limit is reached.[46]

- Random Copolymer Polypropylene (RCP)

RCPs actually consist of an ethylene-propylene copolymer, which is copolymerized in a reactor and contains up to 7% ethylene. The ethylene component significantly alters the properties, resulting in thermoplastic products that exhibit slightly better impact properties, improved clarity, reduced haze, lower melting point or increased flexibility. The incorporated ethylene proves to be a defect in the chain regularity of the PP, which inhibits the crystallisability of the chain. The amount of ethylene incorporated into the chain is usually determined by the balance between thermal, optical and mechanical properties.[46]

- Impact Copolymer Polypropylene (ICP)

ICPs are mixtures of HP and RCP and have a total ethylene content of 6-15 wt%. They are mainly used in applications at cryogenic temperatures where they show an increased impact resistance. The RCP portion of the ICP has an ethylene content of about 40-65 % and is referred to as the rubber phase.[46] A well-known example of this is ethylene-propylene copolymer (EPR), which is added to isotactic PP as a blend material to increase its properties.[50-52] The impact strength of the ICP product is determined not only by the rubber content, but also by the size, shape and distribution of the rubber particles, shape and distribution of the rubber particles in the ICP product. The higher the rubber content of the ICP product, the higher the impact strength. However, this is done at the expense of the stiffness (modulus of elasticity) of the product.[46]

2.1.1. Production and characteristics

The pioneering prerequisites in the last decades were the constant further development of the catalysts which are so important for the production of PP, which made it possible for it to become the mass plastic it is today. In order to cover and guarantee this high demand for the different types of PP, a multitude of production processes for the polymerization of PP were developed. The most important polymerization processes are listed in the following points.

- Slurry (Suspension) Processes

This process was used in the early manufacturing days of polypropylene. The temperature was between 50 and 80 °C and hexane was used as a solvent for the catalyst but also for PP. This resulted in a suspension in which the atactic PP was present in dissolved form and the isotactic in precipitated form. The proportion in this discontinuous process was very large and amounted to over 30 %. In addition, a post-treatment was needed to remove the residue from the catalysts used in order to avoid corrosion of the equipment. This process turned out to be very equipment intensive and expensive, which meant that it was quickly replaced by other processes in the years to come.[47]

- Bulk (“Liquid Pool”) Process

The polymerization was carried out in liquid PP and is known as the bulk or liquid pool process. It was first used in the 1960s and is very similar to the slurry process. However, no solvent is needed and the temperature is 45 - 80 °C for polymerization. Stirred tanks or autoclaves are used for production, but pipe reactors have also been used for this process.[47]

- “Loop Slurry” Process

This is a continuous process operated at a temperature of 70 - 90 °C without any solvent. As the polymerization is carried out in a jacketed reactor in fast circulating liquid propylene, this process could also be considered as a combination of the slurry and bulk process. However, the reactor in which the polymerization takes place is the big difference. Here, a series of tubular reactors, up to 8 "legs", are used, which can increase the rate of this process. Since the construction resembled several loops, Chevron Phillips called this process a loop slurry process, since these loops offered a higher surface area and thus the reaction heat could be better transported away.[47]

- Gas phase Process

Various gas phase processes have been developed and used for more than 40 years. Here, too, no solvent or diluent is used and the temperature of the polymer satiation is between 60 and 80 °C. The individual processes differ in the reactor configuration, the catalysts and the way in which the required components are mixed. Although almost exclusively supported Ziegler-Natta catalysts are used, the catalysts are produced according to different schemes and differ considerably in their composition. Since new processes of this kind use highly stereospecific catalysts, it is no longer necessary to remove the atactic PP.[47] Although they are different in terms of composition, the polymerization in each method takes place in gaseous propylene without other solvents. The propylene gas functions as a reactant and the heat of polymerization is removed with the excess gas, which is returned to the reactor after cooling. The mechanical excitation can be achieved e.g. by the high flow velocity of the gas or stirred vessels depending on the type of reactor. The most important processes are the UNIPOL process, which is also used for PE, the Lummus-Novolen process and the process known today as the Innovene PP process.[47]

- Solution Process

The big difference between the solvent process and the processes described up to that point is the operating temperature of over 100 °C. The process, which was already classified as obsolete, is still used commercially today for atactic PP.[47]

2.1.2. Applications of Polypropylene

Due to the impressive properties of PP, such as excellent chemical resistance, low cost, low density, very good mechanical properties, acceptable melting point, passable rigidity, among others, it can be used in a wide range of applications. This means that it can be assumed that PP is part of our daily lives because it is so versatile. However, there are key areas where it is predominantly used. These include fibers and fabrics, strapping, films, sheet/thermoforming, injection molding, blow molding, automotive and so on.[46]

For fibers, there are various applications such as slit film, staple fibers, nonwovens and monofilaments. Slit film finds its main application in carpet backing, displacing jute fibers due to its better water resistance. Slit films are also found as binding yarns, tarpaulins, mats, grids for erosion control and geotextiles for stabilizing soil layers. Nonwovens are the most common single fiber application for PP. For example, spun bonded nonwovens are strong, while melt-blown nonwovens are soft. However, these nonwovens are often used by combining two types. Monofilaments are made by extruding PP through a film with many small holes and then quenching the monofilaments in a water bath that cools the fabrics. Twisted bundles of monofilaments result in applications such as ropes, twine and fishing nets that are strong and moisture resistant, making them ideal for marine use.[46]

PP films are produced by extrusion processes that can produce a thickness of less than 10 mils, equivalent to 254 µm, and are used for food, tobacco and clothing, among other applications. There are two main classes of film. One is cast film and the other is oriented film. Cast films are converted into products such as bags, films, sheet protectors, adhesive tapes and self-adhesive labels. Bi-axially oriented polypropylene film (BOPP) is another type of film made by extruding the plastic through a round die followed by expansion cooling. The main applications for BOPP films are flexible packaging, with snack packaging being the main application. An opaque film is a special type of BOPP used for packaging products such as candy, soaps, and labels on soft drink bottles.[46]

Injection molding offers a wide range of products and is therefore a popular process for a variety of PP products. It ranges from consumer products such as injection molded toys to medical applications such as disposable syringes. Household applications such as storage systems, household appliances, sports equipment, hand tools, paint brushes and garden furniture, as well as screw caps for bottles and jars are some examples of closure applications made from PP.[46]

When considering bottles, jars, shampoo bottles and lubricant/pesticide containers, these are manufactured using the blow molding process. There are three types of blow molding: extrusion blow molding, where the PP bottles produced are hot fillable and have good contact clarity; injection blow molding to produce relatively small bottles and wide-mouth jars; and injection stretch blow molding to produce biaxial oriented jars and bottles with greater clarity, strength and barrier properties.[46, 53, 54]

Another important sector for products made of PP is the automotive sector. As PP is considered the lightest thermoplastic due to its low density of 0.9 g/ml, much of the plastic in new cars is made of PP, as car manufacturers tend to reduce the overall weight of their cars to save customers some fuel consumption. Interior trim and some exterior components are also made entirely of PP or PP compounds such as doors, pillars, side panels and consoles. But in the meantime, exterior parts made of PP can also be found (air vents, side trims, sill trims and radiator grilles).[46]

This is only a small list of the various areas in which PP is used and it is clear that the variety of products made of PP knows no bounds. Highly technical products are made from PP, but also products that are used for short periods of time. Especially in the case of packaging materials, which account for almost half of the European demand, one can speak of a single use product, which ultimately raises the question of sustainability, but also the issue of recycling such products appears even more important.[55]

2.1.3. Recycling of Polypropylene

In addition to the outstanding properties of PP, it is the negative properties of the material that come into play during recycling. In order to recycle products made of PP without polluting the environment and to create a closed cycle, there are some challenges, such as the fact that it is not miscible with other polymers. The basis of the thermodynamic relationship of the different mixtures is given by the following Formula 1.

$$\Delta G_m = \Delta H_m - T\Delta S_m \tag{1}$$

Where ΔG_m = the free energy of mixing, ΔH_m = the enthalpy of mixing and ΔS_m = the entropy of mixing at the temperature T.

If the free energy of mixing is negative, then binary polymer mixtures are miscible. These theories for achieving miscibility of different polymer blends were observed by Flory as well as Huggins and are described as Flory-Huggins Theory.[56-59] Immiscible polymers enter into phase separation, whereby homogeneous blends are also considered as single-phase systems.[60] To increase the properties of immiscible polymer blends, various additives can promote a certain miscibility of the mixture via compatibilization.[61] For example, the use of styrene-ethylene-propylene copolymers (SEP) and ethylene-propylene rubber (EPR) in HDPE/PP blends was investigated.[62, 63] Various studies are also known for the combination of PP with PE or vice versa. Among others, Eagen et al. [64] reported about a multi-block copolymer consisting of ethylene and propylene which showed best compatibility properties with respect to PP or PE plates.

Another major challenge in the recycling of polypropylene and plastics in general are the degradation processes caused by photo degradation, thermo-oxidative degradation, hydrolytic degradation and mechanical stress during the recycling process.[29] These effects cause the polymer chains to split, which in the case of PP is obviously caused by chain scission (beta-splitting), whereby the molecular weight is strongly reduced. The main cause of the different types of degradation are radical reactions, which initiate polymer chain degradation. PP must always be protected against oxidation processes at temperatures above 100 °C, which is why various antioxidants are used. Primary antioxidants such as sterically hindered phenols, secondary antioxidants such as phosphites or radical scavengers (hindered amine light stability (HALS)) can be used for this purpose.[65] The reaction scheme of the auto-oxidation and the principle or mode of action of the respective antioxidants are shown schematically in the Figure 6.

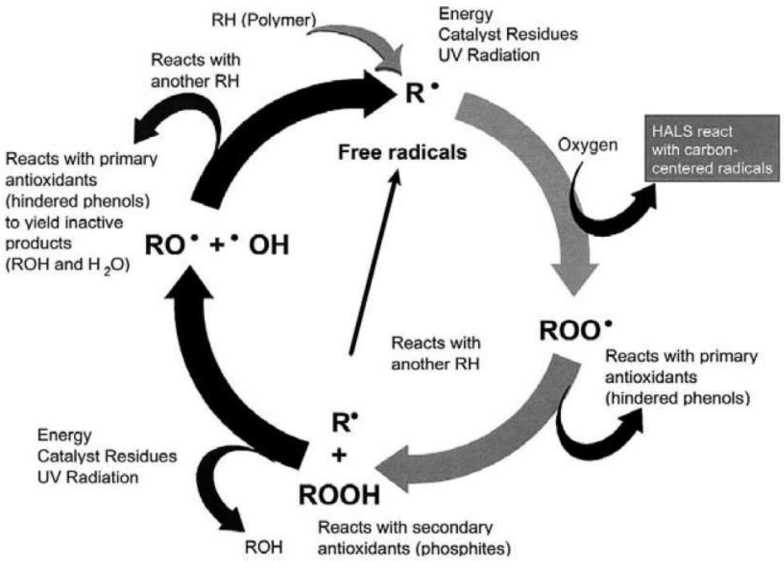


Figure 6: Autooxidation cycle of PP [46]

At the beginning, chain scission of the polymer occurs, e.g. by heat or shear, which results in the formation of an alkyl radical R. This can react further with oxygen to form ROO· or be protected by radical scavengers or primary antioxidants and thus counteract degradation. If this is not the case, in the next step the ROO· will react by hydrogen abstraction with another polymer chain and a hydroperoxide (ROOH) is formed. These are very unstable and decompose into an alkoxy radical (RO·) and a hydroxy radical (HO·). To prevent this, secondary antioxidants can be used which prevent the formation of such radicals.[65]

In addition to the described antioxidants, UV absorbers, quenchers or radical traps can also be used to reduce photo degradation. UV absorbers are additives that convert UV radiation into heat and release it. Typical UV absorbers are benzophenones and benzotriazoles. Nickel compounds are the typical quenchers, which absorb energy by possessing a chromophore group. HALS compounds also serve as radical traps or radical scavengers in photo degradation.[29]

Thermomechanical degradation also plays an important role in the application of PP, which should be counteracted by the use of stabilizers. Klemchuk and Thompson [66] point out that stabilization is necessary during reprocessing. Ma and La Mantia [67] reported that, due to multiple processing, the MFR value of PP increases dramatically and could be counteracted by the use of stabilizers.

Another way to recycle PP is to use additives to improve the properties, which may be very low due to degradation. On the one hand, they should fundamentally improve the properties of PP, but also the miscibility with other heterogeneous materials should be improved. For this purpose, mineral fillers are used to improve the properties but also to save costs. Inorganic fillers such as calcium carbonate, talc, mica, magnesium hydroxide, carbon black and many others can be used.[46] But also organic fillers are mixed with PP.[68] Impact modifiers are widely used to improve the mechanical properties, especially the impact strength of PP. In particular, blending PP with EPDM (ethylene-propylene-diene copolymer) rubber is frequently used for this purpose.[65]

2.1.4. Long Chain Branching of Polypropylene

Linear PP has basically good properties, but its melt strength is restricted and reaches its limits. As a result, processes such as blow molding, foaming or thermoforming cannot be used or can only be used to a limited extent. In order to eliminate this weakness of linear PP, various methods have been developed to help introduce long-chain branching. Four different methods are used to achieve long-chain branching at the backbone of linear PP and thus improve the melt strength behavior.[69]

- Direct polymerization
- Electron beam irradiation
- Compounding
- Reactive Extrusion

The aim is to achieve a higher molecular weight and a broader molecular weight distribution by introducing long chain branches compared to linear PP. In general, a long chain branch is characterized by 0.05 - 0.15 branches/1000 C-atoms and the polydispersity of the branched material is higher than four.[70] In particular, the melting properties of PP are influenced by this.

In recent decades, research has been conducted in this field and in improving the properties of linear PP. In the process, the very "main methods" described above for the production of LCB-PP and their behavior have been investigated. In direct polymerization, the LCB-PP is formed directly during the polymerization reaction. Either by combining an initiator and olefin or by blending with components of low molecular weight with high molecular weight in reactors. Wang et al. [71] reported about polymers with LCB-structure like polypropylene-g-poly(ethylene-co-1-butene) (PP-g-EBR), which was anionic polymerized. In 1990, the Himont company (nowadays LyondellBasell) was able to establish a patent on the market for the production of HMS-PP, which works by means of electron beam irradiation.[72] In addition, a second production method had been developed by the company Borealis for new LCB-PPs. In this reaction, monomers can be grafted below the melting temperature of PP by means of radical reactions of PP and peroxides.[73]

The generation of LCB structures by using electron beam irradiation has been studied in several literatures.[74-77] The method can be used under different atmospheric conditions. However, an oxygen free or at least a reduced-oxygen atmosphere should prevail to prevent the oxidative degradation of the PP.[78]

By using additives, modifiers or resins added to the PP, long chain branching can also be achieved and this is the compounding method. However, the blend material usually already contains LCB-PP, HMS-PP or rubber components to enhance the properties of the actual starting material (linear PP). Fang et al. [79] investigated the blend behavior of linear PP (LPP) with LCB-PP and their film blowing properties. Tabatabaei et al. [80] demonstrated the mode of action of LCB-PP on four different LPPs, and Liu et al. [81] used ultrafine polybutadiene rubber to improve the mechanical properties of PP.

The most common and versatile method for generating LCB-PP is reactive extrusion. In this process, chemical reactions occur between various functional groups and the polymer chain of PP.[82] Grafting is one of the most often and well-known processes. Maleic anhydride is frequently used as a monomer for this purpose. Tang et al. [83] described the preparation of maleic anhydride grafted PP (PP-g-MAH) using a twin screw extruder to react it with an epoxy to enhance the LCB effect. According to Wong et al. [84] styrene is also very suitable as a grafting monomer. Since it is resonance-stabilizing, it can react with the macro-radicals on the PP. In principle, there is a wide range of different monomers that are very suitable for grafting, such as various acrylate compounds [85, 86], which are frequently used due to their basically high reactivity to radicals, but also silane [87] or divinyl benzenes [88]. A schematic representation of grafting by means of monomers is shown in Figure 7.

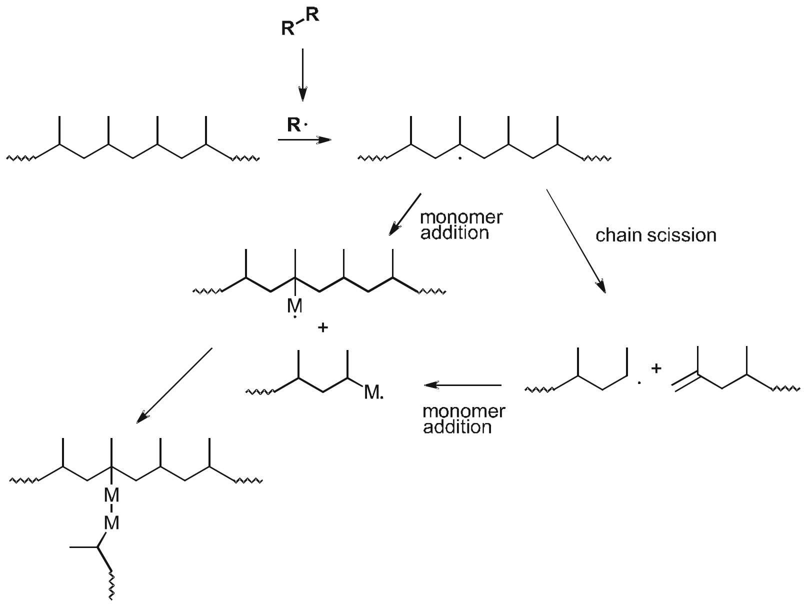


Figure 7: LCB and grafting reaction of resonance stabilizing monomer

Cross-linking agents have also been investigated for the production of LCB-PP. Benzoyl peroxides (BPO) in particular, but also dicumyl peroxides, played an important role in forming three-dimensional networks. For example, according to Su et al. [89, 90] different peroxides were used to graft 1.6-hexanediol diacrylate.

In addition to the variants already listed to achieve long chain branching, peroxides can be used during reactive extrusion. Several factors play a role, such as the choice of peroxide, its concentration and the processing temperature. According to Lagendijk et al. [91], peroxide dicarbonates (PODIC) are a class of peroxides that have a partial stabilizing and initiating effect and thus support the formation of LCB-PP. This type of peroxide thus acts as a co-agent, although the actual reaction mechanism is still largely unclear. The possible reaction scheme is indicated in the following Figure 8.

The formation of free radicals during the decomposition of organic peroxides, e.g. by thermal decomposition, means that they can not only be used as starting materials in chemical reactions but also react with the human organism. The toxicological characteristics of the respective peroxides vary widely, ranging from irritation of the skin and eyes to carcinogenic effects and mutagenic changes.[92]

Dibenzoyl peroxides were used as medicines for the treatment of acne vulgaris, which led to skin irritation and allergic contact dermatitis.[93, 94] Exposure to dicumyl peroxide has caused changes in nasal mucous membranes.[95] For this reason, every organic peroxide is now classified under REACH (Registration, Evaluation, Authorization of Chemicals), which tests and documents the effects and risks to the human organism.

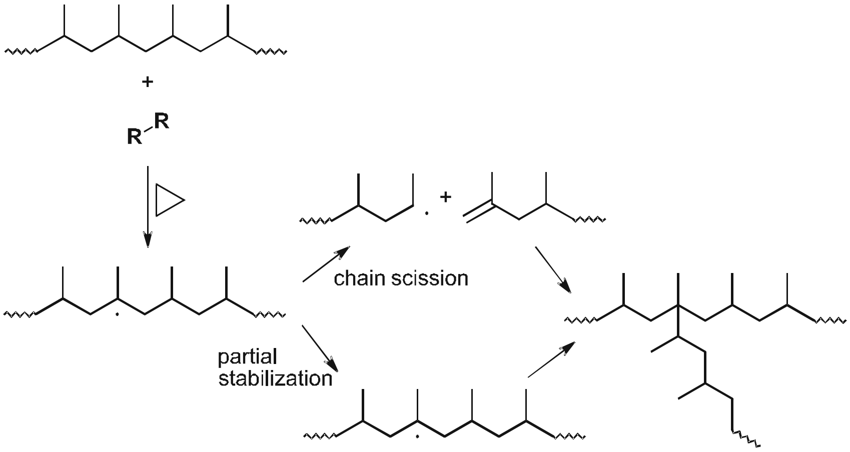


Figure 8: LCB of PP by the using of peroxydicarbonate

In recent years, the mode of action of various peroxides on the long chain branching behavior of PP and the effects on rheological and mechanical properties have been investigated.[96-101] For example, Gotsis et al. [102] represented a study in which peroxydicarbonates with different aliphatic side chains and thus the effects on the branching behavior were investigated.

2.2. Types of Polypropylene used for this work

2.2.1. Virgin Polypropylene

The pure PP materials were purchased from Borealis, whereby three different types were used. The PP HC600TF, which was the main component of this work, was used for the direct introduction of the long-chain branches. On the one hand, it was easy to process and is not overly stabilized, which made it predestined for research purposes.

- PP HC600TF

Is a homopolymer with good processability, stiffness and impact strength. For this reason, it is used in a wide variety of applications such as dark-walled packaging, margarine cups or dairy cups. It is also suitable for the production of monofilaments, tapes, slit and split films. As a result, it can be found in products such as adhesive bag tapes, textile film yarns or fabrics, ropes and yarns. The physical properties of these type of PP are in Table 1 listed.[103]

Table 1: Physical properties of PP HC600TF [103]

Properties	Typical Values	Test method
MFR (230 °C; 2.16 kg)	2.8 g/10 min	ISO 1133
Melt temperature (DSC)	164 °C	ISO 11357-3
Crystallization temperature	110 °C	ISO 11357-3
Charpy Impact Strength (notched)	4 kJ/m^2	ISO 179/1eA

In addition to the direct introduction of LCBs on PP, the benefits of blending materials or so-called "masterbatches" were also investigated in this work. For this purpose, the PP HC600TF was branched with 200 mmol/kgPP dimistryl peroxydicarbonate or dilauroyl peroxide and this was mixed to the PP HD601CF and PP HF700SA in a blend ratio of 90:10.

- PP HD601CF

This is also a homopolymer for unoriented films in the chill-roll process. It is characterized by good mechanical properties, high stiffness and good optical properties. It is used in almost every type of film such as textile packaging films, laminating films and stationary films. But it can also be found in food packaging or flower packaging. Borealis' internal standard film production conditions allow the production of chill-roll films with a thickness of 50 µm. In Table 2 an extract from the data sheet and its physical properties are listed.[104]

Table 2: Physical properties of PP HD601CF [104]

Properties	Typical Values	Test method
MFR (230 °C; 2.16 kg)	8 g/10 min	ISO 1133
Melt temperature (DSC)	162 °C	ISO 11357-3
Molecular weight	medium	-/-

- PP HF700SA

This polypropylene is mainly used for injection molding applications and is a homopolymer. It has excellent mechanical properties and is easy to process. It also has very good flow properties and excellent antistatic behavior. It is highly heat stabilized and can be found in household applications and small appliances. The most important physical properties of PP HF700SA are listed in the Table 3.[105]

Table 3: Physical properties of PP HF700SA [105]

Properties	Typical Values	Test method
MFR (230 °C; 2.16 kg)	21 g/10 min	ISO 1133
Density	905 kg/m^3	ISO 1183
Charpy Impact Strength (notched)	2 kJ/m^2	ISO 179/1eA

- PP HA104E

This homopolymer is characterized by high molecular weight and shows good properties such as stiffness and impact strength. Due to improved processing properties, it is mainly used for pipes, films or profiles. The physical properties of this PP are listed in Table 4.[106]

Table 4: Physical properties of PP HA104E [106]

Properties	Typical Values	Test method
MFR (230 °C; 2.16 kg)	0.75 g/10 min	ISO 1133
Density	905 kg/m^3	ISO 1183
Melt temperature (DSC)	164 °C	ISO 11357-3
Charpy Impact Strength (notched)	4.5 kJ/m^2	ISO 179/1eA

2.2.2. Recycled Polypropylene

PP recyclate only has to consist of the main component PP in which various additives such as fillers, flame retardants or stabilizers are mixed. In addition to the main component, it can also contain other types of plastic such as PE or PS, which are produced as impurities during the recycling process. The composition of recyclates has an enormous effect on the properties of the material.[107]

The recyclates described below have been collected by ourselves (collected) but also provided by a plastics recycler (flakes), Walter Kunststoff GmbH (Figure 9). All materials are post-consumer waste. The properties of the different materials after extrusion with 240 °C are listed in Table 5.

Table 5: Properties of the PP post-consumer waste samples for this work after 240 °C extrusion; measured at TU Wien under standardized conditions

Material	**MFR (g/10min)**	**T_m (°C)**	**E_t (MPa)**	**ε_B (%)**	**a_{tN} (kJ/m^2)**
Flakes of coffee caps	14.4	167	1864 ± 55	748 ± 85	22 ± 4
Flakes of yoghurt cups	6.0	162	2309 ± 51	51 ± 3	50 ± 6
Collected yoghurt cups	5.3	167	1794 ± 143	859 ± 39	49 ± 4
Collected buckets	32.0	151	1570 ± 94	892 ± 73	22 ± 3

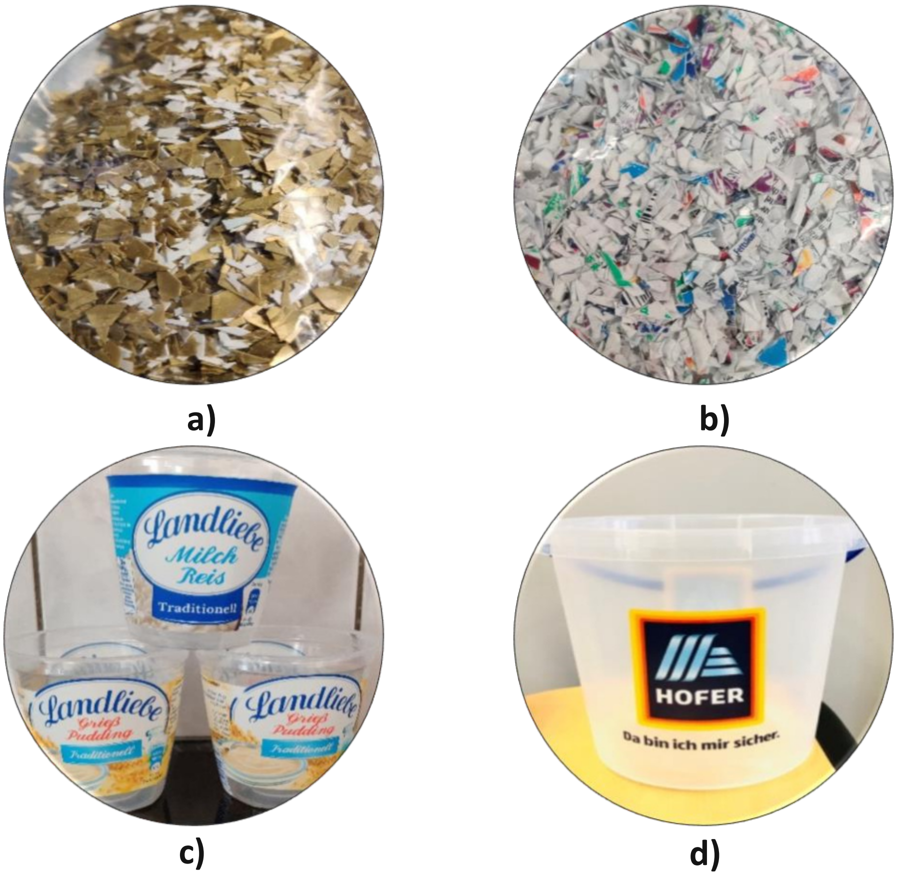


Figure 9: Recycled PP samples for this work; flakes of coffee caps (a); flakes of yoghurt cups (b); collected yoghurt cups (c); collected bucket (d)

2.3. Additives

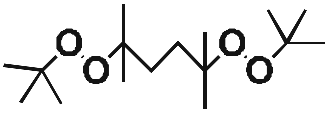
2.3.1. Peroxides

The peroxides used in this work and listed below were obtained and provided by the company Pergan GmbH. The selection of the peroxides as well as their possible reaction properties during reactive extrusion could be made and discussed through personal conversations with Dr. Schmid.

The choice of peroxide has a great influence on the reactive extrusion of PP and for this reason should be very well considered. On the one hand, the formation of peroxide radicals can lead to long-chain branching, but also to chain scission of PP. In addition, various properties of the respective peroxides play an important role in handling them, such as storage temperature and half-life. Basically, according to Klenk et al. [108] the peroxides can be divided into different main groups according to their structure. These are the following groups of peroxides diacyl peroxides, peroxyesters, diperoxyketals, dialkyl peroxides, hydroperoxides, ketoneperoxides, and peroxydicarbonates. In this thesis, the groups dialkyl peroxides, peroxyesters and peroxydicarbonates have been studied, which are among the most effective peroxide groups for cross-linking reactions according to Takamura et al. [109].

- 2.5-Dimethyl-2.5-di-(tert-butylperoxy)-hexane

Belongs to the class of dialcyl peroxides and is a clear liquid used for polymerization (chain degradation of PP (CR-PP) in the extrusion process at a temperature of 200 to 250 °C), curing (of unsaturated polyester resins at a temperature of 140 to 180 °C) and cross-linking (of various components such as NBR, SBR, EP(D)M and EVA for the production of rubber compounds at a processing temperature of 135 °C and a cross-linking temperature of 175 °C).[110] The schematic structure is shown in Figure 10 as well as the properties are listed in Table 6.



2,5-Dimethyl-2,5-di-(tert-butylperoxy)-hexane

MW: 290.4 g/mol

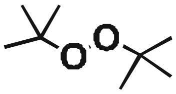
Figure 10: Schematic structure of 2.5-Dimethyl-2.5-di-(tert-butylperoxy)-hexane

Table 6: Properties of 2.5-Dimethyl-2.5-di-(tert-butylperoxy)-hexane [110]

Company name	Peroxan HX
Cas. no.:	78-63-7
Peroxide content	min. 92%
Active oxygen content	10.14 %
10 h half-life temperature	115 °C
Storage temperature	min. 10°C / max. 40 °C

- Di-tert-butyl-peroxide

This peroxide (dialcyl peroxide) is used in various applications such as the polymerization of styrene, ethylene, acrylates, methacrylate and alkyd-styrene resins. The disadvantage is that this peroxide can cause genetic defects, making it extremely difficult to handle. It is also used in the curing of unsaturated polyester resins. It is a clear liquid that is highly volatile and should be used in compounds that begin cross-linking immediately after mixing. In Figure 11 the structure of this peroxide represented and the properties of them are listed in Table 7.[111]



Di-tert-butyl-peroxide
MW: 146.2 g/mol

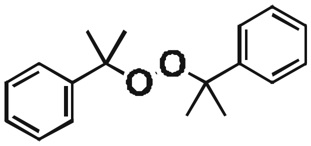
Figure 11: Schematic structure of Di-tert-butyl-peroxide

Table 7: Properties of Di-tert-butyl-peroxide [111]

Company name	Peroxan DB
Cas. no.:	110-05-4
Peroxide content	min. 98%
Active oxygen content	10.72 %
10 h half-life temperature	121 °C
Storage temperature	max. 40 °C

- Bis(1-methyl-1-phenylethylene)peroxide)

Known as dicumyl peroxide, it is one of the most commonly used peroxides. However, it has also recently been replaced by other peroxides due to new guidelines and tightening of the guidelines regarding the health aspects and effects on the human body. The peroxide is present as white crystals and is used for the polymerization of styrene and for the cross-linking of NBR, SBR, EP(D)M, LDPE and EVA rubber compounds.[112] The properties (Table 8) and the schematic structure (Figure 12) are below.



Bis(1-methyl-1-phenylethylen)peroxide
MW: 270.4 g/mol

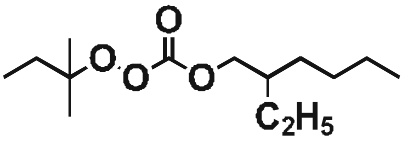
Figure 12: Schematic structure of Bis(1-methyl-1-phenylethylen)peroxide

Table 8: Properties of Bis(1-methyl-1-phenylethylen)peroxide [112]

Company name	Peroxan DC
Cas. no.:	80-43-3
Peroxide content	min. 99 %
Active oxygen content	5.86 %
10 h half-life temperature	112 °C
Storage temperature	30 °C

- Tert-Amyl peroxy-2-ethylhexylcarbonate

Belongs to the group of peroxy esters and is used in the form of a clear liquid. It is mainly used for polymerization of styrene and acrylates as well as methacrylate in solution, mass and suspension (co)polymerization.[113] The schematic structure of this peroxide is shown in Figure 13 an the properties are listed in Table 9.



tert-Amyl peroxy-2-ethylhexylcarbonate
MW: 260.4 g/mol

Figure 13: Schematic structure of tert-Amyl peroxy-2-ethylhexylcarbonate

Table 9: Properties of tert-Amyl peroxy-2-ethylhexylcarbonate [113]

Company name	Peroxan AEC
Cas. no.:	70833-40-8
Peroxide content	min. 94 %
Active oxygen content	5.78 %
10 h half-life temperature	95 °C
Storage temperature	max. 25 °C

- Tert-Butyl peroxy-2-ethylhexylcarbonate

A clear liquid belonging to the group of peroxy esters. Used in the high-pressure polymerization of ethylene in an autoclave or tube process at a temperature of 220 to 270 °C. Polymerization of styrene and acrylates as well as methacrylate is possible. But also the curing of unsaturated polyester resins as well as the cross-linking of EPDM, EPM and NBR can be carried out by means of the peroxide.[114] Also here the structure (Figure 14) and the properties (Table 10) are given.

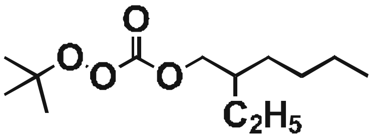


Figure 14: Schematic structure of tert-Butyl peroxy-2-ethylhexylcarbonate

Table 10: Properties of tert-Butyl peroxy-2-ethylhexylcarbonate [114]

Company name	Peroxan BEC
Cas. no.:	34443-12-4
Peroxide content	min. 97 %
Active oxygen content	6.3 %
10 h half-life temperature	98 °C
Storage temperature	30 °C

- Tert- Butyl peroxyisopropylcarbonate

A peroxyester peroxide which is a solution in odorless white spirit. It is preferably used for unsaturated polyester resins at a high temperature of 140 to 160 °C. These compounds have a long storage stability. The polymerization or copolymerization of styrene is carried out by means of bulk or suspension polymerization between 95 and 125 °C. It is also used for the polymerization of acrylates and methacrylate.[115] The structure is shown in Figure 15 and the properties are listed in Table 11.

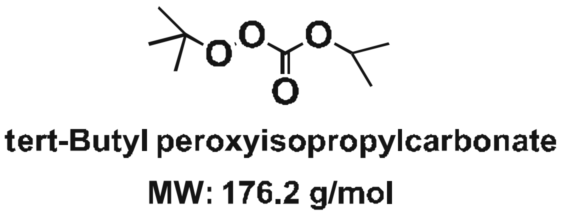


Figure 15: Schematic structure of tert-Butyl peroxyisopropylcarbonate

Table 11: Properties of tert-Butyl peroxyisopropylcarbonate [115]

Company name	Peroxan BIC
Cas. no.:	2372-21-6
Peroxide content	min. 98 %
Active oxygen content	6.81 %
10 h half-life temperature	98 °C
Storage temperature	min. 0°C / max. 25 °C

- Dilauroyl peroxide

Is a diacyl peroxide for the (co)polymerization of vinyl chloride, vinylidene chloride, acrylates and methacrylate. It is in the form of white flakes.[116] In Figure 16 is represented the schematic structure and in Table 12 the properties are listed.

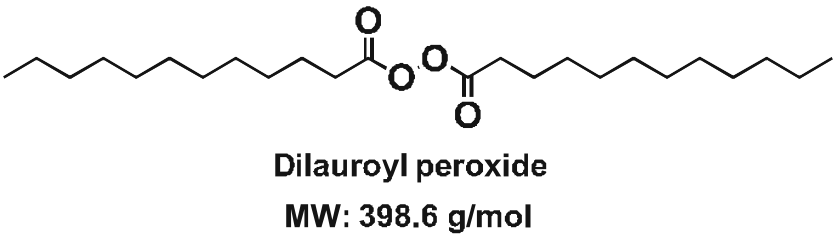


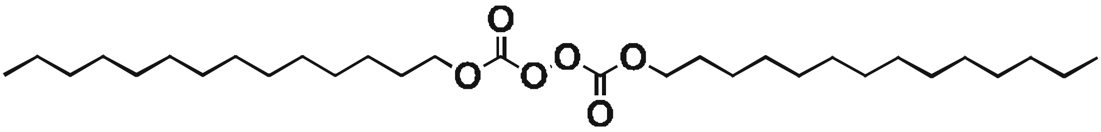
Figure 16: Schematic structure of Dilauroyl peroxide

Table 12: Properties of Dilauroyl peroxide [116]

Company name	Peroxan LP
Cas. no.:	105-74-8
Peroxide content	min. 98 %
Active oxygen content	3.97 %
10 h half-life temperature	61 °C
Storage temperature	30 °C

- Dimistryl peroxydicarbonate

White flakes belonging to the group of peroxydicarbonates and used for the (co)polymerization of vinyl chloride as well as vinylidene chloride at a temperature of 40 to 65 °C. It is suggested that the storage of the peroxide is carried out at freezing temperatures, which may cause problems for the industry.[117] The structure (Figure 17) and the properties (Table 13) are below.



Dimistryl peroxydicarbonate

MW: 514.8 g/mol

Figure 17: Schematic structure of Dimistryl peroxydicarbonate

Table 13: Properties of Dimistryl peroxydicarbonate [117]

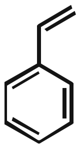
Company name	Peroxan C126
Cas. no.:	53220-22-7
Peroxide content	min. 95 %
Active oxygen content	2.95 %
10 h half-life temperature	48 °C
Storage temperature	15 °C

2.3.2. Monomers

The monomers were used in this work for a preliminary study and an attempt was made to introduce the long chain branching by grafting using the already described peroxide 2.5-Dimethyl-2.5-di-(tert-butylperoxy)-hexane on the PP. In addition, biocompatible monomers were used to reduce the possible toxicity of the unpolymerized monomers and thus eliminate the problem. Styrene, which has already been used as a grafting material, served as a comparative monomer.

The individual monomers with their characterizations are listed in the following points. The concentration of the monomers used was 580 mmol/kg PP.

- Styrene

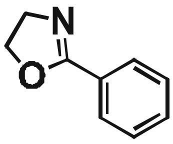


Styrene
MW: 104.2 g/mol

Figure 18: Structure of Styrene

- ➢ Molecular formula: C_8H_8
- ➢ Appearance: liquid, colorless, sweet smelling
- ➢ Storage: refrigerated and in dark containers
- ➢ Non-biocompatible and harmful above a certain lateral dose.

- 2-Phenyl-2-oxazoline

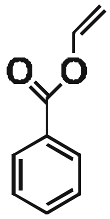


2-Phenyl-2-oxazoline
MW: 147.2 g/mol

Figure 19: Structure of 2-Phenyl-2-oxazoline

- ➢ Molecular formula: C_9H_9NO
- ➢ Appearance: liquid, strong yellow color, characteristic odor
- ➢ Biocompatible

- Vinylbenzoat

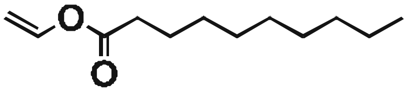


Vinylbenzoat
MW: 142.2 g/mol

Figure 20: Structure of Vinylbenzoat

- ➢ Molecular formula: $C_9H_8O_2$
- ➢ Appearance: liquid, colorless, characteristic odor
- ➢ Biocompatible

- Vinyl decanoate

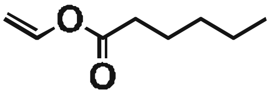


Vinyl decanoate
MW: 198.3 g/mol

Figure 21: Structure of Vinyl decanoate

- ➢ Molecular formula: $C_{12}H_{22}O_2$
- ➢ Appearance: liquid, colorless, characteristic odor
- ➢ Biocompatible

- Vinyl caproate



Vinyl caproate
MW: 142.2 g/mol

Figure 22: Structure of Vinyl caproate

- ➢ Molecular formula: $C_8H_{14}O_2$
- ➢ Appearance: liquid, colorless, characteristic odor
- ➢ Biocompatible

2.3.3. Blend materials

The blend materials used were a linear PP, the PP HC600TF, which has already been described in section 2.2.1. and a commercial available HMS-PP from the company Borealis.

- Daploy™ WB140HMS

This was a long-chain branched homopolymer for foam applications. It is used in the automotive, food and non-food packaging sectors as well as in building and construction. It is characterized by properties such as high stiffness, high service temperatures and excellent processability. In addition, it is used for foam extrusion processes with good foamability, which means that the foamed materials have properties such as good insulation properties and good thermal properties.

3. Methodology

3.1. Reactive Extrusion

Reactive extrusion is versatile and combines melt extrusion with chemical reaction or modification in one step for polymerization of monomers, modification of polymers, compatibilization of immiscible polymer blends or in situ syntheses into a polymer matrix. There are different steps during a reactive extrusion, which include feeding, melting, mixing, devolatilizing and forming. The chemical reaction takes place during the melting phase along the screw axis.[118, 119]

In this thesis, the reactive extrusion was carried out using a single screw extruder, Extron EX-18-26-1.5, with a length/diameter ratio of 1:25, see Figure 23. The extruder is equipped with three independent heating zones (feeding, extrusion and die). Extrusion was performed at a screw speed of 70 rpm and various extrusion temperatures were set, such as 180 °C (165, 180, 220), 200 °C (165, 200, 220) and 240 °C (165, 240, 240).

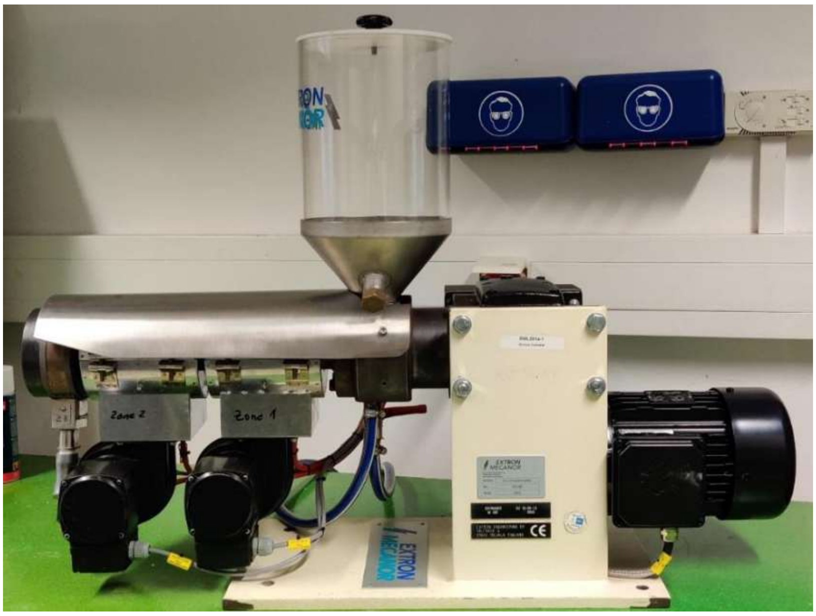


Figure 23: Extron EX-18-25-1.5 Lab Extruder for the reactive extrusion

Since 1950, the extruder has been used as a polymerization reactor and has served as a fixed way to perform polymerizations. A patent of Dow Chemical Company describes a polymerization which was carried out with a single screw extruder as the main device.[120] The first polymerization finally mentioned in the literature that was carried out with an extruder was that for the production of nylon.[121] Later, Mack and Herter [122] proposed twin-screw extruders because of problems with the single-screw extruder during up-scaling. Finally, the combination of a stirred-tank reactor, a single screw extruder and a twin screw extruder was the best option for the production of polyester. Over the years, different approaches and thus different studies have emerged. The free-radical polymerization of methacrylate's using a counter-rotating twin-screw extruder has been analyzed.[123-125] In addition, the extruder was used for polycondensation reactions of urethane [126] and anionic polymerization of ε-carpolactam [127, 128]. Other reactions were studied in different types of extruders such as anionic polymerization of styrene by Michaeli [129] but also radical polymerization of styrene by Kelly [120].

Reactive extrusion is also an attractive tool for the application of grafting or modification reactions. Grafting is carried out by means of free radicals of maleic acid, glycidyl methacrylate or acrylic acid on polyolefin.[126, 130-132] These modified polymers can then be used as blending materials and their properties can be improved by adding metals and glass fibers.[133] During these grafting reactions, unexpected side reactions can occur, such as crosslinking in polyethylene or chain scission in polypropylene.[134]

For reactive extrusion, as for any process, there are some advantages and also disadvantages that need to be considered.[120]

✓ There is a continuous throughput, which is required for operation as a continuous reactor.

✓ Unlike other processes, which operate batch wise, reactive extrusion is a continuous process.

✓ The mixing can be optimized to the specific reaction conditions by the choice of screw geometry/shape.

✓ By using degassing, volatile components and unreacted components can be separated and recycled.

✓ Polymerization by means of extruders requires small amounts of solvents or none at all, which means that no extra separation steps are needed, making the process both cost-effective and environmentally friendly.

☒ Reactor requires a very large volume, which means that the reaction should have a short residence time and the reaction kinetics should be fast.

- ☒ The reaction temperature must not get too high and also the viscosity must be high enough to ensure material transport. Therefore, the reactions in the extruder are limited.
- ☒ In the event of up-scaling, it must be observed that the surface-to-volume ratio decreases, which means that the temperature can no longer be transported away well. Furthermore, the thermal inhomogeneity plays a role.
- ☒ Due to the polymerizations, differences in viscosity can occur, which can lead to instability of the process. This leads to low throughputs or fluctuating turnovers.

The main reactions obtained by means of reactive extrusion can be divided into five categories:[135]

- Bulk polymerization

Is a reaction in which a polymer is formed from the monomer, which is generally soluble again in the monomer. The polymerization reaction is strongly influenced by the heat generated during the reaction and the mixing of the polymer-monomer mixture. The reason for this is the rapid increase in viscosity due to the onset of the polymerization reaction. A distinction is made between addition reactions, in which short-chain polymers are formed in a very short reaction time, and condensation reactions, in which the polymer chains continue to grow throughout the entire reaction time. Thus, bulk polymerization is also referred to as a step growth reaction or a chain growth reaction.[135]

- Graft or functionalization reactions

In this reaction, short monomer units are chemically attached to the monomer backbone and thus functionalized. This results in changes in the chemical and physical composition, which leads to changes in the properties.[135]

- Interchain copolymerization

Here, copolymers are formed by using different polymers (two to three) containing a reactive group to form a graft copolymer. In contrast to graft polymerizations, no monomers are used in this case.[135]

- Coupling or branching reactions

The molecular weight is increased by linking the homopolymer by a polyfunctional copolymer and reacting the polymer chains with each other.[135]

- Degradation reactions

The degradation reaction can be caused by the introduction of heat, shear stress, but also by the use of peroxides. The molecular weight of the polymer chain decreases and the molecular weight distribution becomes narrower.[135]

3.2. Injection Molding

Injection molding is a well-established and proven process for the production of plastic products. These can be produced in large quantities with different geometries in a short time due to the fast production.[136]

A combination of Haake Mini Lab II and Haake Mini Jet 2 (Figure 24) was used to produce the test specimens for tensile testing and impact testing.

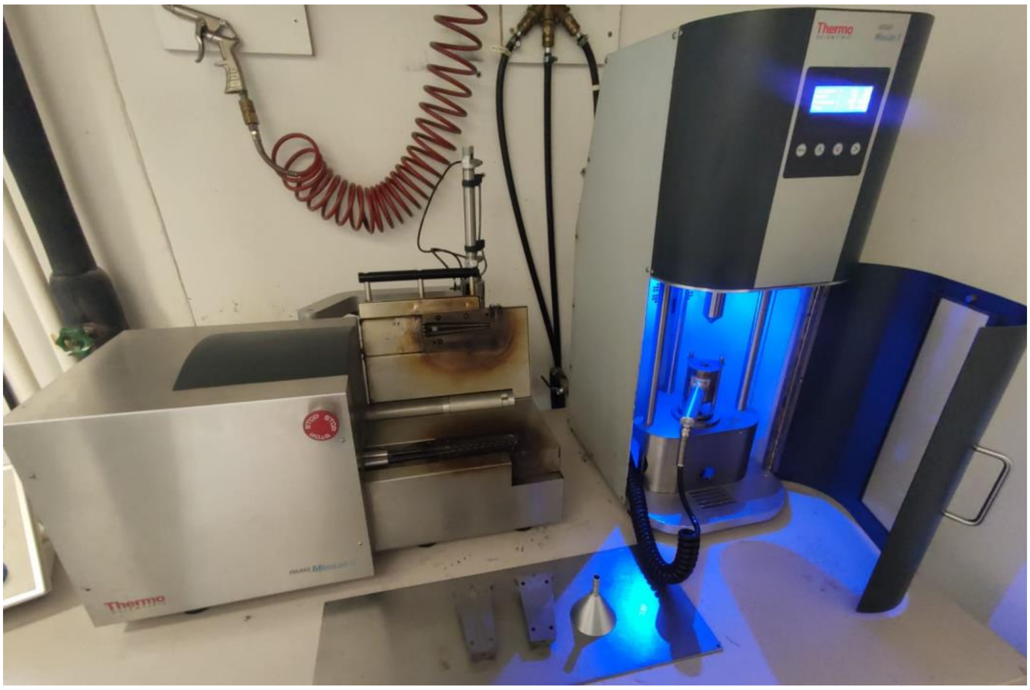


Figure 24: Combination of Haake Mini Lab II and Haake Mini Jet 2 for injection molding

This allowed the respective specimens to be injection molded for the mechanical characterization. The Haake Mini Lab II is a conically shaped twin-screw extruder, which was operated at the respective temperature used during reactive extrusion, see chapter 3.1., (180, 200 or 240 °C). The screw speed during extrusion was 100 rpm. The Haake Mini Jet 2 was used for the actual injection molding. The temperature of the cylinder with which the molten plastic mass was taken from the Haake Mini Lab II was always the same as the temperature at which it was operated (180, 200 or 240 °C). The mold temperature was set at 90 °C and the injection pressure was 350 bar for 10 seconds. The tensile specimens (Figure 25) were prepared according to DIN 572-2 type 5A [137] and the specimens for the impact test according to DIN 8256 method A [138].

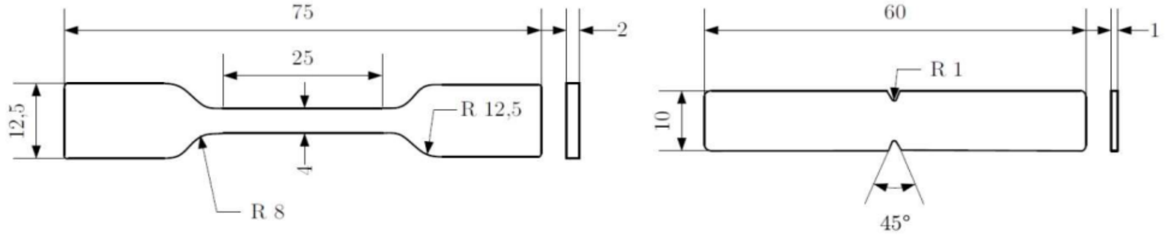


Figure 25: Schematic representation of the specimens for the tensile test and impact tensile test [137, 138]

3.3. Rheology Properties

The rheological investigations were performed with a modular compact rheometer MCR 301 from Anton Paar equipped with a heating chamber CTD 450. The dynamic rheology was measured using a plate-plate measuring system (25 mm) with a gap size of 1 mm and a frequency range between 628 and 0.01 rad/s. The deformation during the measurement increased continuously (logarithmically) from 1 % to 2 % and the measuring temperature was 230 °C. For the extensional rheology measurements, a Sentmanat Extensional Rheometer (SER-HPV1) measurement system was used and measured at a temperature of 180 °C. Strain rates of 0.1 s^{-1}, 1 s^{-1} and 5 s^{-1} were selected. For the start-up curves, plate-plate measurements at 180 °C and shear rates of 0.001 s^{-1} and 0.1 s^{-1} were performed.

The term rheology comes from the Greek and is derived from the word rheos = flow. Thus, rheology deals with the flow behavior of liquids, but also with the deformation behavior of solids. The deformations, which are caused by forces or stresses, can be distinguished between shear, strain, bending, etc. Basically, rheology can be simplified as a two plate model, where the upper plate moves with a shear surface A and a shear force F. The lower plate is fixed and force F acts on it. The distance between the two plates corresponds to the measuring gap h.[139] The schematic measuring principle of the dynamic rheology is shown in Figure 26.

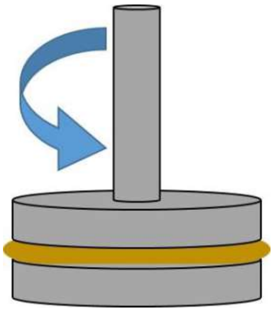


Figure 26: The schematic measuring principle of the dynamic rheology

Two factors are required for the measurement. Firstly, the sample must have wall adhesion and must not slide between the plates, and secondly, a laminar layer flow must prevail. The shear rate can finally be defined as a function of the velocity v (m/s) and the plate spacing h (m).[139]

$$\dot{\gamma} = \frac{v}{h} \qquad (2)$$

Plastics and their melts exhibit viscoelastic behavior, which can be described by means of the viscosity η. This depends on the shear rate. Depending on the area of application, there are different shear rate ranges in which the viscosity curve runs, see Figure 27.[140]

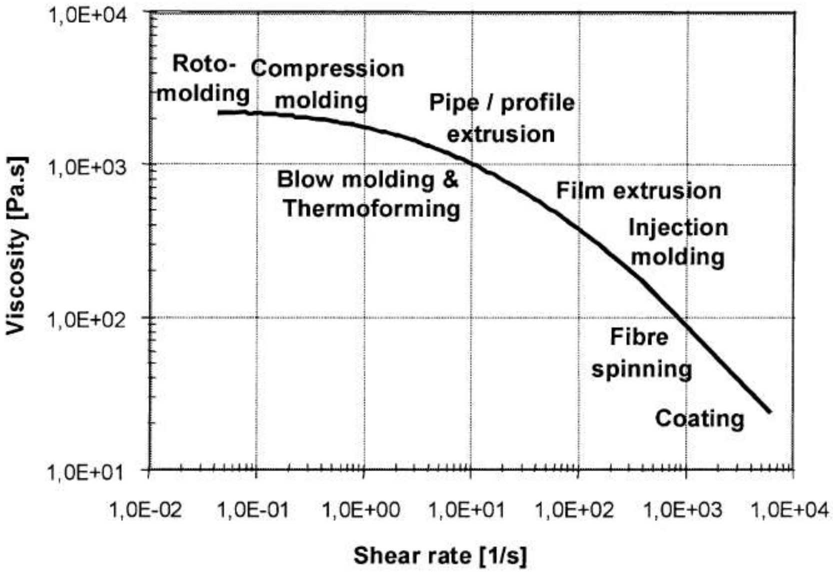


Figure 27: Viscosity curve of PP and its application depending on viscosity [140]

The viscosity curve runs from high shear rates corresponding to a process such as coating to very low shear rates such as compression molding. At these very low shear rates, a kind of plateau is reached which corresponds to the linear viscoelastic behavior where the viscosity is designated as zero shear viscosity η_0. This plays an important role in the rheology of polymers, since it can provide information about the molecular weight. This can be explained by the following Formula 3.[139]

$$\eta_0 = K * M_W^{\alpha} \tag{3}$$

For polymers with low molecular weight (M_w), which is less than the critical entanglement molecular weight M_c, the zero shear viscosity is directly proportional. For branching, however, the molecular weight between the entanglements M_e is given as M_w and is thus no longer proportional to the zero shear viscosity. M_e is specific for each polymer, for polypropylene is 5.1 - 6.9 kg/mol.[141, 142] The factor K depends on the temperature and the tacticity of the polypropylene used and is thus influenced by the chain stiffness of the molten polymer. To describe polymers with high M_w, the coefficient α is approximated as 3.4 for polystyrene as well as 1,4-polybutadiene, 3.6 for polyethylene and 3.4 - 3.6 for polypropylene.[143, 144]

Conclusions about the molecular weight can be drawn not only from the zero shear viscosity, but also from the correlation of the crossover point, which results from the intersection of storage modulus G' and loss modulus G''. By shifting the crossover point horizontally, reference can be made to a higher or lower molecular weight.[145] This is in Figure 28 schematically shown. In case the crossover point moves towards higher shear rates, this is an indication that the molecular weight decreases whereas the molecular weight increases when the crossover point moves towards lower shear rate values. Not only the molecular weight of polymers but also their polydispersity or molecular weight distribution (MMD) correlates very well with the crossover point of the modulus curves. The vertical shift of the point can be used to infer a broadening or narrowing of the MMD.[146, 147]

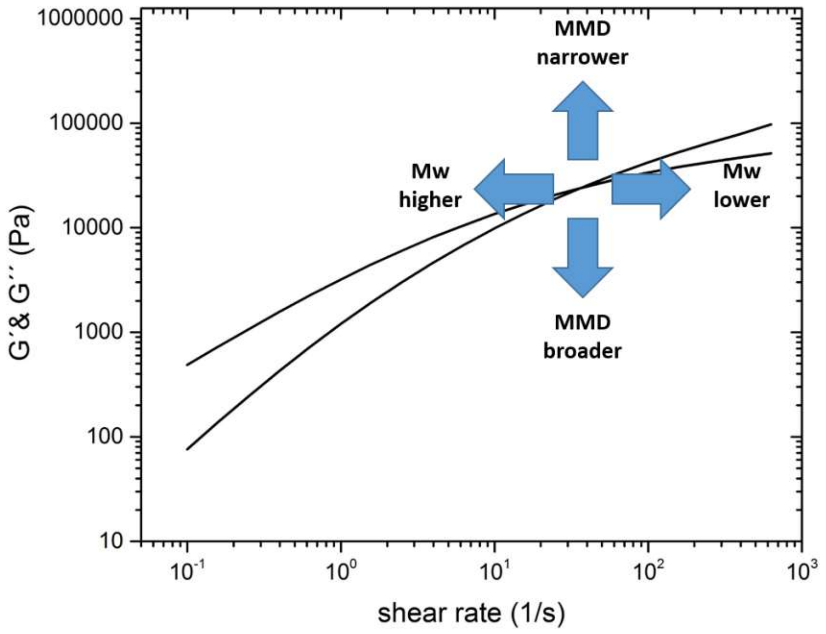


Figure 28: Characteristic Storage and loss modulus curve of PP and the dependence of the cross over point on M_W and MMD

By means of these rheological quantities, a very good statement can be made about the molecular structure of the polymer, which is why the rheological subunits are becoming increasingly important. When LCBs are introduced in polymers, this correlation between molecular structure and viscosity becomes very complex and the exact distribution, how many molecules per LCB, cannot be determined. But of course the viscosity and the course of the loss or storage modulus is affected by the length and distribution of LCBs.

For a definitive statement about a successful LCB, serves the application of extensional rheology. This provides information about strain flow, which is very important in the commercial processing of plastics such as for blow molding, film blowing, film casting, foaming and so on. The nonlinear behavior during strain deformation provides information about structural features of the molecules, which cannot be shown in shear rheology.[144]

To determine strain deformation, a continuous strain is advantageous for polymer melts and is usually measured using a steady simple strain with a constant Hencky strain rate $\dot{\varepsilon}$. The definition of this strain rate can be defined as a function of the length L of the specimen as follows.

$$\dot{\varepsilon} = \frac{d \ln L}{dt} \tag{4}$$

The extensional viscosity can be determined when a uniform extensional flow has been achieved.

$$\lim_{t\to\infty} \eta_E^{+}(t, \dot{\varepsilon}) \equiv \eta_E(\dot{\varepsilon}) \tag{5}$$

In addition, as the strain rate disappears (strain rate $\dot{\varepsilon}$ and shear rate $\dot{\gamma}$ are equal), the extensional viscosity simply becomes three times the zero shear viscosity. This Newtonian fluid behavior was established by Trouton and is referred to as the Trouton factor or ratio and is used to normalize extensional viscosity data.

$$\lim_{\dot{\varepsilon}\to 0} \eta_E(\dot{\varepsilon}) = 3\int_0^{\infty} G(s)\, ds = 3\eta_0 \tag{6}$$

If one compares the strain flow of a linear polymer with that of a branched polymer (LCB polymer), the deviation from the viscoelastic behavior is immediately visible. This deviation from viscoelastic behavior is called strain hardening. In the Figure 29 a typical curve of a non-branched and a branched polymer and the resulting difference is shown.

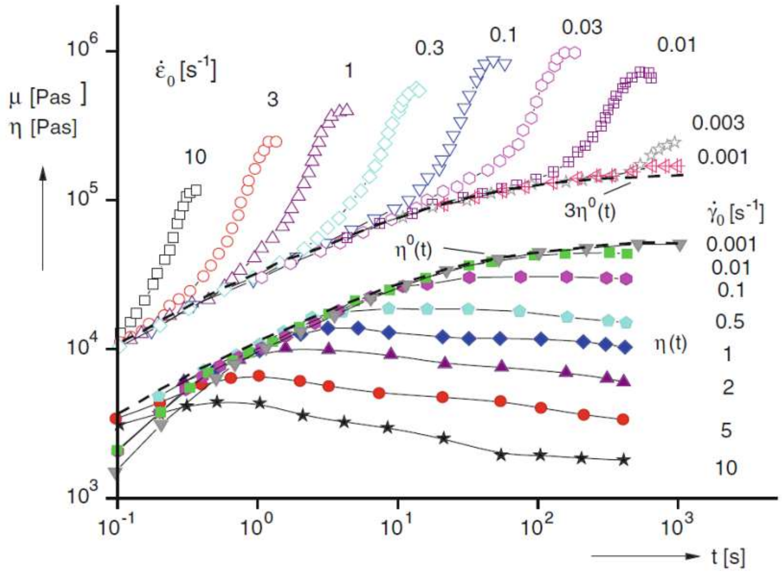


Figure 29: Different elongation viscosities and shear viscosities for LDPE at different strain rates and shear rates [148]

To classify the elongation flow behavior, the linear ratios were compared with the non-linear ratios. In other words, the linear PP is compared with the long chain branched PP. If the strain curves, which were measured at the said strain rates, rise above the LVE curves, this is evidence that LCB-PP or strain hardening is present. In the case of linear PP, the curves do not rise above the LVE curve, but fall, and thus strain-softening behavior is present. This deviation of the LVE curve is described with the strain hardening coefficient or "degree of strain hardening" χ.[149]

$$\chi \equiv \frac{\eta_E^+(t,\dot{\varepsilon})}{3\eta^+(t)} \qquad (7)$$

In recent decades, there has been a lot of research in the literature on the study of extensional rheology in various contexts. Bach et al. [150] studied monodisperse styrene and found that strain softening occurred at low strain rates, whereas strain hardening occurred at higher strain rates. Bhattacharjee et al. [151, 152] studied high molecular weight styrene for strain hardening. The effect on polydispersity was also investigated by elongational rheology. Among others, Münstedt [153] investigated four polystyrenes with different molecular weight distributions and compared their behavior. Blends have also been investigated in which a small amount of high molecular weight material was added to low molecular weight linear polymer and significant strain hardening behavior was observed.[154-157] Also the efficiency of different catalyst systems used to produce branched polymers has been investigated by using elongation rheology and strain hardening behavior.[158-160] In addition, the effects of branched polymers have been analyzed. Kurzbeck et al. [161] used electron beam irradiation for the branching of PP, whereas Hingmann and Marczinke [162] used crosslinking agents to produce branching on PP. This approach was also used by Kasehagen and Macosko [163], who used crosslinking agents to add branches on polybutadiene. Gabriel and Münstedt [164] investigated various polyolefins with different branching forms and were able to show that the number of branches per molecule as well as the number of entanglements per branch play a decisive role in the solidification.

Achieving a homogeneous flow for extensional rheology is more difficult than for shear rheology. There are different possibilities like unaxial (tensile), equibiaxial (biaxial) or planar extension to study the elongation behavior. The first useful and accurate extensometer was developed by Meissner [165] and later further developed and improved by Laun and Münstedt [166]. The cylindrical specimen was clamped in two rotating clamps, which were rotated at a constant speed by gears, thus generating the Hencky strain rate on the specimen. The specimen itself floated in hot oil during this process. Another measurement system that has gained acceptance in recent years is the SER tool (Sentamanat extensional rheometer) from

Sentamanat (Figure 30). Rectangular plates serve as measuring samples, which are attached to rotating drums at the respective ends. These drums are rotated by means of a rotational rheometer and the strain hardening is determined. This device has been shown to provide data that are in good agreement with those of other types of devices.[167]

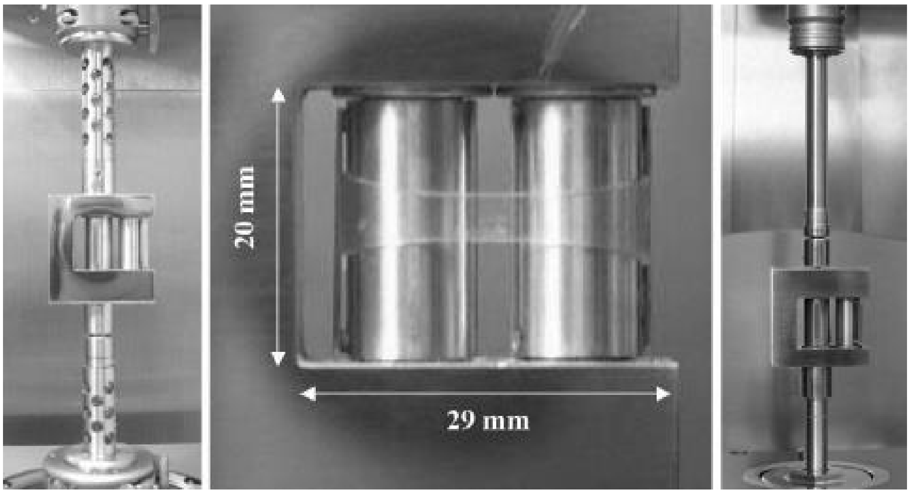


Figure 30: Sentmanat extensional rheology measurement tool [167]

3.4. Melt Flow Rate (MFR)

The MFR device is also used to determine the shear viscosity. It is mainly used in receiving and production control to make quantitative statements about the melt flow behavior of polymers.[168] The measurement of the MFR value for the individual samples in this thesis was carried out according to DIN EN ISO 53735 using a MeltFloW basic from Karg Industrietechnik. The measuring temperature was 230 °C under a weight of 2.16 kg. The resulting shear rates during the measurement (smaller than 20 s^{-1}) do not correspond to the stresses that prevail in most processing operations (larger than 100 s^{-1}).[168]

For the general characterization of the shear rate acting on the starting material during the measurement, the following formula can be used.[169]

$$\dot{\gamma} = 1.85 * MFR \tag{9}$$

For example, if this is applied to PP HC600TF, which has an MFR value of 2.8 g/10min, a shear rate of 4.9 s^{-1} can be calculated.

3.5. Mechanical Properties

There are numerous static and quasi-static test methods for plastics, whereby the tensile test is one of the most important measurement methods. The conventional tensile test, with a constant crosshead speed, is one of the quasi-static test methods.[170] The specimens produced in chapter 3.2. for the tensile test were tested using Zwick050 from ZwickRoell GmbH. The test speed was 10 mm/min and was equipped with an extensometer and a 1 kN load cell. The characteristic values such as the modulus of elasticity (E), yield strength (σ_m) and elongation at break (ε_B) were determined.

In addition to the tensile test (quasi-static test method), the tensile impact test is the pendant to the tensile test and covers the dynamic test methods, whereby a sudden failure of the material results. It is therefore another important mechanical test method that provides indications of the toughness or brittleness of a material. The measurement was carried out according to the standard DIN EN ISO 8256 [138] with an Instron Ceast 9050 pendulum impact tester (maximum impact energy of the pendulum: 2 J, crosshead mass: 15 g). To calculate the notched impact strength with the formula below, the residual width x of the specimen web and the thickness h of the specimen must be specified.[138]

$$a_{tN}\left[\frac{kJ}{m^2}\right] = \frac{E\ [J]}{x\ [mm] * h\ [mm]} * 10^3 \qquad (13)$$

3.6. Differential scanning calorimetry (DSC)

For the thermal analysis of polymers and thus also for plastics, DSC is the most commonly used method. The modified and unmodified PP samples were measured by using TA Q2000 DSC from TA instruments. For this, 5 - 10 mg were weighed into aluminum pans with lids and the measurement was carried out under nitrogen atmosphere (50 ml/min). The measurement program started at room temperature and was heated up to 200 °C at a heating rate of 10 K/min to eliminate the thermal history. Afterwards, the sample was cooled down to room temperature and a second heating cycle (10 K/min) was started until 200 °C was reached again. The characteristic values such as melting temperature (T_m), crystallization temperature (T_c) and enthalpy of fusion (ΔH_m) were determined using TA Universal analysis software. The introduction of long-chain branches changes the polymer structure and thus influences the crystallization behavior. For this reason, DSC measurements are based on the crystallization temperatures and the changes between unmodified and modified PP samples are compared. For long-chain branched samples, the crystallization temperature increases in comparison to linear PP and thus provides higher values.[171, 172]

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5. Summarized Findings

This work focus on the introduction of long chain branching into PP and PP post-consumer waste (PCR). Two options were tackled to introduce the long-chain branching: Grafting with monomers and branching by peroxides. Since a higher extrusion temperature is mandatory for industrial applications in view of higher output rates, the reactive extrusion temperature was elevated, and the degradation behaviour which is enhanced by elevated temperatures, could be controlled. Rheology measurements proved to be a very good tool for detecting degradation and property changes caused by the long-chain branching.

In this thesis the rheological properties (dynamic rheology and MFR measurements), mechanical properties (tensile test and impact tensile test) as well as thermal properties (DSC measurements) were investigated. For the final proof of the introduction of long chains at the backbone of PP, measurements of extensional rheology were conducted at three different strain rates (0.1 s^{-1}, 1 s^{-1} and 5 s^{-1}).

In order to achieve long-chain branching, potential grafting variants with different monomers were investigated. The combination of 2.5-Dimethyl-2.5-di-(tert-butylperoxy)-hexane (20 mmol/kg PP) and styrene (580 mmol/kg PP), which according to Kamleitner et al. [100] already provided very good results, served as a reference system. In addition, various biocompatible monomers (2-Phenyl-2-oxazoline; Vinylbenzoate; Vinyldecanoate; Vinylcaproate) were used with a concertation of 580 mmol/kg PP to replace the "toxic" component styrene. During the use of the biocompatible monomers, the PP was very strongly degraded, which indicated that grafting by using the peroxide (2.5-Dimethyl-2.5-di-(tert-butylperoxy)-hexane) could not be carried out successfully.

To simulate process-like conditions as they are typical in industry, the reactive extrusion was increased from 180 °C to 240 °C. Grafting by using styrene and 2.5-Dimethyl-2.5-di-(tert-butylperoxy)-hexane and the associated reactive extrusion temperature was gradually increased to 180 °C, 200 °C, 220 °C and 240 °C. The rheological investigations and finally the time test indicated that the combination with styrene leads to a drastic degradation of the PP, which is shown in Figure 31. For the time test, 230 °C was selected as the measurement temperature to correlate with the MFR measurement. The measurement was carried out in a nitrogen atmosphere with an amplitude of 1.46 % and an angular frequency of 1.58 rad/s.

However, it must also be noted that for the pure material, the increase in the reactive extrusion temperature results in a significant decrease in viscosity, and thus the material is significantly damaged.

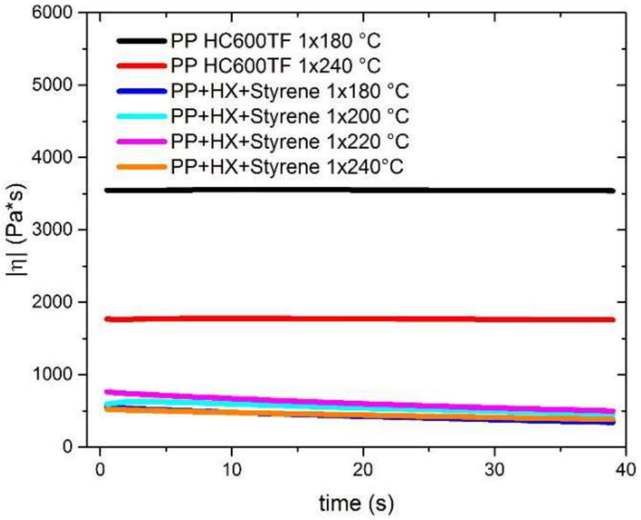


Figure 31: Time test of PP HC600TF and their impact of temperature and by using styrene in combination with 2.5-Dimethyl-2.5-di-(tert-butylperoxy)-hexane

In addition to the possibility of grafting, the branching behaviour of different peroxides (Di-tert-butyl peroxide; Bis(1-methyl-1-phenylethylene) peroxide; tert-Amyl peroxy-2-ethylhexylcarbonate; tert-Butyl peroxy-2-ethylhexylcarbonate; tert-Butyl peroxyisopropyl-carbonate; Dimistryl peroxydicarbonate; Dilauroyl peroxide) and the associated changes in the properties of PP were characterised. When selecting the peroxides, however, it was also necessary to take into account the hazards and risks that could result from them and the effects they have on humans and the environment. Di-tert-butyl peroxide and bis(1-methyl-phenylethylene) peroxide) are classified in the REACH list (Registration, Evaluation, Authorisation of Chemicals) as toxic to plants, persistent, bioaccumulative, mutagenic and toxic. However, these two peroxides with a concentration of 20 mmol/kg PP showed an increase in mechanical properties as well as strain hardening. In view of the toxicity and its effect, these two peroxides were only used as a comparison and were ultimately not pursued further. Five further peroxides with more moderate properties remained for further investigations. These peroxides are part of different classes of peroxides and belong to the groups of peroxy esters (tert-Amyl peroxy-2-ethylhexylcarbonate; tert-Butyl peroxy-2-ethylhexylcarbonate; tert-Butyl peroxyisopropyl-carbonate), diacyl peroxides (Dilauroyl peroxide) and peroxydicarbonate (Dimistryl peroxydicarbonate). The differences of the chemical structure and their decomposition products into symmetric or asymmetric products at a reactive extrusion temperature of 180 °C as well as 240 °C were analysed. The peroxide concentration for all was 20 mmol/kg PP based on their molecular mass. **(Publication I)**

Reactive extrusion is a very popular method for generating long-chain branches due to its fast reaction times, simple infrastructure and ease of use. During the process, radical polymerisations result from the use of peroxides, which decompose into radicals by thermal impact. In addition to the desired LCB reaction, possible side reactions such as disproportionation or cross-linking can occur with regard to the monomers, but also β-scission, especially in the case of PP. Due to the numerous reaction possibilities, the mechanism of how LCB occurs by means of peroxydicarbonates is widely unclear. A first assumption about a possible reaction mechanism was made by Lagendijk.[91] This is shown in Figure 8 in chapter 2.1.4. He assumes that alkyl carbonate groups are formed by the decomposition of peroxydicarbonates, which react further with the PP used by hydrogen abstraction. The decomposition reaction of peroxydicarbonate was also described by Buback et al. [173] and shown by electron spray ionisation mass spectroscopy of the peroxide end groups. The radical centres, which formed on the PP can subsequently react through radical recombination's with regard to other PP chains as well as peroxide radicals and thus form the LCBs. In principle, it is also possible that the radicals polymerise with the products formed by β-scission. Dilauroyl peroxide, which was explained in more detail by Takamura et al. [109], shows a similar decomposition product to peroxydicarbonate (Dimistryl peroxydicarbonate). This leads to the hypothesis that this peroxide behaves similarly to peroxydicarbonate in terms of the reaction mechanism, since dilauroyl peroxide also has the same symmetrical structure as peroxydicarbonate.

The use of peroxides during reactive extrusion generally led to a degradation of the material at both extrusion temperatures 180 °C and at 240 °C. This could be seen from the MFR values, which increased compared to the original material, but also from the dynamic rheological tests (viscosity, G´ and G´´). The degradation behavior for the PP was significantly stronger for the asymmetric peroxides than when using the symmetric peroxides. The introduction of LCB at the backbone of PP was successfully demonstrated by the use of the peroxides in all cases, at both reactive extrusion temperatures 180 °C and at 240 °C. At the given conditions, the symmetrical peroxides (Dimistryl peroxydicarbonate and Dilauroyl peroxide) showed an increase or at least a constant elongation at break, but also in the case of impact strength. Comparing all these components determined in this study, the symmetric peroxides showed a better performance compared to the asymmetric peroxides. In addition, these results show promising "upcycling" possibilities for PP recyclates by modifying with Dimistryl peroxydicarbonate and Dilauroyl peroxide. **(Publication I)**

The degradation behavior of PP and the introduction of long chain branches always oppose each other and behave like an equilibrium. The temperature plays an important role because at an elevated temperature the equilibrium of PP shifts towards degradation **(Publication I)**, but also the concentration of the peroxide used can lead to degradation due to the radicals released during the reaction. Therefore, the influence of the concentration was investigated by using Dimistryl peroxydicarbonate and Dilauroyl peroxide. For this purpose, a concentration series of 10, 20, 100 and 200 mmol/kg PP of these two peroxides was used **(Publication II)**. It was found that even with low concentrations the introduction of long chain branching was possible and by higher concentrations a reasonable compromise between degradation and LCB can be reached. Furthermore, the behavior of the already modified LCB-PP after the first extrusion step at 180 °C (the actual reactive extrusion step) was investigated after a further additional extrusion step at 240 °C. This second extrusion step was intended to reflect industrially oriented processing. **(Publication II)**

With the increase of the concentrations of peroxides, the degradation of the PP was also increased, which was basically expected due to the tendency of the PP to β-scission. This could be shown by the investigations of the melt flow properties. In order to prevent further degradation of the already branched material during reprocessing, Irganox 1010 was used as a stabilizer. By using Irganox 1010 (0.5 wt%), it was possible to counteract the degradation behavior in the second extrusion step at 240 °C. **(Publication II)**

The thermal investigation by means of DSC showed a trend towards higher values for the crystallization temperature as well as for the melting enthalpy at the lower concentrations and then dropped again as the concentration increased. This was the case for both Dimistryl peroxydicarbonate and Dilauroyl peroxide. When investigating the elongation behavior, it was found that no clear trend can be established whether the concentrations or the single or double extrusion play a role. However, in general it can be said that the elongation rheology measurements detected a strain hardening behavior in all modified samples. The elongation at break study for the first extrusion step at 180 °C showed that the modified samples with Dimistryl peroxydicarbonate followed the same trend as virgin PP. In contrast, the modification with Dilauroyl peroxide demonstrated a significant increase at this temperature. This effect was observed after the second extrusion at 240 °C for both peroxides. In comparison, the impact strength was drastically increased with increase in the concentrations of peroxides. **(Publication II)**

In addition to the homopolymers, block-copolymers are also studied, such as Eltex Tub 350-HM00, Total PPC 16040 and Borealis PP BA202E. These materials are all characterized by high stiffness and are used in various pipe applications. It was found that when using copolymers, the introduction of long chain branching by means of peroxydicarbonates proved to be difficult. As can be seen in Figure 32, Eltex Tub 350-HM00 and Total PPC16040 no indication of long-chain branching in extensional rheology is visible. Whereas with PP BA202E a slight deviation of the strain hardening curves can be seen which indicating strain hardening. One possible explanation for this behavior is the low MFR value of the Eltex Tub 350-HM00 and Total PPC 16040 materials used. This is 0.3 g/10 min, compared to 0.85 g/10 min for PP BA202E. Due to the higher molecular weight, it could be possible that the peroxydicarbonate cannot react with the PP chains during reactive extrusion and thus long chain branching may not occur.

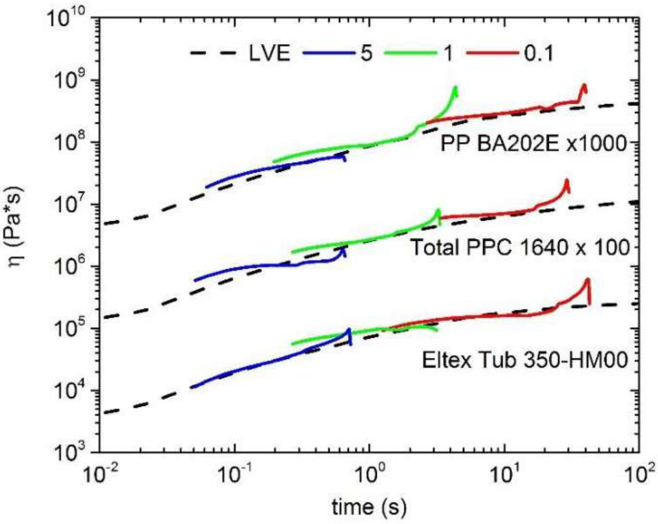


Figure 32: Elongation rheology of modified copolymers

A major goal of this work was to investigate PP post-consumer waste and to enhance the performance of the material and bring new application possibilities. To investigate this, flakes of yoghurt cups was modified with a concentration of 200 mmol/kg PP of peroxide (Dimistryl peroxydicarbonate and Dilauroyl peroxide). The modification of these flakes showed a significant strain hardening behavior at both processing temperatures as well as a dramatic increase in mechanical properties (elongation and impact strength). In this study could be shown that the direct use of peroxides allows successful "upcycling" of recyclates, which can be reused depending on the desired requirement profile. **(Publication II)**

The direct introduction of peroxides is not the only way to introduce long-chain branching to PP and thus improve the properties. This can also be achieved by mixing materials that already contain long-chain branching. Fang et al [79] and Stange et al [174] reported that the addition of LCB-PP as a blend material to new linear PP increases the melt stiffness and especially the work hardening. According to Mc Callum [175], the mechanical properties of virgin PP could also be increased by the addition of LCB-PP. Since the modification with 200 mmol/kg PP of Dimistryl peroxydicarbonate and Dilauroyl peroxide showed promising results for both virgin PP and recycled PP **(Publication II)**, this concentration was used for the implementation of the “masterbatches”. The homopolymer PP HC600TF was used for the production of the “masterbatches”, which was mixed with the appropriate concentration (200 mmol/kg PP) of Dimistryl peroxydicarbonate or Dilauroyl peroxide at a reactive extrusion temperature of 180 °C. The two “masterbatches” produced on the basis of Dimistryl peroxydicarbonate and Dilauroyl peroxide were used as blend material with an amount of 10 wt% in a further extrusion step. In order to be able to classify the performance possibilities and the results of these "masterbatches", a linear PP and a commercially available HMS-PP were also investigated by blending 10 wt% in the mixtures. The use of so-called "masterbatches" eliminates the problems associated with the use of peroxides on a large scale. By using "masterbatches" there are no storage problems in terms of temperature compared to the respective peroxides and also the handling during the process is much less dangerous. In this study, two virgin PPs (PP HD601CF and PP HF700SA) and three post-consumer waste PPs (flakes of coffee caps, flakes of buckets and flakes of yoghurt cups) with different MFR values were used as original material. The extrusion temperature, in which the blend materials were incorporated was carried out at 240 °C in order to be industry oriented. **(Publication III)**

The rheological results showed that the viscosity of the original materials could be improved or at least kept constant by using blends with “masterbatches”. This shows that this method could be carried out successfully although large differences in the MFR values had to be considered when blending the individual materials with the respective blending materials. The determination of the storage and loss modulus of the samples and its evaluation of the crossover point provided the result that the molecular weight as well as the molecular weight distribution could be broadened in comparison to the respective original materials. Another important finding was provided by the extensional rheology of the blends. Blends with the linear PP had no strain hardening, whereas by using the “masterbatches” a significant increase in strain hardening was observed. Thus, the properties can be enhanced by the use of “masterbatches” compared to linear PP used as blend material. Compared to the blends with HMS-PP, the two "masterbatches" were able to keep up in strain hardening. The mechanical properties also showed that the “masterbatches” produced were successfully modified in their blend series. Especially the impact tensile strength could achieve the best values for both compared to the other blend materials. Overall, the use of the long-chain branched “masterbatches” based on Dimistryl peroxydicarbonate and Dilauroyl peroxide provides an improvement in all areas such as melt flow properties, melt strength properties and mechanical properties. As a result, such modified "masterbatches" with peroxides could become very relevant for the "upcycling" of PP in the future. Especially the results of the PP post-consumer waste starting materials in this study were very successful and promising in consideration of new recycling opportunities.

With regard to the recycling of plastics, grade purity is still a major requirement that must be fulfilled. However, as PP covers a wide range of products and is used in many different areas, from pipes to consumer goods and packaging materials, it is possible that different streams are mixed together during recycling. These have different melting properties, which in turn are reflected in the MFR and thus make processing more difficult. In order to investigate the miscibility of PPs with different molecular weights, four different PPs were studied as virgin materials and were used as binary blends as well as a quaternary blend (25:25:25:25). This was intended to simulate a mixed fraction that could also possibly arise during recycling. The studies were carried out at 180 °C (laboratory conditions) and 240 °C (process simulation). In addition, a further processing temperature was investigated to find a possible average value at 200 °C.

The following abbreviations are used in Figure 33 and Figure 34 as well as for the Table 14:

- PP1 → PP HA104E
- PP2 → PP HC600TF
- PP3 → PP HD601CF
- PP4 → PP HF700SA

A study series was carried out without Dimistryl peroxydicarbonate and one with 20 mmol/kg PP Dimistryl peroxydicarbonate to show a possible introduction of LCB in comparison. The following results have all been analyzed at a processing temperature of 200 °C and are also exemplary for the other processing temperatures.

Figure 33 compares the MFR values of the two series. The unmodified materials and blends show that they are easily miscible at 200 °C and thus have a certain compatibility with each other. The same trend can be observed for the modified PPs and blends. In addition, the use of 20 mmol/kg PP Dimistryl peroxydicarbonate does not lead to strong degradation of the materials at this reactive extrusion temperature.

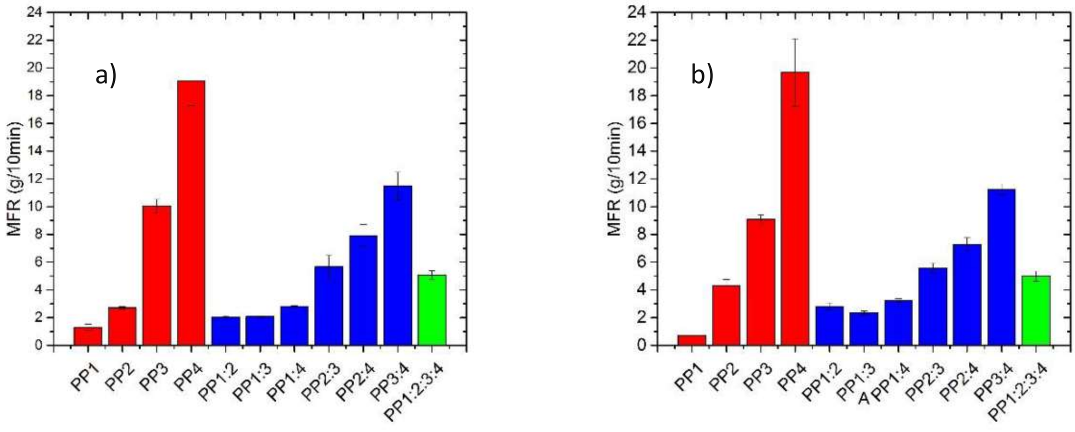


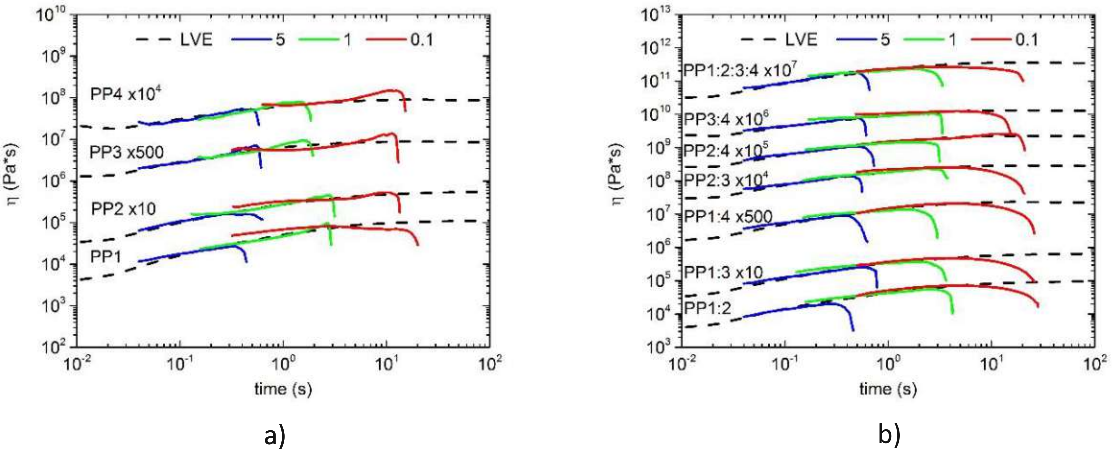
Figure 33: MFR values of (a) unmodified and (b) modified PP samples and PP-blends after a extrusion temperature of 200 °C; measured at 230 °C and 2.16 kg load

Looking at the mechanical properties in Table 14, it becomes clear that the modulus of elasticity decreases slightly by modifying with Dimistryl peroxydicarbonate, the elongation at break remains constant throughout and the impact strength is significantly increased. This could already indicate a successful introduction of long chain branching.

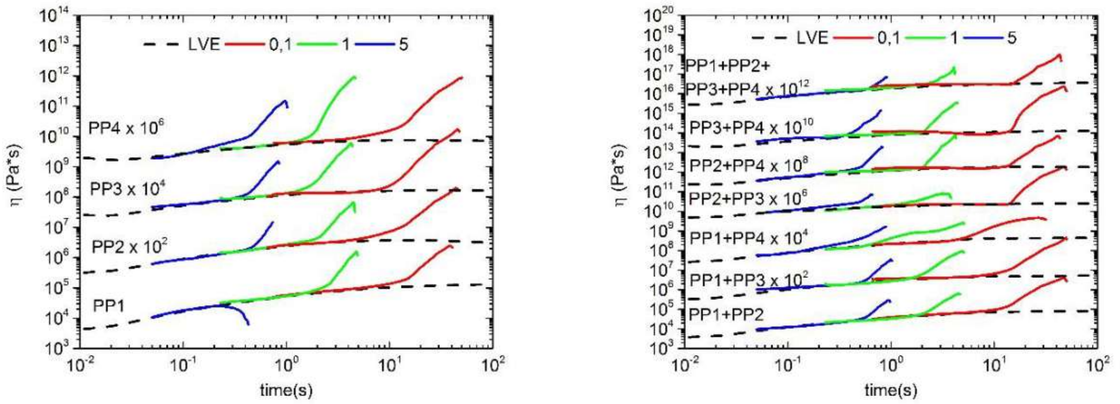
Table 14: Summarizing mechanical properties of all samples

Samples	Without Dimistryl peroxydicarbonate			With Dimistryl peroxadicarbonate		
	E_t (MPa)	ε_B (%)	a_{tN} (kJ/m^2)	E_t (MPa)	ε_B (%)	a_{tN} (kJ/m^2)
PP1	2203 ± 115	438 ± 100	66 ± 8	2001 ± 116	251 ± 126	118 ± 17
PP2	2240 ± 120	597 ± 102	54 ± 11	1643 ± 68	702 ± 94	79 ± 6
PP3	2228 ± 81	593 ± 46	40 ± 6	2019 ± 185	576 ± 21	68 ± 10
PP4	2148 ± 146	499 ± 107	29 ± 3	1740 ± 174	45 ± 25	46 ± 5
PP1:2	2430 ± 179	613 ± 63	54 ± 9	2176 ± 156	540 ± 85	94 ± 12
PP1:3	2358 ± 142	623 ± 96	48 ± 5	2252 ± 282	590 ± 87	73 ± 6
PP1:4	2390 ± 82	555 ± 113	50 ± 8	2062 ± 124	545 ± 36	70 ± 7
PP2:3	2250 ± 166	545 ± 24	35 ± 7	2341 ± 84	635 ± 70	57 ± 3
PP2:4	2432 ± 64	638 ± 74	39 ± 6	2254 ± 206	594 ± 40	56 ± 4
PP3:4	2471 ± 103	581 ± 71	38 ± 6	2219 ± 120	588 ± 24	54 ± 5
PP1:2:3:4	2436 ± 105	555 ± 71	47 ± 6	2350 ± 248	461 ± 92	67 ± 7

The elongation rheology curves of all samples are shown in Figure 34. It can be clearly seen that there is a deviation of the elongation rheology curves from the start-up curve and that all modified samples show strain hardening.



a) b)



c) d)

Figure 34: Elongation rheology of all (a) unmodified and (c) modified PP samples and all (b) unmodified as well as (d) modified PP-blends

Basically, this study showed that it is possible to mix different PPs with different molar masses and to modify them with Dimistryl peroxydicarbonate in order to increase the properties or to extend the property portfolio compared to the original material. The blend of all PPs should show that it is possible to recycle or upcycle from different PP streams.

Within the framework of the project [176], it was shown, that no introduction of LCB on PP filled with talc or glass fiber reinforced was possible, (no strain hardening was observed by using extensional rheology). It was supposed that the filler used interferes with the reactive extrusion or that it reacts preferentially with the peroxide radicals, thus inactivating them.

Based on highlighted results in Publication III, a further attempt was undertaken and the possibility of introducing LCB indirectly was tried. For that reason, filled polymer systems have been blended with these "masterbatches". For this study, two materials were used, one filled with talc (40%), PP MD441U (VPP1), and one with glass fiber (30%), PP GB311U (VPP2). The processing temperature was 240 °C and 10 wt% “masterbatch” based on Dimistryl peroxydicarbonate (MB-Podic) and Dilauroyl peroxide (MB-LP) was added. The MFR values and the mechanical property values such as modulus of elasticity, elongation at break and impact strength are given in the Figure 35. Looking at the series of VPP1, the MFR value increases due to the modification with Dimistryl peroxydicarbonate and also due to the use of the “masterbatches”. When blending with the “masterbatches”, the increase in MFR values is related to the fact that the “masterbatches“ have MFR values of 7.7 (MB-PODIC) and 6.0 g/10min (MB-LP). The impact strength and elongation at break remain more or less constant for the VPP1 series, whereas the modulus of elasticity, which is very high for PP, decreases slightly. For the series of VPP2 it can be summarized that the MFR values and the impact strength remain almost constant when using the “masterbatches” compared to the original material. The modulus of elasticity decreases slightly, while the elongation at break increases a little. All in all, no major changes in the mechanical properties could be achieved by using the “masterbatches”.

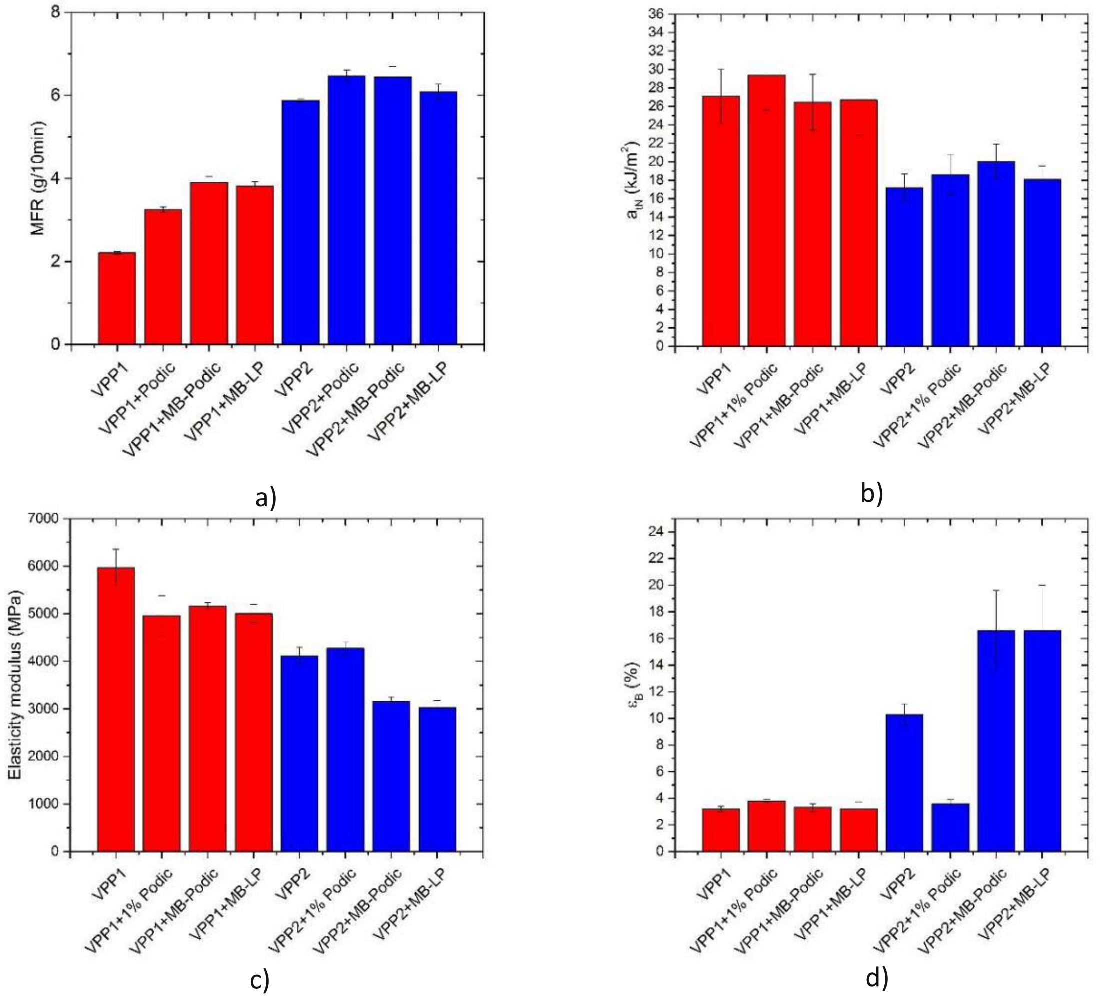
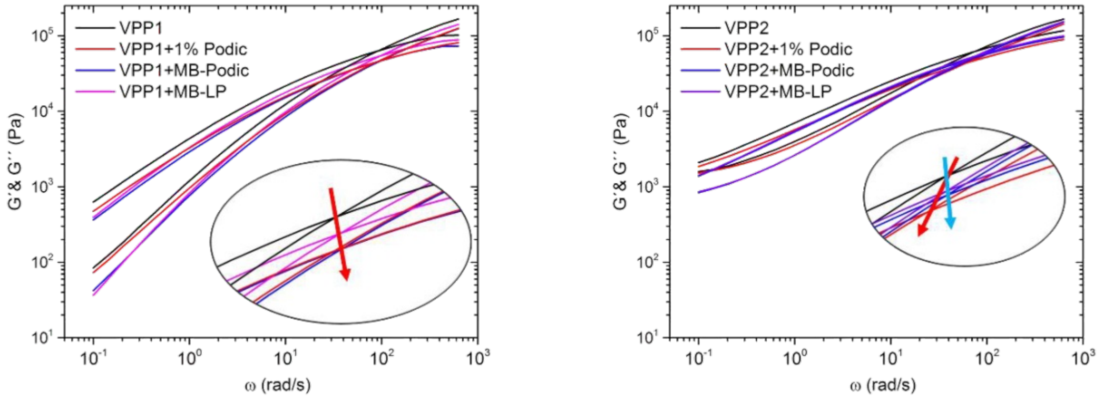


Figure 35: MFR values (a) and mechanical properties, tensile impact strength (b), elasticity modulus (c), elongation at break (d) of all samples

In addition to the mechanical properties, the rheological properties and the effects of the “masterbatches” were also investigated. The curves of G' and G'' of the respective specimens are shown in Figure 36. VPP1 clearly shows that the crossover point moves towards the lower right, which leads to a degradation and to a broadening of the molecular weight distribution. Looking only at the effects of the “masterbatches” in the series of VPP2, the same trend as in VPP1 can be seen. The only difference compared to VPP1 is that the direct modification carried out in [176] has another trend and display increase of the molar mass. In addition, VPP2 tends to cross-link as at low frequencies the curve of G' and G'' are converging again and almost form a second crossover point. For a possible explanation of this unexpected curve progression, gel content determinations should be made and could provide information.

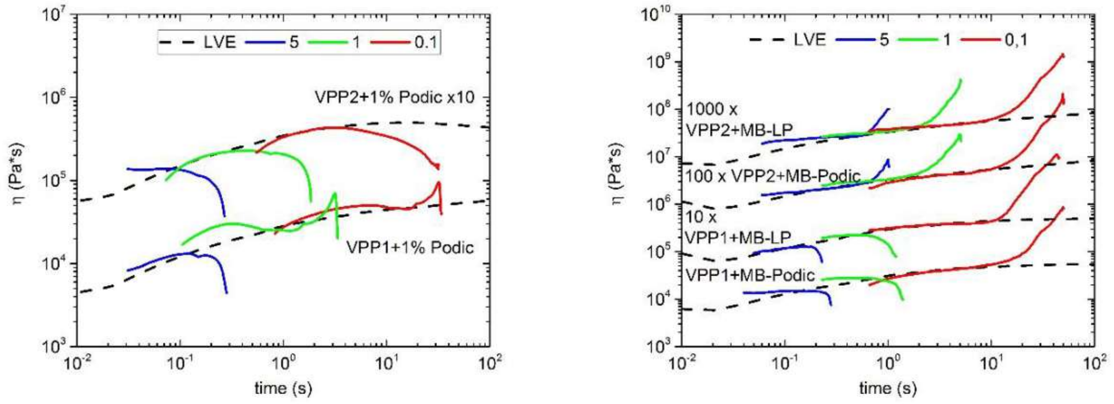


a)

b)

Figure 36: Dynamic rheology measurements of all samples; measured at 230 °C

Finally, the elongation rheology of the respective samples was examined to determine if there are long-chain branches and thus if strain hardening is detectable (Figure 37). The direct modification did not show any strain hardening in both materials, whereas in VPP1 a clear strain hardening is visible at least at the strain rate of 0.1 s^{-1} by blending with “masterbatches”. After considering the elongation rheology, an improvement of the properties of the filled system can be assumed by using “masterbatches”, which makes the indirect method suitable for filled systems.



a)

b)

Figure 37: Elongation rheology of all samples; measured at 180 °C

6. Concluding Statement & Outlook

The research carried out within the framework of this thesis has led to finding a way to not only recycle polypropylene but to improve the properties and thus provide a possible "upcycling", which allows the PP to be used in new applications.

Basically, it was shown that the use of peroxides is suitable for directly modifying the polypropylene by means of reactive extrusion and thus achieving long-chain branching. Two classes of peroxides have proven to be highly effective. One is Dimistryl peroxydicarbonate and the other is Dilauroyl peroxide. **(Publication I)**

Another result of this thesis was to use high concentrations of these two peroxides (100 or 200 mmol/kg) to investigate their behavior with regard to single and double extrusion. The highlight, however, was that the modification was very successful also on PP post-consumer waste. It can be used as a potential "upcycling" method for recycling material **(Publication II)**

For the production of the so-called “masterbatches”, virgin PP (PP HC600TF) was modified with a concentration of 200 mmol/kg PP Dimistryl peroxydicarbonate or Dilauroyl peroxide at a reactive extrusion temperature of 180 °C. The use of "masterbatches" based on Dimistryl peroxydicarbonate and Dilauroyl peroxide by blending with an amount of 10 wt% showed a clear trend. The blends also led to an improvement in the respective material properties of various virgin PPs and also recycled PP samples such as yoghurt cups, buckets or coffee caps. **(Publication III)**

In addition, it could be shown that the miscibility of different PPs was possible and the introduction of LCBs by using Dimistryl peroxydicarbonate was possible also in blends of PP with different molar masses. This allows an "upcycling" of these different PPs. Furthermore, it was possible to partially circumvent the problem with the filled PPs by using “masterbatches” and to achieve a successful improvement of the elongation rheological properties here as well.

Overall, the present work offers a promising opportunity for the recycling of polypropylene and potentially a way to take a step in the direction of sustainability in the future. It was shown that the modification of PP by the direct method could be carried out very successfully at different conditions (temperature, extrusion steps, peroxide concentration). In addition, the indirect modification by using "masterbatch" via compounding turned out to be a promising method to upgrade virgin PP and recycled PP.

Looking forward to these results, the following points would be of interest and would make sense in further work.

- The reaction mechanism and the LCB behavior of Dimistryl peroxydicarbonate and Dilauroyl peroxide during reactive extrusion should be investigated.
- With regard to Dimistryl peroxydicarbonate and Dilauroyl peroxide, a scale-up to a larger extruder that is used in industry would be very informative with regard to its influencing factors such as temperature, mechanical shearing but also handling. The LCB behavior on larger quantities of virgin PP and recycled PP could be used and investigated.
- Based on the excellent melt strength properties obtained from this work on virgin PP and recycled PP, these modified materials could be used in new applications such as films. For this purpose, it would be advisable to test the LCB-PPs on a film blowing line and determine their properties.
- For the further processing of the “masterbatches”, the use of stabilizers such as Irganox 1010 could be considered and what effects this has on the reprocessing of the material.
- Concerning the “masterbatches” based on Dimistryl peroxydicarbonate and Dilauroyl peroxide, it would be promising to apply the production of these already on recycled PP and to use this again for recycled materials. This would create a closed cycle and open up new possibilities with regard to the "plastics problem". First successful experimental results could be obtained here.
- Further studies could be carried out with the “masterbatches” for filled systems. To find out where the limits are and to investigate a possible dependency on the filler content.

polymers

MDPI

Article

Influence of Different Types of Peroxides on the Long-Chain Branching of PP via Reactive Extrusion

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Abstract: Long-chain branching (LCB) is known as a suitable method to increase the melt strength behavior of linear polypropylene (PP), which is a fundamental weakness of this material. This enables the modification of various properties of PP, which can then be used—in the case of PP recyclates—as a practical "upcycling" method. In this study, the effect of five different peroxides and their effectiveness in building LCB as well as the obtained mechanical properties were studied. A single screw extruder at different temperatures (180 and 240 °C) was used, and long-chain branched polypropylene (PP-LCB) was prepared via reactive extrusion by directly mixing the peroxides. The peroxides used were dimyristyl peroxydicarbonate (PODIC C126), tert-butylperoxy isopropylcarbonate (BIC), tert-Butylperoxy 2-ethylhexyl carbonate (BEC), tert-amylperoxy 2-ethylhexylcarbonate (AEC), and dilauroyl peroxide (LP), all with a concentration of 20 mmol/kg. The influence of the temperature on the competitive prevalent reactions of degradation and branching was documented via melt mass-flow rate (MFR), rheology measurements, and gel permeation chromatography (GPC). However, via extensional rheology, strain hardening could be observed in all cases and the mechanical properties could be maintained or even improved. Particularly, PODIC C126 and LP signaled a promising possibility for LCB in this study.

Keywords: polypropylene; reactive extrusion; peroxide; long-chain branching; strain hardening

1. Introduction

In 2018, the global production of plastic amounted to 359 million tons, in other words an increase in the order of 3% compared to 2017. Various plastic products are used in a wide range of different applications. The three biggest markets of plastic products are packaging (39.9%), building and construction (19.8%), and automotive (9.9%). In these three areas, polypropylene (PP) is strongly represented, for example, in sectors such as food packaging, hinged caps, microwave containers, pipes, automotive parts, bank notes, etc. Taking into consideration the separation of low-density polyethylene (PE-LD) and high-density polyethylene (PE-HD) into two independent groups, PP (with an amount of 19.3%) was the most relevant polymer for the production of plastic products in 2018 [1].

PP's significance is due to desirable characteristics, such as excellent chemical resistance, high melting point, high tensile modulus of elasticity, high stiffness, low density, and low cost. It also shows excellent flexural fatigue resistance, can be stabilized to provide good thermal aging stability, and is easy processed by injection molding, extrusion, and spinning [2,3]. Nevertheless, linear, i.e. unmodified, PP is challenging in processes like thermoforming, film blowing, blow molding, extrusion coating, and foaming, because of the lack of melt strength and strain hardening [4].

Over the past few years, different basic concepts have been studied in the literature to achieve high melt strength PP (PP-HMS) using different methods [5–9]. According to Chikalikar et al. [10], it is possible to increase the melt strength of PP in different ways:

- Increasing the average molecular weight of PP
- Broadening the molecular weight distribution by incorporating high and low molecular weight chain fractions
- Blending PP with polymers such as PE-LD
- Introducing long-chain branching (LCB) on the backbone of PP, which is the most popular method to obtain PP-HMS
- PP-LCB can be achieved in different ways, but reactive extrusion is the most popular process. This type of process offers very short reaction times, little or no use of solvents, simple product isolation steps, and relatively low infrastructure costs [11,12]. In the literature, PP-LCB is a well-studied topic with different approaches to improve the properties of linear PP and their disadvantages [13–22]. In addition to introducing LCB onto the backbone of PP, further competition reactions can take place. PP in particular tends to undergo chain scission reactions, so-called β-scission, which creates smaller unsaturated fragments of chains [23,24]. There is a possibility that cross-linking occurs, but a prediction of this phenomenon is very difficult. The phenomenon of β-scission caused by the use of peroxides is also known as controlled rheology PP (PP-CR). This leads to a reduction in viscosity, which results in a reduction in average molar mass and a narrowing of PP's molar mass distribution (MMD) [25]. Additional side reactions could occur, such as disproportionation or a combination of free peroxide radicals. In particular, at higher temperatures, the equilibrium shifts to β-scission or disproportionation, which negatively affects the branching [24]. For this reason, the extrusion temperatures in scientific works are mainly at lower temperatures (180 °C). However, in practice, high temperatures have been used for the extrusion process, which means that additional effects may have occurred such as increased chain scission or different reaction rates during the extrusion. Figure 1 shows a schematic representation of the LCB reaction process confronted with the β-scission of PP. In the first step, the peroxide decomposes under homolytic scission into two primary radicals, which abstract a hydrogen atom from the PP backbone and therefore a PP macroradical is generated. There are now two possible reactions that can take place—on the one hand, the LCB, and on the other hand, the β-scission of PP [26,27].

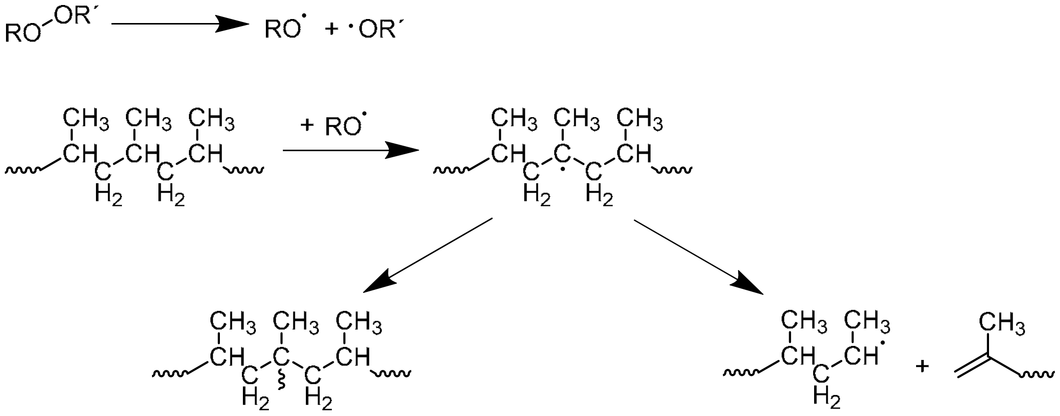


Figure 1. Reaction scheme of long-chain branching (LCB) confronted with β-scission of polypropylene (PP).

Lagendijk et al. [28] and Gotsis et al. [29] demonstrated that reactive extrusion using peroxydicarbonate (PODIC), a special class of organic peroxides with different lengths of aliphatic side chains, is a promising method to generate PP-LCB. In recent studies undertaken by our group, we demonstrated that PODIC could be used for upcycling linear isotactic PP with different molar masses and also that the properties of PP with impurities of PE could be improved successfully [30–32].

The LCB of PP via reactive extrusion depends on a number of various aspects such as mixing efficiency, shear rate, temperature, and residence time. One of the most important aspects is the choice of the peroxide, which has the largest impact on the reaction. Many attributes need to be addressed [12]. One of the most important attributes of peroxides is the initiator half-time, which is related to their efficiency. Furthermore, the maximum storage temperature is very important and presents a huge challenge to the storage facilities. The peroxide's primary requirement is the ability to abstract a H atom from the backbone of PP, making it possible to generate PP-LCB. This behavior has been investigated since peroxides play an important role in the modification of PP [33,34]. Klenk et al. [35] reported that peroxides can be classified into seven different types depending on their reactivity based on their chemical structure, namely diacyl peroxides, peroxyesters, diperoxyketals, dialkyl peroxides, hydroperoxides, ketoneperoxides, and peroxydicarbonates. Additionally, Takamura et al. [36] described the effectiveness of peroxides in cross-linking processes depending on their decomposition rates. Three groups of peroxides, that is, group I (diacyl peroxides), group II (peroxyesters), and group III (dialkyl peroxides), were investigated and showed an increase in the lifetime of the peroxides from group I to group III. The choice of the right peroxide plays an important role in generating PP-LCB and the associated opportunity to improve the properties of isotactic PP [27,37–39]. Therefore, the influence of five different peroxides and their long-chain branching behavior in conjunction with isotactic PP will is the topic of this study. In order to prove long-chain branching of PP and the associated property changes, the mechanical and rheological behaviors of the samples were investigated.

2. Materials and Methods

2.1. Materials

Five different peroxides supplied by Pergan GmbH (Bocholt, Germany) were used for the study, and the structure of each peroxide is shown in Figure 2. Differences can be seen in the structure of the peroxides and their decomposition products. The peroxides PODIC C126 (dimyristyl peroxydicarbonate; Pergan GmbH, Bocholt, Germany) and LP (dilauroyl peroxide; Pergan GmbH, Bocholt, Germany) provide two symmetrical reactive units. In comparison, the decomposition products of the peroxides tert-butylperoxy isopropyl carbonate (BIC; Pergan GmbH, Bocholt, Germany), tert-butylperoxy 2-ethylhexylcarbonate (BEC; Pergan GmbH, Bocholt, Germany), and tert-amylperoxy 2-ethylhexylcarbonate (AEC; Pergan GmbH, Bocholt, Germany) result in two unsymmetrical units.

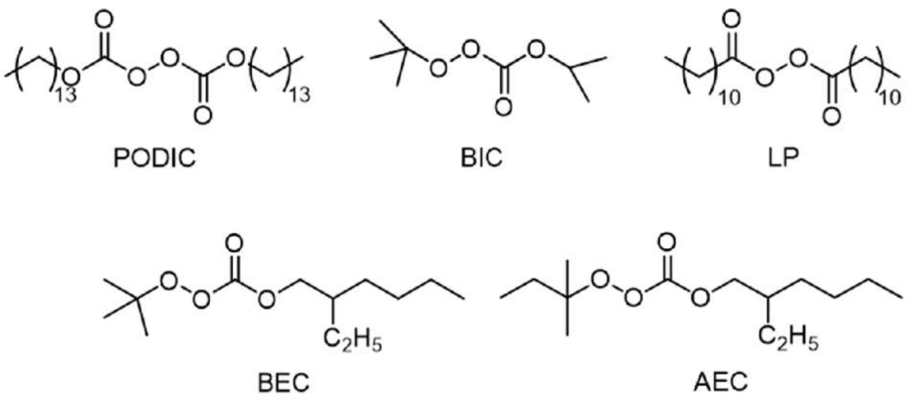


Figure 2. Schematic structure of the peroxides.

PODIC C126 (Peroxan C126, flakes) is used for the (co)polymerization of vinyl chloride and vinylidene chloride. BIC (Peroxan BIC, solution in odorless white spirits) is a peroxyester for the (co)polymerization of styrene, acrylates, and methacrylates and for the curing of unsaturated polyester resins. In addition, BEC (Peroxan BEC, liquid) and AEC (Peroxan AEC, liquid) are counted among the group of peroxyesters and both are also used for the (co)polymerization of styrene, acrylates, and methacrylates. LP (Peroxan LP, flakes) is an example for the diacylperoxide group and is used for the curing of highly filled methacrylic resins, typically with other peroxides of different reactivity. The characteristics of the different peroxides are summarized in Table 1.

Table 1. Characteristics of the peroxides.

Peroxide	CAS-No.:	Max. Storage Temperature (°C)	Molecular Weight (g/mol)	Active Oxygen Assay (%)	10 h Half-Life Temperature (°C)
PODIC C126 *	53220-22-7	15	514.8	2.95	48
LP *	105-74-8	30	398.6	3.97	61
BIC **	2372-21-6	25	176.2	6.81	98
BEC **	34443-12-4	30	246.3	6.17	98
AEC **	70833-40-8	25	260.4	5.78	95

* symmetrical peroxide; ** unsymmetrical peroxide.

Isotactic PP homopolymer with a melt mass-flow rate (MFR) of 2.8 g/10min was supplied by Borealis (HC 600TF, Vienna, Austria). This is a PP grade for different thermoforming applications.

2.2. Sample Preparation

The sample preparation i.e., the reactive extrusion, was done in an Extron EX-18-26-1.5 single screw extruder (Extron Engineering, Ltd, Akaa, Finland) with an length/diameter (L/D) ratio of 25:1 and 3 independent heating zones (feeding zone, extrusion zone, and die zone). The screw had the following dimensions: screw diameter of 18 mm, channel depth of 1 mm, pitch length of 14 mm, and flight width of 2.5 mm. The reactive extrusion was carried out with a screw speed of 70 rpm at 180 (165, 180, and 220 °C) and 240 °C (165, 240, and 240 °C) to simulate industry-related requirements. According to Giles et al. [40], the calculation of the shear rate ($\dot{\gamma}$) in an extruder screw is done by using Equation (1), where D is the screw diameter in mm, N is the screw speed in rpm and h is the channel depth in mm. Therefore, a shear rate of 66 s^{-1} in the screw channel of the extruder was calculated according to the above-mentioned parameters.

$$\dot{\gamma} = (\pi \times \mathrm{D} \times \mathrm{N}) / (60 \times \mathrm{h}) \tag{1}$$

The different peroxides were directly mixed with the PP granulate and added to the extruder. All formulations had the same peroxide concentration (20 mmol) with respect to their molar mass, whereby the various contents of percent by weight (wt %) occur. Sample names and compositions are given in Table 2.

Table 2. Sample compositions and processing temperatures.

Sample	Extrusion Temperature (°C)	Sample Specification
PP 180/PP 240	180/240	Virgin PP granulate
PODIC 180/PODIC 240	180/240	20 mmol/kg PODIC C126 (1 wt %)
BIC 180/BIC 240	180/240	20 mmol/kg BIC (0.5 wt %)
BEC 180/BEC 240	180/240	20 mmol/kg BEC (0.5 wt %)
AEC 180/AEC 240	180/240	20 mmol/kg AEC (0.5 wt %)
LP 180/LP 240	180/240	20 mmol/kg LP (0.8 wt %)

For further sample preparation, the modified PP compositions were shredded with a universal cutting mill "Pulverisette 19" (Fritsch, Idar-Oberstein, Germany) with a 4 mm square perforation sieve and a high-performance cyclone to achieve a better separation.

2.3. Characterization of Molar Mass and Viscosity

The characterization of the molar mass and the viscosity of the different samples was done by using dynamic rheology measurements, extensional rheology, high-temperature gel permeation chromatography (HT-GPC), and MFR measurements.

For the dynamic rheology, i.e., the frequency sweep, measurement discs with a diameter of 25 mm and a thickness of 1.2 mm were compression-molded at 180 °C or 240 °C and a pressure of 30 bar. The dynamic rheology was done on a plate–plate system using an Anton Paar MCR 301 rheometer (Graz, Austria), which was equipped with a CTD 450 heating chamber (Anton Paar, Graz, Austria) under nitrogen at 230 °C. This temperature was selected to obtain a better correlation between the dynamic rheology results and the MFR measurements, which used the same temperature. The gap size was 1 mm, the chosen frequency range was between 628 and 0.01 rad/s, and the deformation during measurement was raised logarithmically from 1% to 2%.

For extensional rheology, 8 mm wide stripes were cut from sheets with dimensions of 60 mm × 60 mm × 0.8 mm, which were produced by compression molding at 180 °C or 240 °C. A Sentmanat Extensional Rheometer (SER-HPV 1, Xpansion instruments, Tallmadge, OH, USA) for Anton Paar rheometers was used at 180 °C and with three different strain rates ($\dot{\varepsilon} = 5\ \mathrm{s}^{-1}$; $1\ \mathrm{s}^{-1}$; $0.1\ \mathrm{s}^{-1}$). The steady shear experiments for the start-up curves were done with a plate–plate system at 180 °C and two different shear rates ($0.001\ \mathrm{s}^{-1}$ and $0.1\ \mathrm{s}^{-1}$).

The molar mass distribution (MMD) was determined on a high-temperature size exclusion chromatographer (HT-SEC) from Polymer Char (Valencia, Spain). The measurements were carried out at 160 °C with 1,2,4-trichlorbenzene as eluent and, for the detection, an infrared detector (IR5-Detector, Polymer Char) was used.

The measurements of the MFR at 230 °C and under 2.16 kg weight were done according to the DIN EN ISO 1133 method A, in g/10min, with a MeltFloW basic (Karg Industrietechnik, Krailling, Germany).

2.4. Mechanical Testing—Tensile Test and Tensile Impact Strength

According to ISO 527-2-A5 the test specimens for tensile test were performed by injection molding with a Haake Mini Lab II (Thermo Fisher Scientific, Waltham, MA, USA). The temperature of the twin-screw extruder was selected between 180 °C and 240 °C. The injection molding parameters were set with a 90 °C mold temperature and an injection pressure of 350 bar. The test machine (Zwick 050, ZwickRoell GmbH & Co. KG, Ulm, Germany) was used with a test speed of 10 mm/min and was equipped with a 1 kN load cell and an extensometer.

The impact tensile test specimens (60 mm × 10 mm × 1 mm) were prepared by injection molding under the same conditions. The test specimens were notched on both sides and tested according to ISO 8256/1A on an Instron Ceast 9050 (2 J hammer, crosshead mass = 15 g; Darmstadt, Germany).

3. Results and Discussion

3.1. Melt Flow Properties

Lagendijk et al. [28] reported that the branched PP, which was modified with various structures of PODIC via reactive extrusion, showed a slightly lower MFR compared to that of the linear PP. Generally, the molecular structures of polymers affect the MFR at low shear rates. To determine the shear rate of the MFR equipment's die, the following Equation (2) can be used [41,42]. In this study, the virgin PP with an MFR of 2.8 g/10min has a shear rate value of approximately 5 s^{-1}.

$$\dot{\gamma} = 1.85 \times \text{MFR} \tag{2}$$

On the one hand, a high MFR value is the result of chain mobility because of the β-scission and, on the other hand, long-chain branching or cross-linking reduces the MFR values [27,43]. The MFRs of the unmodified and modified PP for this study under different extrusion temperatures are shown in Figure 3. It can be seen that the MFRs increase to high values for the unsymmetrical peroxides BIC, BEC, and AEC at 180 °C and 240 °C. In this case, the degradation and the associated β-scission of the PP chain are predominant. On the one hand, the peroxides are responsible for the scission; however, the temperature of the reactive extrusion is another aspect of the chain scission reaction, which is very important. The virgin PP that was extruded shows a slightly increasing MFR value in comparison to the virgin granulate with an MFR of 2.8 g/10 min. The symmetrical peroxides PODIC and LP show values minimally higher compared to that of the extruded PP. The modification with PODIC presents the lowest MFR value after extrusion at 180 °C and with LP presents the lowest MFR value at the 240 °C extrusion temperature. However, the modification with LP shows an unexpected behavior and does not follow the trend compared to that of the other peroxides. In all other cases, including the unmodified PP, the MFR values are higher at a modification temperature of 240 °C compared to 180 °C. This suggests that the temperature during extrusion plays an important role in the modification and branching of PP. The low MFR values for the PODIC and LP modifications is the first sign of the highest branching efficiency of these two types of peroxides in comparison to the unsymmetrical ones.

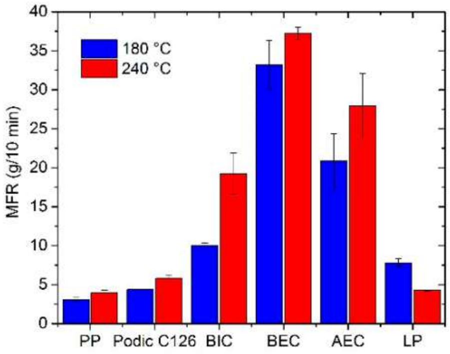
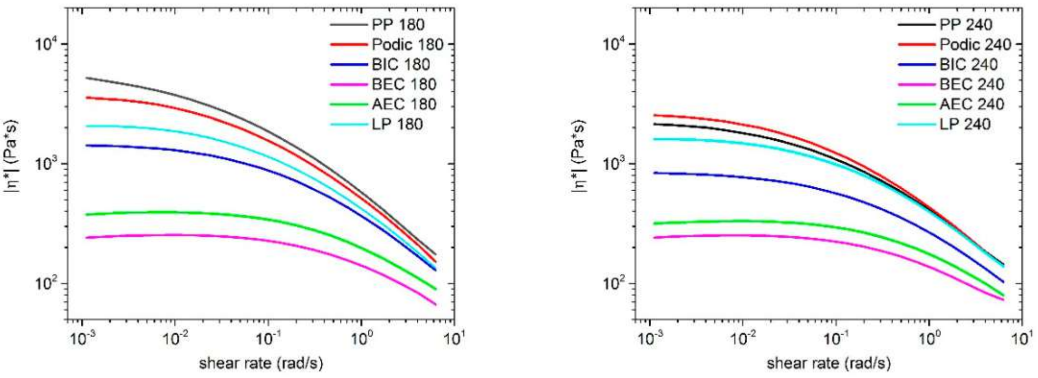


Figure 3. Melt mass-flow rate (MFR) of extruded PP (without peroxide) and modified PP (with different peroxides) at 180 °C and 240 °C; virgin PP has an MFR of 2.8 g/10 min.

3.2. Dynamic Rheology

In the literature, linear viscoelastic rheology is a very well established technique for the detection of LCB, due to the high sensitivity of the LCB structure and with its associated structure change of molecular chains [44–48]. The complex viscosity (η*) is very sensitive to the LCB structure and the peroxide-induced degradation of PP. On the one hand, the presence of very low LCB can change the zero-shear viscosity (η_0) and the shear thinning degree of modified PP [49]. On the other hand, the peroxide-induced degradation of PP and the resulting β-scission can also change these behaviors [25]. For a better comparison to the MFR values, the complex viscosity versus angle shear rate for all samples measured at 230 °C are shown in Figure 4. The samples reactively extruded at 180 °C are presented in Figure 4a, whereas those modified at 240 °C are presented in Figure 4b.



(**a**) (**b**)

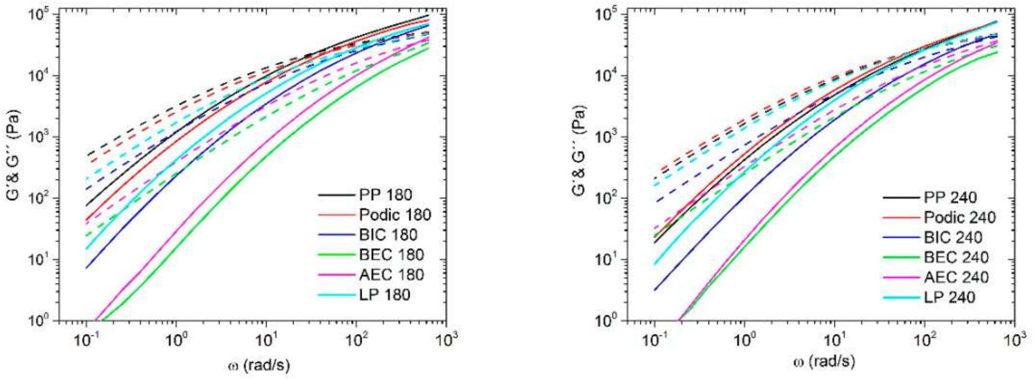
Figure 4. Complex viscosity versus shear rate of samples extruded at (**a**) 180 °C; (**b**) 240 °C; measured at 230 °C.

For the modification at 180 °C, the curves of all modified PP samples are located below the curve of the virgin PP. In the presence of the various peroxides, the complex viscosity decreased obviously at low frequency and the Newtonian zone became broader, caused by the chain scission during the peroxide-induced reactive extrusion process. However, PODIC and LP show approximately the same behavior as the virgin PP. In particular, PODIC and LP have a higher shear thinning behavior at higher frequencies compared to that of the unmodified PP. By adapting the process temperature to 240 °C, the shear thinning effect for PODIC and LP is even more pronounced. Particularly, PODIC at higher temperature shows an increasing complex viscosity compared to that of the unmodified PP. Moreover, the shear thinning effect was significantly more distinct with respect to the other samples. A higher viscosity compared to that of the virgin PP and a higher shear thinning effect at higher frequencies are an indication of a larger amount of LCB, which could be generated during the reactive extrusion at 240 °C.

In addition, the trend of the viscosity curves shows nearly the same trend as the MFR values. For example, the viscosity curves of BEC display the lowest viscosity level at both extrusion temperatures (180 and 240 °C), and therefore the highest MFR values.

In addition to the complex viscosity, the storage modulus G′ and loss modulus G″ (dashed lines) play an important role in the dynamic rheology. Both parameters provide information about viscous and elastic effects and the influence of shear rate or frequency on material functions [50]. The curves of G′ and G″ of 180 and 240 °C extruded materials are presented in Figure 5. In all cases except for PODIC at 240 °C, it can be observed that the curves i.e., the crossover point of the modified PP, tend to have higher frequencies. Furthermore, it can be seen that not each curve has a crossover point. In particular, BEC displays no crossover points in both cases, which is attributable to the high MFR values. Morshedian et al. [51] reported that as the MFR increases, the crossover point shifts to higher frequencies.

In the literature, it is well established that changes in molecular mass M_W and molecular mass distribution (MMD) of different polymers can be detected by the position change of the crossover point [51–54]. This means that there is a critical frequency ω_C and a critical modulus G_C for each crossover point. The vertical shift of G_C provides information about the MMD, which means that an increasing G_C indicates a narrower MMD. The change in M_W can be determined with the shift of ω_C. The horizontal shift towards higher frequencies indicates a decrease in M_w [55].



(**a**) (**b**)

Figure 5. Storage and loss moduli as a function of angular frequency of samples extruded at (**a**) 180 °C; (**b**) 240 °C; measured at 230 °C.

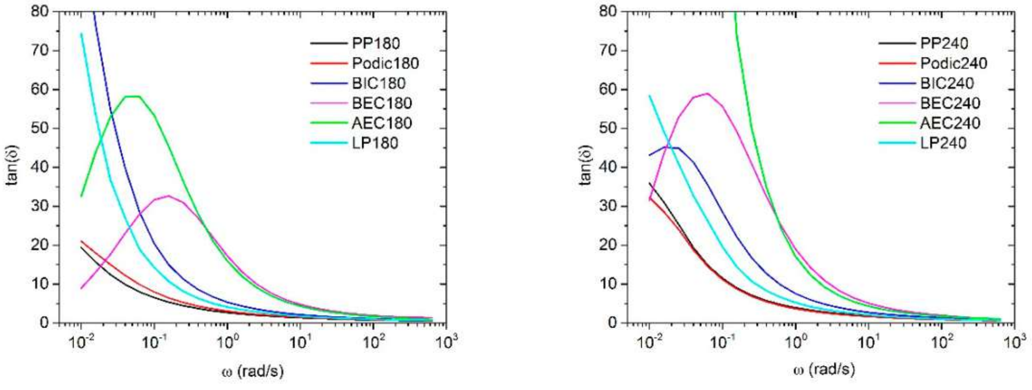
The values of ω_C and G_C of the unmodified and modified samples are presented in Table 3. At 180 °C, the modification with the peroxides leads to a lower molecular mass, which is represented by higher ω_C values compared to those of the unmodified PP. Moreover, the MMD is lower in comparison to the unmodified PP, caused by the higher G_C values. The modification at 240 °C shows almost the same results regarding ω_C and G_C. For BEC and AEC, a crossover could not be obtained for the 240 °C extrusion temperature in the investigated angular frequency range. No data supported statement can therefore be made, but it can be assumed that a possible crossover point would occur at a frequency higher than 628 rad/s. The degradation of PP using these peroxides is very strong. Only PODIC presented a higher MW and MMD compared to PP at 240 °C, which indicates that LCB dominated in this case.

Table 3. Summary of the rheological data from the frequency sweep measured at 230 °C.

Sample	ω_C (rad/s)	G_C (kPa)	Comment
PP 180	36	23.9	
PODIC 180	50	24.5	MW ↓, MMD ↓
BIC 180	139	29.0	MW ↓, MMD ↓
BEC 180	-	-	(MW ↓, MMD ↓) *
AEC 180	460	33.6	MW ↓, MMD ↓
LP 180	84	25.6	MW ↓, MMD ↓
PP 240	98	27.1	
PODIC 240	66	23.5	MW ↑, MMD ↑
BIC 240	308	32.6	MW ↓, MMD ↓
BEC 240	-	-	(MW ↓, MMD ↓) *
AEC 240	-	-	(MW ↓, MMD ↓) *
LP 240	114	28.4	MW ↓, MMD ↓

* no crossover point detected but estimated from the general trend of the curves.

According to Wood-Adams et al. [56], the presence of LCB can be evaluated by using the plot of the loss angle δ and tanδ as a function of the frequency ω. Furthermore, De Maio and Dong [57] reported that higher elasticity leads to higher melt strength, which means that melt strength and tanδ are related to each other. The curves of all samples are shown in Figure 6. Normally, the linear polymer melt represents a monotonic decrease in tanδ by increasing ω. This behavior demonstrates the unmodified PP and the modified PP with PODIC at 180 °C. Their curves have nearly the same trend; only the gradient of PP is more pronounced. By comparison, BIC and LP show a typical terminal behavior of liquid-like materials because of the rapid decrease of tanδ with the increase of ω. BEC and AEC have an unexpected curve progression, which is not usual for conventional PP. Li et al. [48] and Sugimoto et al. [58] reported a similar unexpected rheological behavior of tanδ for their investigated samples. It is known in the literature that binary blends show a two-step rubbery plateau, which can only be seen for high molecular weight components [59–62]. However, the modification at 240 °C presented nearly the same behavior, whereas BIC also showed a second plateau and the curves of all samples displayed a steeper curve progression compared to that of the modification at 180 °C. The formation of such an unexpected curve progression supports the hypothesis of a strong degradation when using AEC, BEC, and BIC (at a higher temperature). All of them presented high MFR values, the lowest viscosity curves, and crossover points at high frequencies, or even no crossover points, which indicates that a possible degradation (β-scission) of PP is predominant.



(**a**) (**b**)

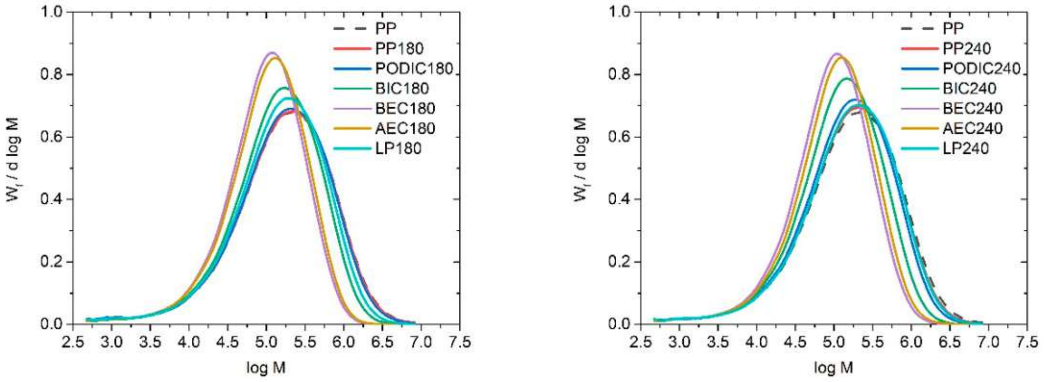
Figure 6. tanδ of the unmodified and modified PP with extrusion temperature of (**a**) 180 °C and (**b**) 240 °C; measured at 230 °C.

3.3. Molar Mass Determination

In addition to determining the MMD using dynamic rheology, high-temperature gel permeation chromatography (HT-GPC) measurements were performed. GPC is one of the most important methods to determine the MMD of polymers [63]. GPC measurement, a well-established concept in the literature, provides a further possibility to determine the molecular structure and any modifications made to polymers [51,64–68].

The corresponding curves of the GPC measurements are illustrated in Figure 7. The MMD of the virgin PP (without extrusion) was used for both cases as reference (dashed lines). In Figure 7a, the curves present nearly the same behavior compared to those of the reference PP and the unmodified PP. Only AEC and BEC show a significant change in MMD curves. The distribution becomes narrower and the peak maximum of MMD is distinctively increased and shifts to lower M values. The distribution of all samples, which were extruded at 240 °C, and the reference PP are shown in Figure 7b. It can be observed that all curves have nearly the same trend as the MMD curves at 180 °C. Therefore, the temperature difference during extrusion (180 °C or 240 °C) has no influence on the MMD via GPC. Only the use of the different peroxides presented a change in the distribution.

Additionally, the GPC results are listed in Table 4. PP and PODIC (both extruded at 180 °C) display almost similar molecular mass with only slight differences in their distributions. With the addition of the other peroxides, M_w and M_w/M_n decreased in all systems, especially BEC and AEC, which indicates the occurrence of degradation. The modification at 240 °C presented slightly the same trends for the molecular mass and polydispersity compared to those of the modification at 180 °C. Only LP 240 shows a lower degradation in comparison to LP 180. Therefore, PP 240, PODIC 240, and LP 240 display similar values, which means that LCB and degradation occur concurrently.



(**a**) (**b**)

Figure 7. MMD of virgin PP as well as unmodified and modified PP samples at (**a**) 180 °C and (**b**) 240 °C.

Table 4. Summary of the GPC data; molar mass and polydispersity of all extruded samples at 180 °C or 240 °C.

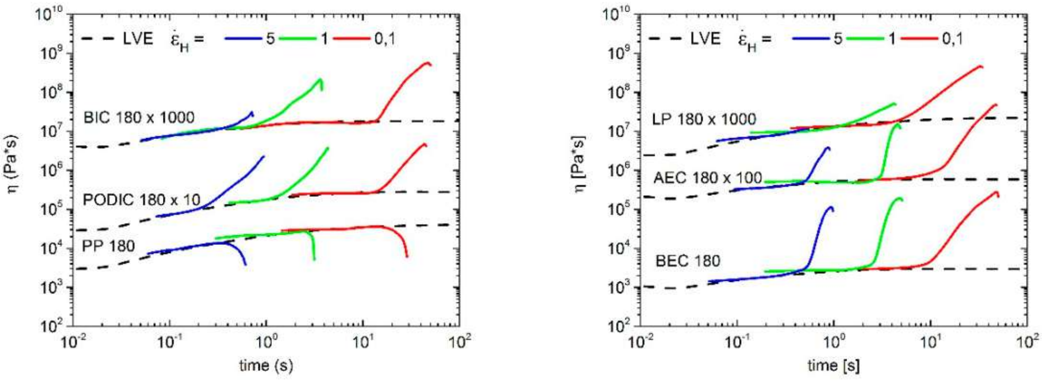
Sample	M_w (kg mol^{-1})	M_n (kg mol^{-1})	M_w/M_n
PP 180	379	63.2	6.0
PODIC 180	359	62.8	5.7
BIC 180	263	57.4	4.6
BEC 180	164	48.3	3.4
AEC 180	179	50.1	3.6
LP 180	307	59.9	5.1
PP 240	354	62.2	5.7
PODIC 240	309	60.5	5.1
BIC 240	230	54.1	4.2
BEC 240	160	46.8	3.4
AEC 240	179	50.0	3.6
LP 240	341	62.0	5.5

3.4. *Extensional Rheology*

For a better verification of LCB, additional extensional rheology measurements were performed on the different formulations. According to Münstedt et al. [69], the extensional behavior of a material is very important for many processing operations such as thermoforming, blow molding, film blowing, film casting, foaming, and so on.

In previous work performed by our group, some polymers, especially PP-LCB, have a pronounced increase of extensional viscosity compared to their virgin linear materials [32,70]. This phenomenon is called strain hardening, which is strongly related to LCB and the nascent changes in the molecular structures of PP [28,29].

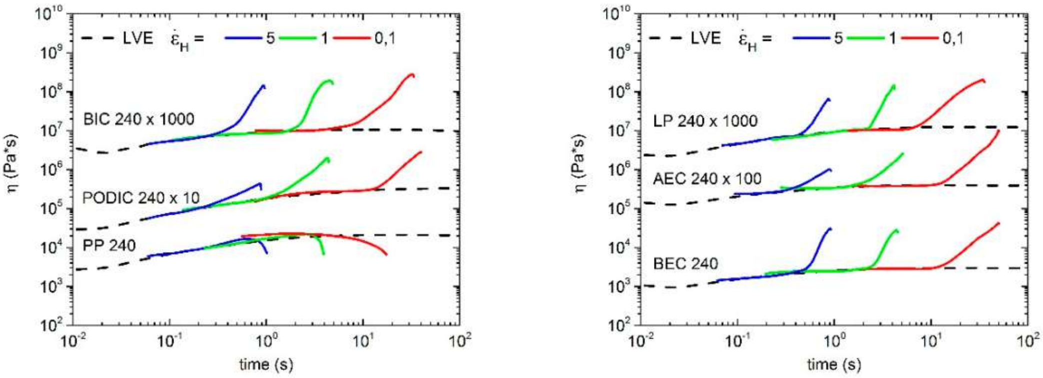
As shown in Figure 8, the linear PP at 180 °C does not exhibit a strain hardening behavior and therefore there is no remarkable deviation from the linear viscoelastic curve (LVE). The LVE confirms an increase that is three times the shear viscosity [71]. In addition to the previously mentioned linear PP, extensional rheology measurements of all modified PP samples demonstrate a strain hardening behavior at three different Hencky strain rates at 180 °C. LP does not display a deviation from LVE and therefore no strain hardening threat at the highest Hencky rate. However, all in all, the modification with the different peroxides and the LCB induced by reactive extrusion at 180 °C were successfully obtained.



(**a**) (**b**)

Figure 8. Extensional rheology of the different PP samples, (**a**) unmodified PP, PODIC and BIC; (**b**) BEC, AEC and LP, extruded at 180 °C; measured at 180 °C.

The extensional rheology curves of all PP-LCB extruded at 240 °C are plotted in Figure 9. As expected, the linear PP at this temperature does not show any strain hardening, whereas all of the modified PP samples have a strong increase of the extensional rheology curves. This means that long-chain branching of PP is possible at temperatures higher than 180 °C, which is very important for different applications in the industry.



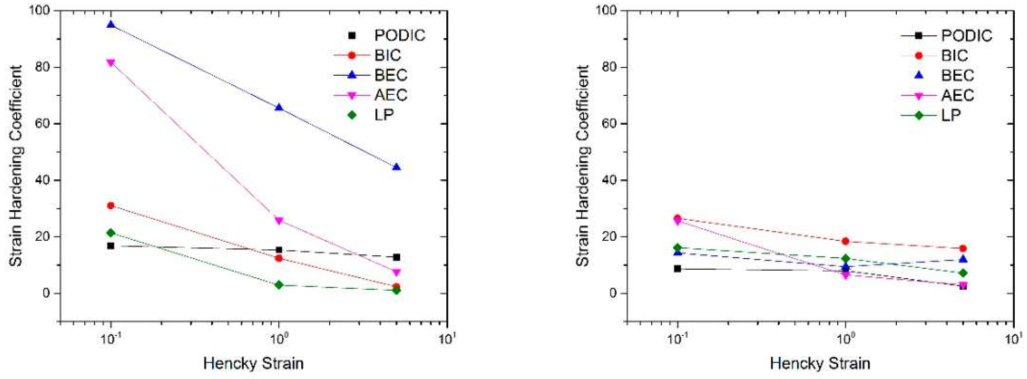
(**a**) (**b**)

Figure 9. Extensional rheology of the different PP samples, (**a**) unmodified PP, PODIC and BIC; (**b**) BEC, AEC and LP, extruded at 240 °C; measured at 180 °C.

With the strain hardening coefficient SH, it is possible to quantify the strain hardening behavior of each sample according to Equation (3), where η_e (t) is the maximum extensional viscosity of the Hencky strain rate and η_e^0 (t) is the extensional viscosity of the LVE curve.

$$\mathrm{SH} = \eta_e\,(t)/\eta_e^0\,(t) \tag{3}$$

The calculated strain hardening ratios of all samples are given in Figure 10. The modification at 180 °C for BEC and AEC achieve very high strain hardening values at a Hencky strain of 0.1. However, the SH factor decreases significantly by increasing the Hencky strain for both peroxides. A similar curve progression displays BIC and LP at 180 °C. Only PODIC shows a constant behavior. In comparison, the modification at 240 °C shows lower strain hardening coefficients for all mixtures and more linearity in the logarithmic plot.

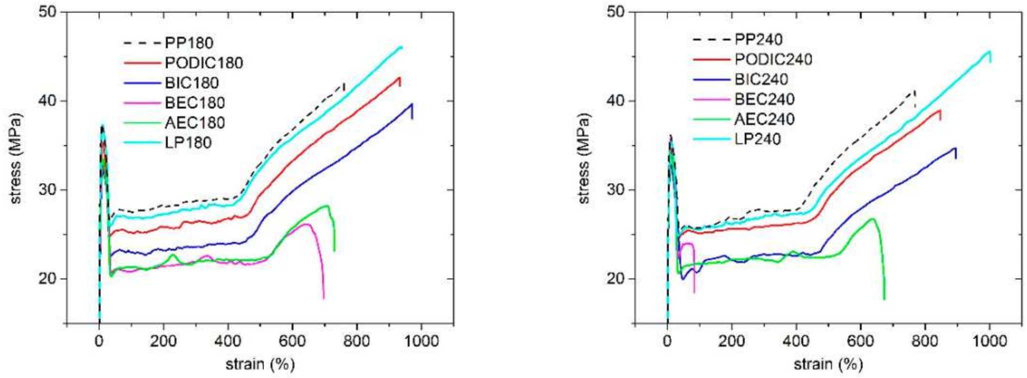


(**a**) (**b**)

Figure 10. Strain hardening coefficient at different strains rates (0.1, 1, 5); modified at (**a**) 180 °C and (**b**) 240 °C.

3.5. Mechanical Properties

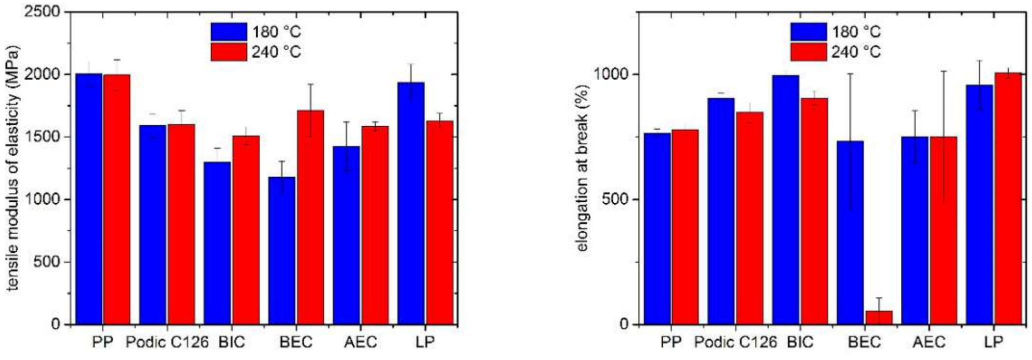
The tensile test plays an important role in determining the mechanical properties of polymers such as tensile strength, yield point, and elongation at break [72–75]. In Figure 11, the stress–strain plots at extrusion temperatures of 180 and 240 °C are shown, and the obtained results of tensile modulus of elasticity and elongation at break are presented in Figure 12. For the stress–strain plots, exemplary curves of each sample are illustrated. The stress–strain curves at the 180 °C extrusion temperature show consistently high strain values, which is an indication that cross-linked networks do not exist [76]. Furthermore, it can be seen that the yield point decreases significantly when using BIC, BEC, and AEC for the modification, whereas the yield point of PODIC decreases slightly and LP shows the same value compared to PP 180. In particular, the modification with PODIC, BIC, and LP displays a well-improved strain hardening behavior, which could be the result of the entanglement from introducing LCB. The different levels of the curves suggest that the degradation of PP-LCB could play a role, because BIC, BEC, and AEC illustrate the lowest levels of the curves.



(**a**) (**b**)

Figure 11. Stress–strain plots of unmodified PP and modified PP extruded at (**a**) 180 °C and (**b**) 240 °C.

All in all, the stress–strain plot at the 240 °C extrusion temperature presents the same results as those of the plot at 180 °C, except that BEC 240 °C has a very brittle behavior compared to the other curves at 240 °C and also to the stress–strain curve of BEC 180 °C. It is also apparent that the strain hardening of LP 240 is more significantly pronounced compared to that of PODIC 240 and BIC 240.



(**a**) (**b**)

Figure 12. Results of the tensile test: (**a**) tensile modulus of elasticity and (**b**) elongation at break of the model mixtures extruded at 180 °C and 240 °C.

On the one hand, the tensile modulus of elasticity of unmodified and modified PP and, on the other hand, the elongation at break are displayed in Figure 12. After the reactive extrusion, the tensile modulus of elasticity for the unmodified PP is nearly constant. After adding the different peroxides, the tensile modulus of elasticity decreases significantly. Kamleitner et al. [30] reported a similar behavior for modifications with PODIC and suggested this phenomenon with the formation of LCB and long-chain aliphatic decomposition products from the peroxide. It is shown that all modified formulations at 240 °C have consistent values of tensile modulus of elasticity. Compared to these, the values at 180 °C vary slightly more depending on which peroxide is used. However, by using LP as peroxide for the reactive extrusion, the highest tensile modulus of elasticity values can be achieved.

The elongation at break can be increased or held constant by adding peroxide. The single exception is shown for the formulation with BEC at 240 °C. In this case, the elongation at break was close to zero and all samples show a brittle behavior. However, the peroxides PODIC and BIC obtained higher values and, therefore, the LCB of PP has a strong effect on the tensile strength. Specifically, the modification with LP shows the highest elongation at break at both temperatures. It was possible to increase the values by about 30% compared to the unmodified PP samples.

The results of tensile impact tests are shown in Figure 13. At 180 °C, the unmodified PP and the samples with PODIC and BIC have nearly the same impact tensile strength. Compared to this, BEC and AEC show a slight downward trend. Interestingly, the impact tensile strength of LP increased to 62 kJ/m^2, which conforms to 50% more than unmodified PP.

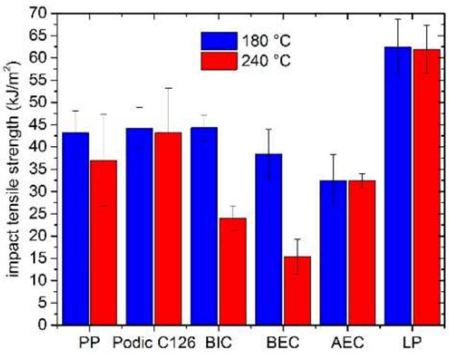


Figure 13. Results of the impact tensile test of the different model mixtures prepared at 180 °C and 240 °C.

Additionally, the reactive extrusion at 240 °C shows that PODIC can maintain the same level of tensile impact strength as at 180 °C. In comparison, the unmodified PP loses a little of its impact strength after extruding at 240 °C. By adding AEC, BIC, or BEC, the impact strength decreases significantly. However, by adding LP, a strong enhancement can be achieved. The impact strength can be maintained at the same level as LP at 180 °C and, compared to unmodified PP, the modification with LP at 240 °C raises the value by about 70%.

4. Conclusions

In this study, the effects of different peroxide types (symmetrical and unsymmetrical structure) on the LCB behavior of PP was investigated. The PP-LCB samples were prepared via reactive extrusion in melt by temperatures of 180 °C and 240 °C. As expected, it was found that, for the virgin PP, the temperature of the extrusion process plays an important role regarding its melt behavior. After increasing the extrusion temperature to 240 °C, the MFR value was higher and the complex viscosity was lower in comparison to the values at 180 °C.

The modification with peroxides showed different results. It was demonstrated that the reactive extrusion with unsymmetrical peroxides (BIC, BEC, and AEC) led to higher MFR values and showed lower complex viscosity curves. In comparison, the use of symmetrical peroxides (PODIC and LP) showed small deviations from the virgin PP, which means that the application of these two peroxides is more stable. This trend was better depicted by applying frequency sweep and performing GPC measurements. It can be concluded that the unsymmetrical peroxides did not show a crossover point in the suggested frequency area in comparison to all other samples. The curves shifted to higher frequencies, which means that the values of MW and MMD were lower compared to those of the unmodified PP. This was the case for BEC and AEC at the 180 °C extrusion temperature and for BIC, BEC, and AEC extruded at 240 °C. Additionally, the GPC measurements showed for BEC 180, AEC 180, and BIC 240 a shift of the MMD peak maximum to lower M values, i.e., a narrower progression of MMD. These results suggested that the degradation with unsymmetrical peroxides was more fundamental compared to symmetrical peroxides. Furthermore, these measurements allowed us to conclude that PODIC and LP provide the best opportunities to generate LCB-PP.

The strain hardening behavior was measured using extensional rheology. It was demonstrated that, for all peroxides, an improvement in strain hardening as well as in melt strength was achieved. This knowledge and the previously discussed results show the competition between degradation and LCB reactions.

Furthermore, it was shown that the mechanical properties of the samples modified by using peroxides are very dependent on the extrusion temperature. The elongation at break values of the samples that were extruded at 180 °C showed that, on the one hand, the modification with peroxides could be held constant in the case of BEC and AEC compared to PP 180 and that, on the other hand, it could be improved by using PODIC, BIC, and LP. In comparison to PP 180, the modification resulted in an improvement, that is, in the case of PODIC nearly 20%, for BIC 30%, and for LP 25%. At the extrusion temperature of 240 °C, the improvements were not so significant with the peroxides. However, in comparison to PP 240, the elongation at break values could be increased with PODIC by nearly 10%, with BIC by about 15%, and with LP by nearly 30%. For the tensile impact test, the modification with the unsymmetrical peroxides (BIC, BEC, and AEC) had the tendency to lower impact tensile strength values, which is an indication of chain scission and the related degradation, compared to the unmodified PP at both extrusion temperatures [25,77,78]. Nevertheless, the modification with PODIC showed in both cases a constant level in comparison to the unmodified PP. In particular, the use of LP improved the impact tensile strength. At 180 °C, an improvement of about 40% was achieved, and for the extruded samples at 240 °C, the improvement increased to about 60% compared to PP 240.

All in all, it can be concluded that the modification of PP with PODIC and LP (symmetrical peroxides) offers the best possibilities to generate PP-LCB at an extrusion temperature of 180 °C and also 240 °C. In both cases, an improvement of their properties can be achieved, such as higher elongation at break values or higher impact tensile strength and the availability of strain hardening.

These results are very promising in view of possible "upcycling" options to recycle individual PP flows in commercialized products. Furthermore, reactive extrusion at higher temperatures—which are common in industrial practices—was successfully performed.

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ARTICLE

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Upcycling of polypropylene with various concentrations of peroxydicarbonate and dilauroyl peroxide and two processing steps

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Abstract

The influence of two peroxides (peroxydicarbonate/dilauroyl peroxide) with various concentrations (10–200 mmol/kg PP) and their effective opportunity to introduce long chain branched (LCB) were investigated. The dependence of a single and double extrusion step and the changes of the properties were studied. Experiments were carried out in a single screw extruder at 180°C for the first extrusion step (modification) and at 240°C for the second extrusion step (processing simulation). Melt flow rate and dynamic rheological properties were studied at a measuring temperature of 230°C. For the definitive determination of long chain branched polypropylene (LCB-PP) served the extensional rheology measurements. The mechanical properties were examined via tensile test and impact tensile test. Summarized, LCB (melt strength) could be observed via extensional rheology for all modified specimens and the mechanical properties were maintained or even improved for the modified samples. Particularly, samples containing dilauroyl peroxide display excellent mechanical properties in this study.

KEYWORDS
extrusion, mechanical properties, polyolefins, recycling, rheology

1 | INTRODUCTION

Polyolefin, mostly low-density polyethylene (PE-LD), high-density polyethylene (PE-HD) and polypropylene (PP), are among the most widely used and produced polymeric materials in the world. They are used in different industry sectors for example packaging, food industry, biomedical applications, films, bags.[1–4] The operating life from most of these polyolefin products are lower than 1 month.[5,6] In the European Union, Norway and Switzerland (EU28 + NO/CH) the production volume of plastic was about 62 million tons in 2018, whereby around 50% are used for single-use disposable application like packaging.[7,8] Around 12 million of tons accumulates only of PP, which represents a percentage share of 19.3%. In one of the biggest segments of PP, the packaging sector, the recycling rate was increased by 92% in the period of 2006–2018.[7]

For the efficient recycling four different main techniques have become well-established: reuse (primary), mechanical recycling (secondary), chemical recycling (tertiary) and energy recovery (quaternary).[9–13] In the last years the mechanical recycling got more and more important, because it is a general environmental-friendly approach and an economic viable practice, with the possibility to save 20–50% in terms of the market price of virgin material.[4,14–17] 17 However, mechanical recycling is a process in which plastic solid waste will be recycled via mechanical means in a new recycled material and therefore converted in new plastic products. The drawback of this option is that the process deteriorates the properties of the recyclable material, including degradation of polymers, heterogeneity of plastic wastes and presence of low molecular weight compounds.[5,18,19] To improve the quality of the new material and make them suitable for new applications a lot of reprocessing techniques of mechanical recycling have been developed and widely applied in the recycling industry.[20]

One of the most popular methods to improve the properties of PP and achieve high melt strength PP (HMS-PP) is the possibility to introduce long chain branching (LCB) on the backbone of PP.[21] By using reactive extrusion for LCB-PP a lot of advantages of this process could be generated like very short reaction times, low infrastructure costs and no use of solvents, which makes it very popular.[19] In literature, LCB-PP is very well-known as an innovative tool that presents a really good possibility for a “up-cycling" process of PP, which compensates the loss of mechanical properties during the mechanical recycling process.[22–29] In general, LCB could result in an increase of the molar mass, a broadening of the molar mass distribution and increasing of strain hardening.[30–33] Vested with these attributes, PP can be used in processes like foaming, film blowing and thermoforming.[34] According to Lagendijk et al., it is possible to generate LCB-PP from a linear isotactic PP homopolymer by using peroxydicarbonates (PODIC) as a peroxide.[35] This peroxide acts as initiator and co-agent at the same time and enables a successful branching reaction. A study of PODICs with long aliphatic side chains and their high branching efficiency was presented by Gotsis et al.[31] However, in the last years different approaches were followed, in which various peroxides and their influences on property changes of PP were investigated.[36–43] The melting behavior and the associated changes of the molecular structure, especially molar mass (MW) and molar mass distribution (MMD), of PP were mainly carried out.

In general, the determination of MW and MMD is normally measured by using gel permeation chromatography (GPC). This method is not always the best solution, especially for many polymers such as PP, which sometimes must be dissolved in very toxic solvents or needs high temperature chromatography column for the measurements.[44–47] In comparison to GPC measurements the dynamic rheology has become more and more a promising alternative in the last few years.

Rheological properties in melts are strongly influenced by the presence of long chain branches and generally changes in the chain structure can be shown. Compared to GPC, low frequency rheology measurement is a more appropriate and reliable technique for detecting changes in molecular structure.[48–52] Thus, dynamic rheology has become more and more a promising alternative in the last few years. Especially in the case of long-chain branching extensional rheology seems to be a more effective method because the occurrence of a typically small change of the molar mass distribution detected by GPC could result from chain-extension or from long-chain branching, whereas a little chain-extension does not result in such a dramatic change in the strain-hardening behavior as it results from long-chain branching. It is possible to determine the MMD and MW of polymers from data, which are obtained from a frequency sweep experiment. For this purpose, the crossover modulus GC and the crossover frequency ω_C, where the storage modulus G' and loss modulus G'' are equal, is used.[53,54] According to Bernreitner et al., respectively, Zeichner and Patel, it is possible to correlate the width of MMD to the value of GC and MW to the value of ω_C.[55,56] Furthermore, rheology measurements are extremely sensitive to molecular structure of polymers and proved to be a reliable technique for verifying the existence of long chain branching.[22,30,57–64] Especially the extensional rheology is extremely influenced by changes in the molecular structure, like broader MMD on the basis of LCB, and it is known that the variation of branching topologies affected the viscoelastic behavior differently.[65–69]

The focus of this work is the investigation of two different types of peroxides – on the one hand PODIC C126, which is a peroxydicarbonate peroxide, and on the other hand dilauroyl peroxide, which represents the group of diacyl peroxides. We studied the effects of concentration of these peroxides and processing conditions (extrusion temperature and single/double extrusion) on rheological and mechanical properties of LCB-PP. The modification and the introduction of the long chains to the PP was carried out in a first extrusion step at a temperature of 180°C (modification step). Furthermore, the modified material was to be extruded again in a second extrusion step at 240°C in order to achieve an industry-oriented temperature and thus ensure a possible process simulation for the LCB-PP.

2 | EXPERIMENTAL

2.1 | Materials

The PP (HC 600TF) was an isotactic homopolymer from Borealis with a melt flow rate (MFR) of 2.8 g/10 min, which is used for thermoformed packaging applications. In addition, a recycled PP was used, which corresponded to a post-consumer waste (yoghurt cups) and was provided by the company Walter Kunststoffe GmbH. The peroxides, which we used for the modification of PP were the PODIC C126 (dimyristyl peroxydicarbonate; 10 h half-life time at 48°C) and PEROXAN LP (dilauroyl peroxide; 10 h half-life time at 61°C) provided by Pergan in white powder form. Additionally, the half-lives of the two peroxides are given at 180°C, since the first extrusion modification (long chain branching) takes place during reactive extrusion at this temperature. Modification with PODIC C126 is spontaneous at this temperature because no half-life could be calculated at this temperature. Whereas the half-life for PEROXAN LP is 0.3 s at a temperature of 180°C. The difference between the two peroxides and their results can be explained by the fact that the two peroxides belong to different classes of peroxides (peroxydicarbonate and diacyl peroxide). In addition, both peroxides decompose into different peroxide products, which are shown in Figure 1.[70,71] For the heat stabilization Irganox 1010 was used, which was supplied by BASF.

2.2 | Sample preparation

The first extrusion (A; modification step) and also the second extrusion (B; for the already extruded or modified PP) were carried out in an Extron EX 18–26-1.5 single screw extruder with a screw diameter of 18 mm and L/D ratio of 25:1. It was also equipped with three independent temperature zones (feeding zone/extrusion zone/die zone) and the screw rotation speed was 70 rpm. The virgin PP and the peroxides, with various concentrations, were mixed directly and added to the extruder. The sample names and the compositions of the formulations are given in Table 1.

The first extrusion for the modification of PP, which include the introducing of long chains on the PP backbone, was done at 180°C with a temperature profile of 165, 180 and 220°C. Afterwards the modified PP samples were shredded with a universal cutting mill "Pulverisette 19" with a 4 mm square perforation sieve and a high-performance cyclone to achieve a better separation. One half of the new received granules were mixed with 0.5 wt % Irganox 1010 and could therefore be used for a second extrusion at a higher temperature. The extrusion temperature for the second extrusion step was 240°C with a temperature profile of 165, 240 and 240°C. Therefore, these materials were extruded two times—one time at 180°C by using the peroxides for the LCB (modification step) and an additional time at 240°C (processing simulation step)—and shredded afterward with the above-mentioned universal cutting mill. For comparison reasons also unmodified PP was extruded at 180 and 240°C.

2.3 | Different scanning calorimetry

The thermal behavior of the unmodified and modified PPs at the various extrusion steps was investigated by using TA Q2000 DSC from TA instruments. The samples (5–10 mg) were integrated in aluminium pans and the measurements were done under nitrogen atmosphere. The samples were heated up from room temperature to 200°C with a rate of 10 K/min to eliminate the thermal history, cooled down to room temperature and heated up a second time to 200°C also with a rate of 10 K/min. For the determination of melting (T_m) and crystallization temperature (T_c) as well as the melting enthalpy (ΔH_m) the TA Universal analysis software was used.

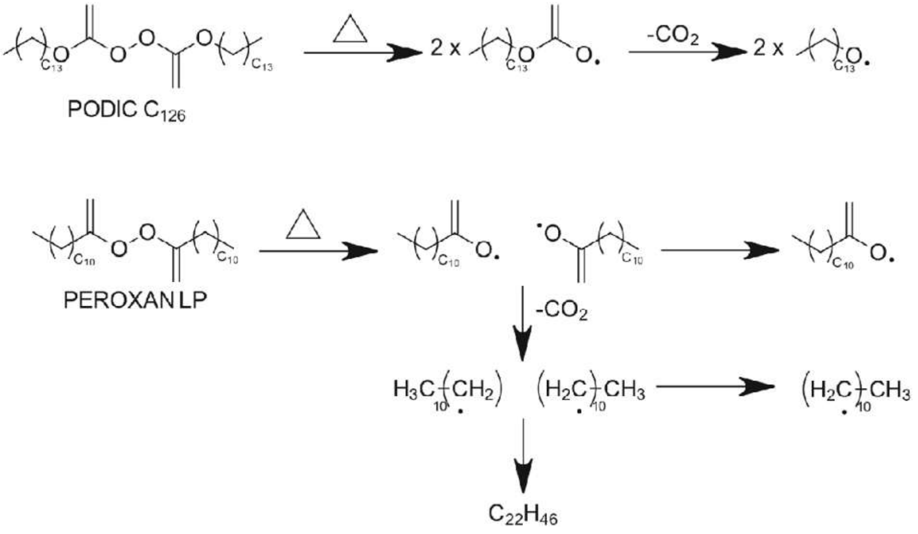

FIGURE 1 Scheme of the peroxide structure of PODIC C126 and PEROXAN LP and their decomposition products according to Buback et al for dialkyl peroxydicarbonates and according to Takamura et al for diacyl peroxides

2.4 | Melt flow rate

According to DIN EN ISO 1133 method A, the measurements of the MFR (g/10 min) were done with a MeltFlow basic from Karg Industrietechnik at 230°C and a weight of 2.16 kg.

2.5 | Gel content

The insoluble gel content was determined by adding 300 mg of polymer in a filter paper and refluxing this sample in xylene for 24 h.

2.6 | Dynamic rheology

The dynamic rheology was performed at 230°C under nitrogen on a plate-plate system (25 mm diameter) by using an Anton Paar MCR 301 rheometer, which was equipped with a heating chamber CTD450. The gap size of the plate-plate system was 1 mm, the frequency range was between 628 and 0.01 rad/s and the deformation was raised logarithmically from 1% to 2%. The necessary disc shaped specimens with a diameter of 25 mm and a thickness of 1.2 mm were prepared via a compression mold with a pressure of 30 bar at 180°C for the first extruded material or at 240°C for the second extruded samples.

TABLE 1 Samples and sample specifications

Samples for the first extrusion step at 180°C	Sample specifications for the first extrusion at 180°C	Samples for the second extrusion step at 240°C
PP-A	Virgin PP granulate HC 600TF	PP-B
PODIC A0.5	10 mmol/kg PODIC C126 (0.5 wt%)	PODIC B0.5
PODIC A1	20 mmol/kg PODIC C126 (1 wt %)	PODIC B1
PODIC A5	100 mmol/ kg PODIC C126 (5 wt%)	PODIC B5
PODIC A10	200 mmol/kg PODIC C126 (10 wt%)	PODIC B10
LP A0.5	10 mmol/kg PEROXAN LP (0.4 wt%)	LP B0.5
LP A1	20 mmol/kg PEROXAN LP (0.8 wt%)	LP B1
LP A5	100 mmol/kg PEROXAN LP (4 wt%)	LP B5
LP A10	200 mmol/kg PEROXAN LP (8 wt%)	LP B10
RecPP-A	Post consumer PP (yoghurt cups)	RecPP-B
RecPP PODIC A10	200 mmol/kg PODIC C126 (10 wt%)	RecPP PODIC B10
RecPP LP A10	200 mmol/kg PEROXAN LP (8 wt%)	RecPP LP B10

Abbreviations: DSC, differential scanning calorimetry; PODIC, peroxydicarbonates; PP, polypropylene.

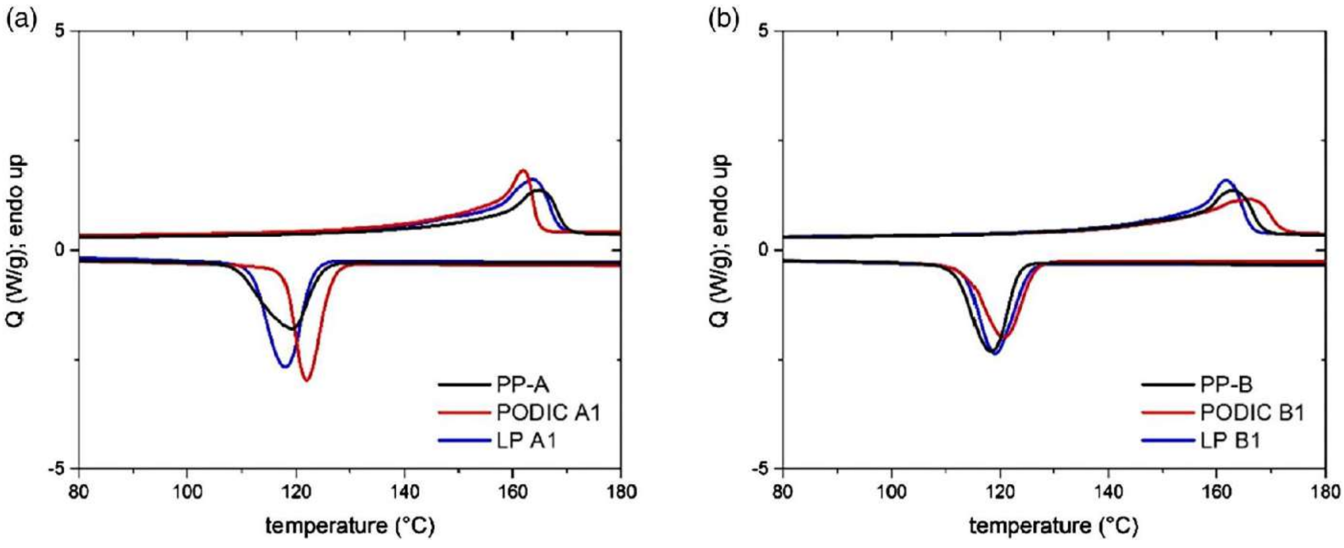

FIGURE 2 Exemplary differential scanning calorimetry (DSC) thermograms of unmodified polypropylene (PP) and modified PP with 20 mmol PODIC and LP extruded at 180°C and a second extrusion at 240°C [Color figure can be viewed at wileyonlinelibrary.com]

2.7 | Extensional rheology

A Sentmanat Extensional Rheometer (SER-HPV 1) from Xpansion instruments was used for an Anton Paar rheometer at 180°C and three different strain rates ($\dot{\varepsilon}$ = 5 s^{-1}; 1 s^{-1}; 0.1 s^{-1}). For these measurements, stripes with 8 mm width were cut from 60 mm × 60 mm × 0.8 mm sheets, which were produced by compression molding at 180°C, respectively, 240°C. With a steady shear experiment at the plate-plate system the start-up curves were measured at two different shear rates of 0.001 s^{-1} and 0.1 s^{-1}.

2.8 | Tensile test and tensile impact strength

The tensile test machine (Zwick 050) from ZwickRoell GmbH was equipped with a 1 kN load cell, an extensometer and the test speed of 10 mm/min was used. The test specimens according to ISO 527-2-5A were produced by injection molding with a Haake Mini Jet II from Thermo Fischer Scientific. The mold temperature was 90°C and an injection pressure of 350 bar was selected.

The impact tensile specimens with 60 mm × 10 mm × 1 mm were injection molded by using the same conditions like the test specimens for the tensile test. The samples of the tensile impact test were notched on both sides and tested according to ISO 8256/1A. For the test an Instron CEAST 9050 impact pendulum with 2 J hammer and a cross head mass of 15 g was used.

3 | RESULTS AND DISCUSSION

3.1 | Thermal properties

The melting and crystallization behavior of the unmodified and modified PP samples, which were modified at the first extrusion step at 180°C and also extruded again for a second extrusion step at 240°C was analyzed by using differential scanning calorimetry (DSC). Exemplary thermograms for the unmodified and modified PP samples are displayed in Figure 2. In both figures are shown the unmodified PP samples and the samples modified with 20 mmol peroxide (PODIC A1/B1 and LP A1/B1).

In Table 2 a summary of all samples (unmodified and modified samples with different content of peroxide) of the second heating run and their crystallization temperature (Tc), melting temperature (Tm) and the enthalpy of fusion (ΔHm) for the both extrusion steps are shown.

TABLE 2 Summary of the results of the DSC measurements (second heating run)

Sample	T_m (°C)	T_C (°C)	ΔH_m (J/g)
PP-A/PP-B	164/163	119/118	99/101
PODIC A0.5/B0.5	163/163	123/124	108/108
PODIC A1/B1	162/164	123/123	109/107
PODIC A5/B5	163/162	120/124	100/104
PODIC A10/B10	162/161	119/122	97/101
LP A0.5/B0.5	163/162	112/114	102/102
LP A1/B1	162/162	119/119	102/104
LP A5/B5	165/164	114/115	111/112
LP A10/B10	160/161	110/112	91/90

Abbreviations: DSC, differential scanning calorimetry; PODIC, peroxydicarbonates; PP, polypropylene.

The molar mass, molar mass distribution and the chain irregularity would be influenced via long chain branching during the reactive extrusion. Therefore, the crystallization behavior of LCB-PP is affected and according to the literature the values of Tc are higher compared to the unmodified PP.[72–76] If both peroxide modifications are considered independently of each other, the first extrusion step at 180°C shows that when PODIC C126 is used, the crystallization temperatures reach a higher level at the lower concentrations and then fall again with increasing peroxide concentration until they reach the same level at the highest concentration of Podic C126 (200 mmol) compared to unmodified PP. PEROXAN LP, on the other hand, tends to have lower crystallization temperatures compared to unmodified PP. The effect just described can also be observed for the second extrusion step at 240°C for both peroxides. Also the enthalpy of fusion values shows the same trend by first increasing and finally decreasing at the highest peroxide concentration for both peroxides. Straight the samples with the highest peroxide concentration, especially LP A10 or LP B10 have a lower Tc, Tm and ΔHm in comparison to the unmodified PP which could be an indication that degradation effects due to higher concentration of the peroxides are more pronounced and competitive reactions hinder long chain branching. However, Teh et al reported that the decrease of ΔHm and Tm could be also an indication for LCB-PP.[77]

As expected, it is very difficult to determine the long chain branching behavior of the modified samples exclusively with DSC measurements. But DSC measurements provide a good method to get a first impression about possible LCB reactions during the extrusion steps.

3.2 | Melt flow properties

The MFR measurements provide information about the influences and changes of the molecular structure of PP by using different peroxide concentrations during reactive extrusion at 180°C and the further process simulation step at 240°C. An increased MFR suggest a higher chain mobility because of the chain scission during the reactive extrusion with peroxides, whereas a reduction of the MFR values represent long chain branching or crosslinking of PP.[78–80] Lagendijk et al reported, that in the case of modification of PP with PODIC it was possible to reduce the MFR values slightly.[35]

In Figure 3 the MFR values of the unmodified and modified PP samples are shown for the first extrusion at 180°C and the second extrusion at 240°C.

For the first extrusion step at 180°C it can be seen, that the MFR value of the unmodified PP increases from an initial value of 2.8 g/10 min to 3.5 g/10 min, which reflects that the extrusion process lead to degradation, although no peroxide is added. By adding small amounts of peroxydicarbonate and dilauroyl peroxide (PODIC A0.5 and LP A0.5) the MFR values were kept nearly at a constant level in comparison to the unmodified PP. For the other samples with a higher amount of peroxides (PODIC A5, PODIC A10, LP A1 and LP A10) the values increased significantly, which is due to the fact of the higher concentrations of peroxides and the associated competing degradation reaction toward the LCB reactions. In both cases, the MFR increases with increasing concentration of peroxides (up to 100 mmol) and decreases again (200 mmol peroxide) for the samples that were extruded at 180°C. That the MFR value for the samples with the highest concentration of peroxides (200 mmol) decreases in both cases was not expected. This effect could be possibly related to the fact that different reaction mechanisms take place during reactive extrusion. During extrusion, radical polymerization takes place which can lead to chain scission, especially in the case of PP, but also to the introduction of long-chain branching. In addition, disproportionation reactions of the resulting peroxide radicals can play a role.[81] Especially with PP, these two concurrent reactions (β-scission and branching) play an important role and a suitable balance must be found between these reaction mechanisms. Since the MFR value of the samples with the highest peroxide concentration (200 mmol) decreases again, one could consider that the balance is more on the side of the LCB and thus possibly the degradation was counteracted compared to the samples with 100 mmol peroxide content.

A more clear trend can be deduced for the MFR values after the second extrusion step at 240°C, as shown in Figure 3(b). It is clear to see that the MFR values growth gradually with the increase of the concentrations of the peroxides. The samples with the lowest concentration of peroxides show the lowest values of MFR, whereas the samples with the highest concentration of peroxides present the highest MFR values. Comparing the values with the lowest and the highest concentration of peroxydicarbonate and dilauroyl peroxide it appears that the values are nearly the same in both cases.

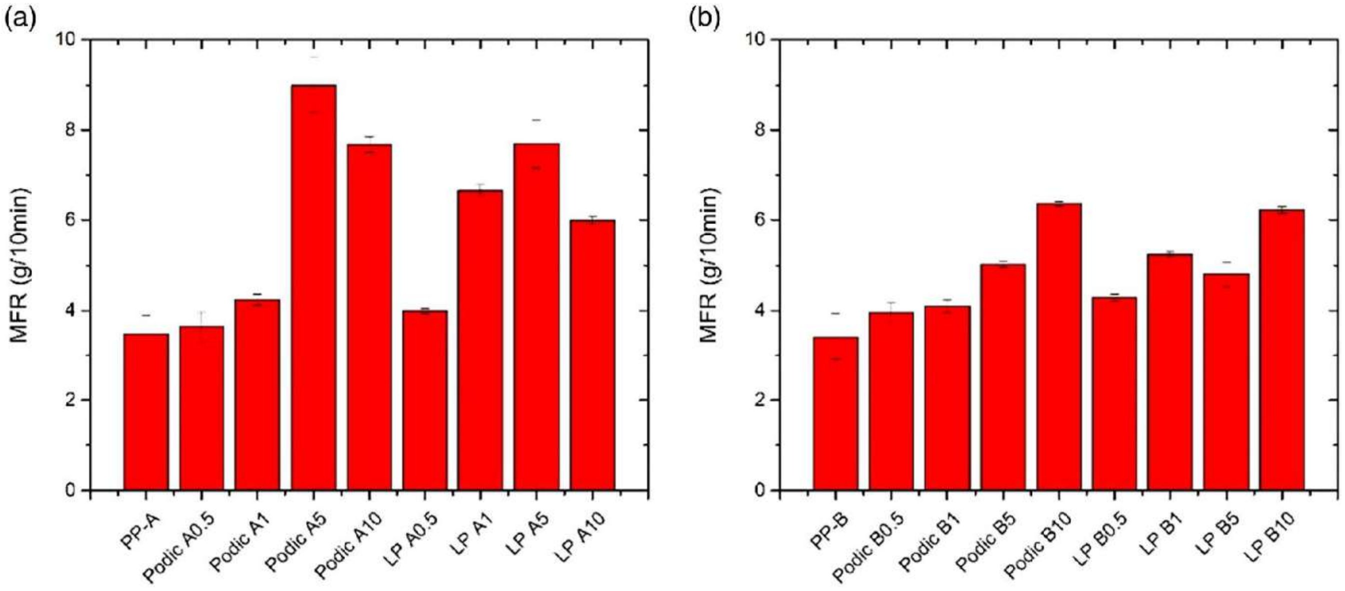

FIGURE 3 Melt flow rate (MFR) measurements at 230°C with 2.16 kg of the unmodified and modified PP samples for the first extrusion step at (a) 180°C and for the second extrusion step at (b) 240°C [Color figure can be viewed at wileyonlinelibrary.com]

However, it could be observed, that the samples display lower MFR values after the second extrusion, especially for the samples, which demonstrate higher MFR values after the first extrusion step. As a reduction in MFR is generally caused by cross-linking, the individual materials, which were extruded at 180°C as well as at 240°C, were boiled with xylene for 24 h on reflux to determine the degree of cross-linking. No undissolved mass or gel could be observed in any sample. Therefore, it can be assumed that the lower MFR values of the second extrusion (240°C) were not caused by crosslinking or highly branched gel particles.

Since the determination of the gel content of the respective formulations did not show any corss-linked gel particles, this can be excluded as a reason for the lowering of the MFR values after the second extrusion. It is known that free radical scavengers prevent the degradation of PP. Irganox 1010 is one of the most common agents used as a primary antioxidant for PP. The resulting phenoxyl radical is produced by H-absorption, which is used to stabilize the PP and thus prevent further degradation. However, there are other resonance structures, such as the quinonoid, which react further with the polymer free radicals.[82]

Thus, it could be possible that the Irganox 1010 partly contributes to the formation of LCB in the second extrusion step. This could be explained by the reduction of the MFR values. For a wide range of PP applications, different stabilizers are used depending on the requirements. Predominantly, almost 40% antioxidants and 45% light stabilizers are used.[83] Therefore, stabilization is very essential in the field of plastic recycling to counteract degradation.[84]

3.3 | Dynamic rheology

The dynamic rheology is very efficient and sensitive for the detection of LCB or molecular structure changes.[73,85–87] Malmberg et al. reported, that a very low level of LCB can change the zero shear viscosity and the shear thinning degree.[88] The complex viscosity |η*|versus shear rate, which was measured at 230°C for a better comparison to the MFR values, are shown in Figure 4.

The curves for the first extrusion step at 180°C are represented in Figure 4(a). It can be seen that the curve of unmodified PP and PODIC A0.5 exhibit a congruent course, whereas the curves with higher concentrations of PODIC C 126 decrease to lower viscosity values compared of them. In general, the curves of LP (dashed lines) show a lower level compared to the curves of PODIC C126, which indicates that the chain scission is more pronounced in the case of LP.

In the case of LP, it could be seen that with the increase of the dilauroyl peroxide concentration the viscosity curve decrease continuously. However, the curves of peroxydicarbonate display nearly the same trend with exception of the curve with highest peroxide content of PODIC C126 (200 mmol). This viscosity curve presents a converse behavior, which is reflected in the fact that the curve of PODIC A10 is minimal higher than PODIC A5. A reason for this behavior could be that with higher peroxide concentration more LCB-PP can be generate and thus stabilized the formulation, which was also shown between the MFR values of these samples. Figure 4(b) shows the curves after the second extrusion step at 240°C, which are measured at 230°C. Considering the curves with peroxydicarbonate first, a general decrease of

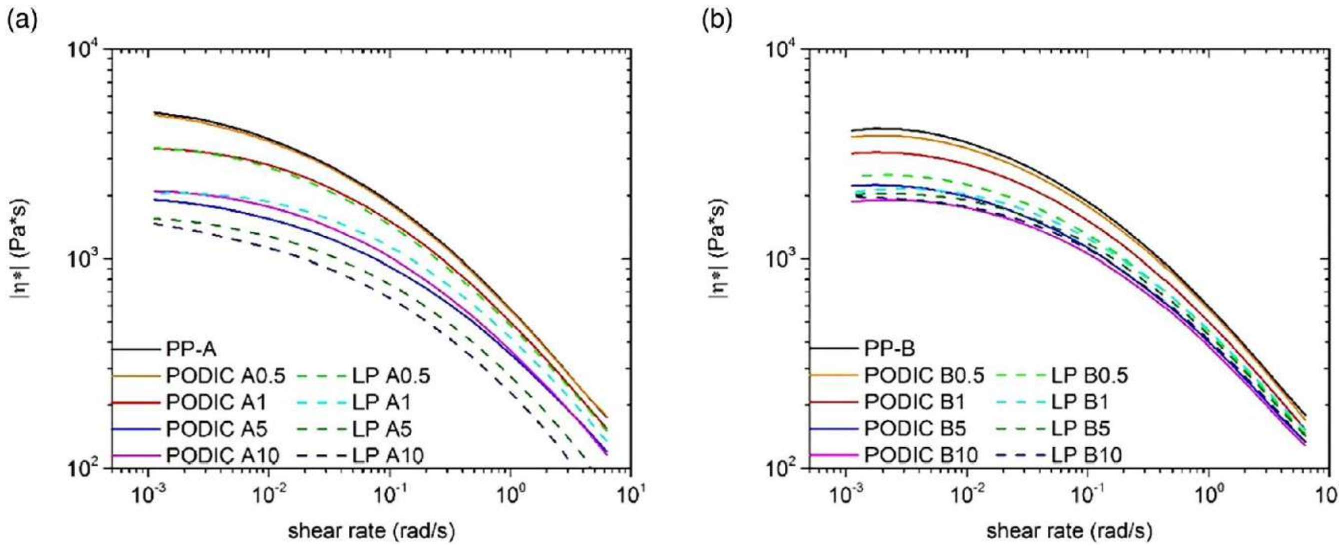

FIGURE 4 Complex viscosity versus shear rate of all samples for the first extrusion step at (a) 180°C and for the second extrusion step at (b) 240°C; measured at 230°C [Color figure can be viewed at wileyonlinelibrary.com]

the curves with an increasing amount of peroxide can be identified. The same behavior is represented by the curves of dilauroyl peroxide (dashed lines). However, the curves with the highest peroxide content of 200 mmol (LP B10 and PODIC B10) have the same curve progression and the same level of complex viscosity at low shear rates.

All in all, the behaviors of the complex viscosity curves of all samples, the unmodified PP and the modified PP with peroxydicarbonate (PODIC C126) and dilauroyl peroxide (PEROXAN LP), reflect a very well correlation to the results of the MFR measurements.

The dynamic rheology, especially the storage modulus G′ and the loss modulus G″, play an important role for the determination of viscoelastic properties of a polymer melt, which is mainly influenced by the molecular structure (M_W and MMD).[55,89–94] The curves of G′ and G″ for all samples after the first extrusion at 180°C are shown in Figure 5.

All of them show a crossover point between G′ and G″, whereas the modification of peroxydicarbonate presents, that with increasing of the peroxide content the curves and therefore the crossover point tends to higher frequencies. This can be attributed to the higher radical concentration and the associated enhancement of chain scission. However, it could be also observed, that the less amounts of peroxydicarbonate have nearly the same behavior than the unmodified PP. Furthermore, it was observed that there is no difference in the curve progression between the PODIC A5 and PODIC A10. This behavior could be an indication, that above a certain amount of peroxide a specific level has been reached and therefore no more degradation of PP is obtained.

The modification with dilauroyl peroxide and the curves of G′ and G″ after the first extrusion with 180°C are shown in Figure 5(b). The samples with the LP present nearly the same behavior compared to the samples, which were modified with PODIC C126. However, it is notable here that the less concentrations of LP show a larger deviation from the unmodified PP compared to the modification with PODIC C126. All in all, it can be seen a very well tendency that with an increasing amount of the peroxide concentration the curves of G′ and G″ tend to higher frequencies. Nevertheless, the curves with a high amount of LP (100 and 200 mmol) are very close together, thereby the assumption is confirmed that over a certain level of peroxide content no further degradation initiated from LP takes place. For the second extrusion step, which was extruded at 240°C, the curves are shown in Figure 6.

The samples modified with peroxydicarbonate represent after the second extrusion step the same curve progression than the samples of peroxydicarbonate after the first extrusion step. The samples PODIC B0.5 and PODIC B1 and their curves are close to the curve of the unmodified PP sample, whereby the samples with higher concentration of PODIC C126 (PODIC B5 and PODIC B10) are again shifted to higher frequencies. Also the samples modified with dilauroyl peroxide represent the same behavior after the second extrusion as the extruded LP samples at 180°C. The curves of LP modified samples with a small amount (10 and 20 mmol) are very close together and display nearly the same curve progression

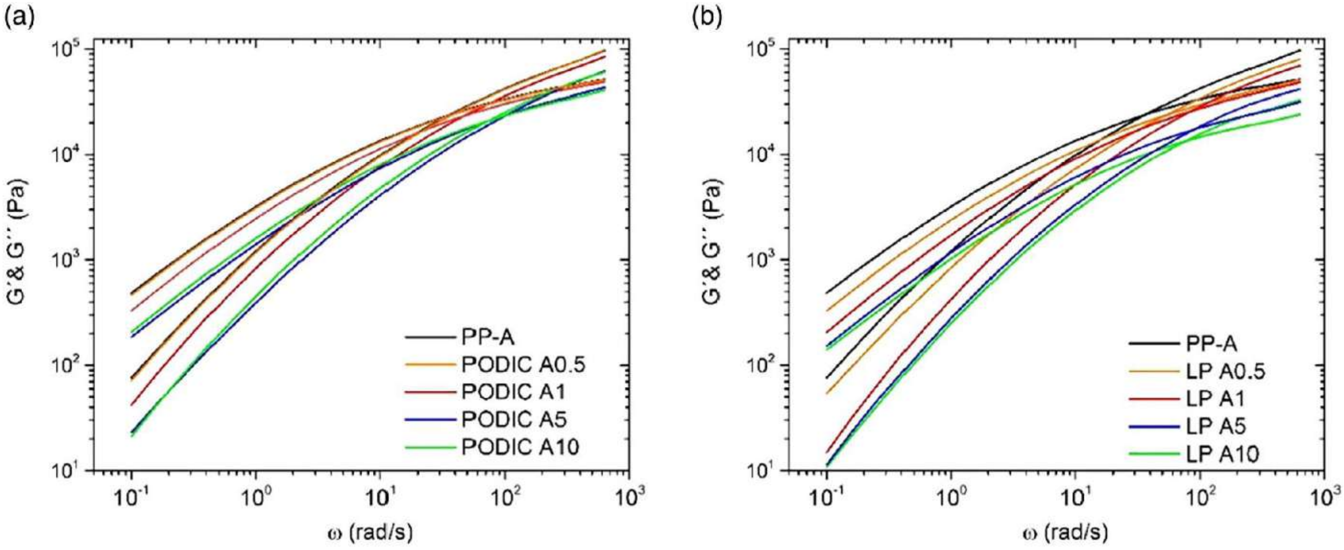

FIGURE 5 Storage and loss moduli as function of angular frequency for the first extrusion step at 180 °C for the samples with (a) peroxydicarbonates (PODIC) C126 and (b) PEROXAN LP; measured at 230°C [Color figure can be viewed at wileyonlinelibrary.com]

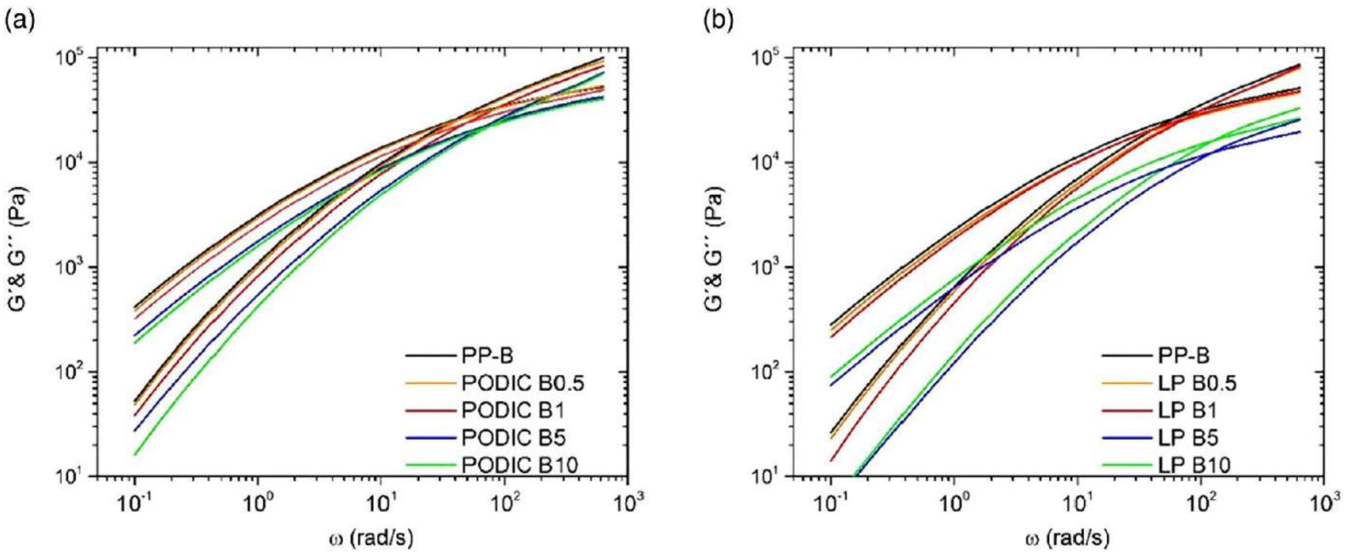

FIGURE 6 Storage and loss moduli as function of angular frequency for the second extrusion step at 240°C for the samples with (a) peroxydicarbonates (PODIC) C126 and (b) PEROXAN LP; measured at 230°C [Color figure can be viewed at wileyonlinelibrary.com]

TABLE 3 Summary of the rheological data from frequency sweep measured at 230°C

Sample	ω_C (rad/s)	G_C (kPa)	Comment	Sample	ω_C (rad/s)	G_C (kPa)	Comment
PP-A	36.4	23.9		PP-B	39.6	25.6	
PODIC A0.5	37.6	23.9	MW ↓, MMD ~	PODIC B0.5	43.2	25.7	MW ↓, MMD ~
PODIC A1	48.0	23.4	MW ↓, MMD ↑	PODIC B1	48.7	23.6	MW ↓, MMD ↑
PODIC A5	103.9	23.9	MW ↓, MMD ~	PODIC B5	71.8	22.6	MW ↓, MMD ↑
PODIC A10	73.6	20.9	MW ↓, MMD ↑	PODIC B10	74.7	22.0	MW ↓, MMD ↑
LP A0.5	52.8	23.5	MW ↓, MMD ↑	LP B0.5	61.9	23.8	MW ↓, MMD ↑
LP A1	83.6	25.6	MW ↓, MMD ↓	LP B1	76.0	26.5	MW ↓, MMD ↓
LP A5	89.1	17.3	MW ↓, MMD ↑	LP B5	126.3	12.5	MW ↓, MMD ↑
LP A10	76.3	13.4	MW ↓, MMD ↑	LP B10	130.4	16.3	MW ↓, MMD ↑

Abbreviations: MMD, molar mass distribution; MM, molar mass; PODIC, peroxydicarbonates; PP, polypropylene.

like the unmodified sample (PP-B). However, the difference to the previous curves (extruded at 180°C) is, that in the case of the second extrusion at 240°C the curves of LP are very close together to the unmodified, whereby these curves are partially or completely overlapped. The curves with the high peroxide concentration of dilauroyl peroxide (100 and 200 mmol) display a big shift to higher frequencies in comparison to the curves of LP modified samples. For a better overview about the performance of G′ and G″ and the results of the crossover points of each curve the data of ω_C (critical frequency) and G_C (critical modulus) are summarized in Table 3.

With these results a clear statement could be given regarding the changes of the molecular structure (M_W and MMD) during the reactive extrusion process. The vertical shift of G_C provides information about the MMD and the change of the M_W can be determined with the horizontal shift of ω_C. The resulting values show that M_W decreased if the values of ω_C shift to higher frequencies and the MMD is getting broader if the G_C values are lower. The unmodified PP samples, which were first-time extruded at 180°C and second-time extruded at 240°C were used as reference for the determination.

It could be observed, that the molecular weight of all modified samples are decreasing compared to the unmodified PP for the extrusion at 180°C as well as 240°C. Nonetheless, the molecular weight distribution could be kept almost constant and could be certainly improved. Only the MMD values of LP A1 and LP B1 show an increase in the results of the G_C values, which demonstrated that the distribution becomes narrower. Apart from this, it is noticeable that the values of ω_C and

G_C between the both extrusion steps do not increase sharply and it is possible to keep the values of M_W and MMD at a constant level.

According to Gahleitner et al it is possible to guarantee a correlation between rheological behavior and the molecular structure of polypropylenes.[55] The molecular weight and the molecular weight distribution as well as the change due to the use of the two peroxides can be analyzed from the results of the rheological investigations. This is possible with the use of two proportionalities, log (M_W)/ log (w_C) and (M_W/M_n)/($1/G_C$), which were proposed by Zosel and Zeichner.[56,95]

The following table (Table 5) show the results of the unmodified and modified samples. As in the rheological investigation, it can be seen that the molecular weights of the modified samples decrease after the first extrusion at 180°C as well as after the second extrusion at 240°C. The molecular weight distributions also show the same trend as in the results of the rheological analysis, that with an increase in the peroxide concentration, a larger molecular weight distribution occurs in comparison to the starting material.

Figure 7 represents the plots of the mechanical loss tan(δ) versus the frequency ω for the first and second extrusion step.

It has been reported, that the presence of LCB and the increase of elastic response with decrease of tan(δ) at low frequencies could be evaluated.[96–98] For the first extrusion step (Figure 7(a)) two independent curve progressions could be observed. On the one hand the unmodified PP and the modified samples, where PODIC A0.5, PODIC A1 and LP A1 are implemented, demonstrate a monotonic decrease in tan(δ) by increasing ω and on the other hand the other modified samples have an unexpected behavior, which is not usual for PP.[10,99]

Such two-step rubbery plateau is known for binary blends, which can be identified for high molar mass components.[100–102] However, these curves display a lower tan(δ) compared to the unmodified PP at low frequencies, which indicates that the LCB could be achieved. This behavior is more visible in Figure 7(b) because all modified samples demonstrate a lower tan(δ) value compared to the unmodified PP after the second extrusion step at 240°C. However, the modified samples of PODIC B0.5, PODIC B1, PODIC B5 and LP B1 represent a typical terminal behavior, as before at the first extrusion step at 180°C, of liquid-like materials because of the rapid decrease of tan(δ) with the increase of ω.

3.4 | Extensional rheology

Münstedt et al reported, that the extensional viscosity shows more sensitivity towards MMD compared to the shear viscosity.[103] The increasing of the extensional behavior, which is also known as strain hardening, is very important for many processing operations like thermoforming, foaming, film blowing and so on.[104]

As can be seen in Figure 8, the unmodified PP for the first extrusion step (180°C) and also for the second extrusion step (240°C) demonstrate no strain hardening and therefore no remarkable deviation for all three Hencky strain rates ($\dot{\varepsilon}$ = 5 s^{-1}; 1 s^{-1}; 0.1 s^{-1}) from the linear

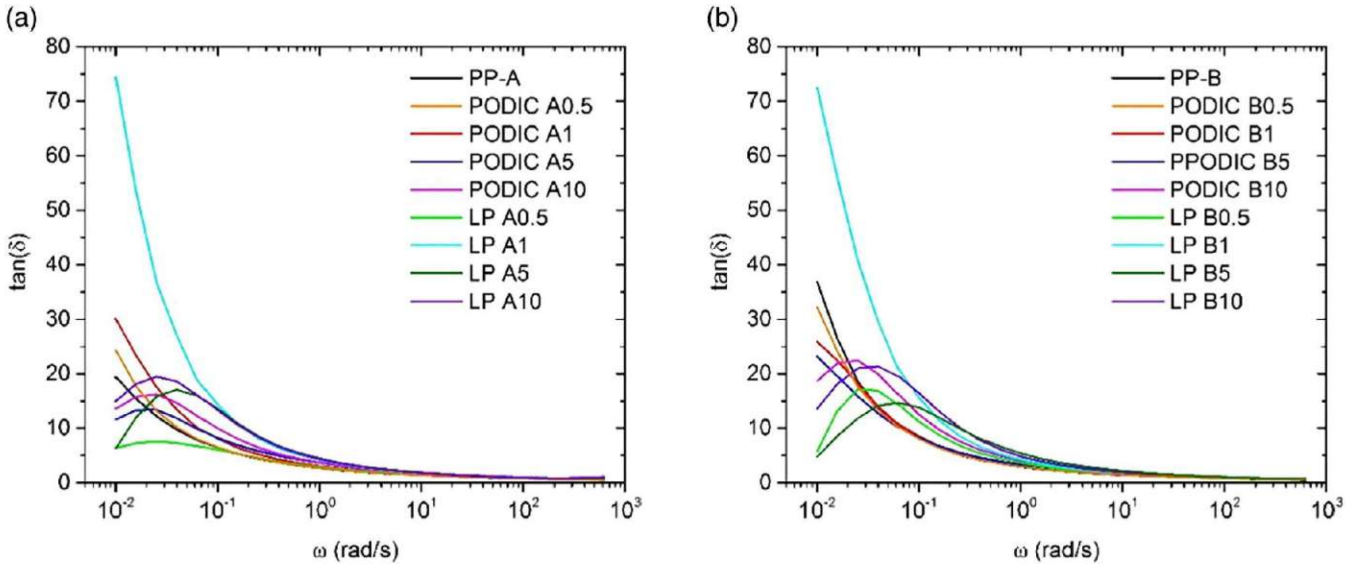

FIGURE 7 Tan δ of the unmodified PP and modified samples for the first extrusion step at (a) 180°C and for the second extrusion step at (b) 240°C; measured at 230°C [Color figure can be viewed at wileyonlinelibrary.com]

viscoelastic start-up curve (LVE), which is expected for linear polymers.[105,106] However, for the first extrusion step at 180°C (Figure 8(a)) the modified samples with peroxydicarbonate represent consistently strain hardening behavior, indicating that PODIC C126 induced LCB to the linear polymer backbone successfully.

After the second extrusion step at 240°C (Figure 8(b)) the strain hardening behavior declined slightly, especially for the highest Hencky strain rate of 5 s^{-1}. Nevertheless, a strain hardening behavior at the other Hencky strain rates was obtained for all samples, starting with the lowest concentration up to the highest concentration of peroxydicarbonate.

Additionally the results of the extensional rheology measurements of the modified samples with PEROXAN LP can be observed in Figure 9 for the first extrusion step at 180°C and the second extrusion step at 240°C.

An increase of the extensional viscosity for the various strain rates can also be achieved successfully, especially the samples with higher concentration of dilauroyl peroxide (LP A1, LP A5 and LP A10) with a concentration of 20 to 200 mmol PEROXAN LP demonstrate for all three Hencky strain rates an improvement of the strain hardening behavior. The samples with lower concentration of dilauroyl peroxide (LP A0.5) represent, that with the highest Hencky strain rate of 5 s^{-1} no deviations from the linear viscosity start-up curve were visible. In the case of the sample LP A0.5 the concentration (10 mmol) could be too low to introduce LCB on the backbone of PP. However, after the second extrusion step at 240°C (Figure 9(b)) for the most materials the extensional behavior has nearly the same values in comparison after the first extrusion step and it was possible to kept constant the strain hardening behavior after a further procedure step. After the second extrusion step the sample of LP B1 show the same behavior like the modified samples with peroxydicarbonate, which demonstrated a slightly decline of the extensional behavior from the first extrusion step at 180°C to the second extrusion step at 240°C. Nevertheless, a successful introduction of LCB on the linear backbone of PP during the reactive extrusion for both peroxides and their various concentrations was achieved.

In order to quantify the effect of strain hardening of each modified sample, the strain hardening coefficient (SH) is used and calculated according to Equation (1), which is defined as the ratio of the maximum extensional viscosity, η_e (t), of each Hencky strain rate and the extensional viscosity of the LVE curve, ηe0 (t), which correspond to the threefold of the shear viscosity.

$$SH = \frac{\eta_e(t)}{\eta_e^0(t)}. \tag{1}$$

The ratios of strain hardening of each modified sample and for both extrusion steps are given in Figure 10.

In most cases of the first extrusion step it could be observed, that the SH coefficient is very high for the lowest strain rate of 0.1 s^{-1} and decrease by increasing the strain rates. According to Bonten, at high strain rates it can be assumed that the extensional viscosity will decrease because the polymer chains are aligned and thus move more easily against each other.[107] Only the modified sample LP A1 do not follow the observation compared to the other samples and represent the highest SH

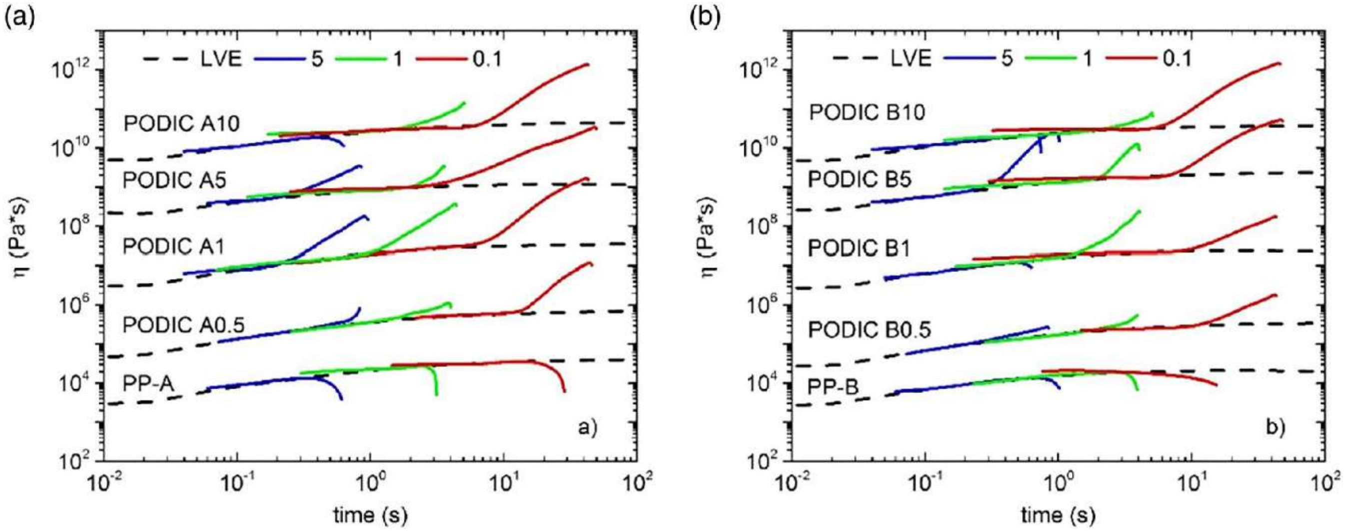

FIGURE 8 Extensional rheology of the unmodified polypropylene (PP) and modified samples with different concentrations of peroxydicarbonates (PODIC) C126 for (a) the first extrusion step at 180°C and (b) the second extrusion step at 240°C; measured at 180°C (PP2; 10 × 0.5 wt% 1000 × 1 wt%; 100,000 × 5 wt%; 2,000,000 × 10 wt%) [Color figure can be viewed at wileyonlinelibrary.com]

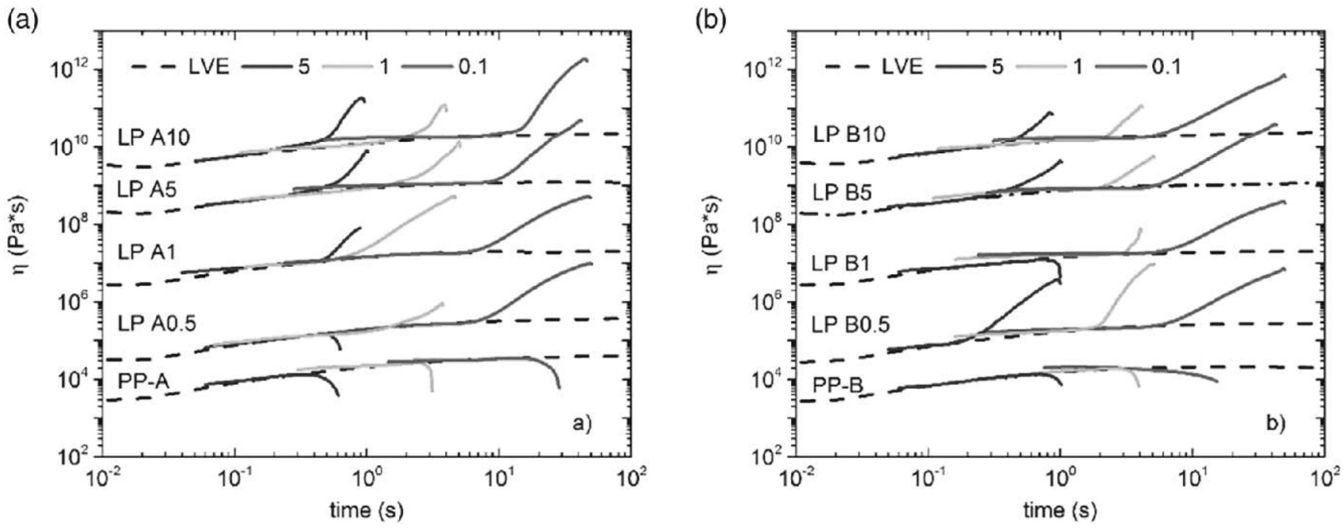

FIGURE 9 Extensional rheology of the unmodified polypropylene (PP) and modified samples with different concentrations of PEROXAN LP for (a) the first extrusion step at 180°C and (b) the second extrusion step at 240°C; measured at 180°C (PP2; 10 × 0.5 wt%; 1000 × 1 wt%; 100,000 × 5 wt%; 2,000,000 × 10 wt%)

coefficient at a strain rate of 1 s^{-1}. Also this behavior can be seen in the Figure 10(b) for the samples PODIC B1 and LP B0.5 at the second extrusion step. For the second extrusion step (240°C), there was also a noticeable tendency for the SH coefficient for the most modified samples to be kept constant or even increased compared to the first extrusion step (180°C).

3.5 | Mechanical properties

For the determination of the mechanical properties of polymers the tensile test, by using the values of tensile modulus of elasticity, tensile strength and the elongation break, as well as the impact tensile test play an important role.[108–110] In Figure 11 the strain stress curves (exemplary) for the unmodified PP and the modified samples are shown, which were obtained from the tensile test.

It can generally be observed that the stress for the first extrusion step at 180°C and the second extrusion step at 240°C reach high values, whereby a cross-linking of the samples can be excluded.[111] Furthermore you can see that by the use of peroxydicarbonate or dilauroyl peroxide during the extrusion steps effect the stress–strain values.

In addition to the stress–strain curves, the summarized values of the tensile modulus, tensile strength and elongation at break are given in Table 4.

For the first extrusion step the actual modification step displays for both peroxides, that with increasing the peroxide content the tensile modulus of elasticity decreased significantly. This phenomenon becomes more clearly after the second extrusion step, whereby the samples with the highest peroxide concentrations (PODIC B10 and LP B10) display in both cases the lowest tensile modulus of elasticity values.

According to the DIN EN ISO 527-1 standard the value of the tensile strength corresponds to the first maximum of the elongation curve. These values are given in Table 4 for all samples (unmodified or modified). If we now look at the unmodified and modified samples for the two extrusion steps independently of each other, we can see that the tensile strength changes only slightly between these two steps. It can even be assumed that the additional extrusion step has no influence on the tensile strength when comparing the same samples. However, the amount of peroxide plays an important role in the tensile strength. A clear tendency can be seen. The more peroxide is used the more tensile strength is lost and the values decrease more and more. For the first extrusion step this means a decrease in tensile strength of 16.4% for PODIC A10 and 18.7% for LP A10. In comparison, for the second extrusion at 240°C a decrease of 18.8% for PODIC B10 and 13.7% for LP B10 was observed. Always related to the unmodified starting material PP-A or PP-B.

The elongation at break values for the first extrusion step and the second extrusion step are represented in Table 4. The use of peroxides during the extrusion steps effect that the values of elongation at break could be increased or can be at least maintained compared to the unmodified PP. After the first extrusion step at 180°C the peroxide PODIC C126 represents a constant level for the elongation at break of the modified samples, whereby the sample with the lowest concentration of peroxydicarbonate (PODIC A0.5) slightly

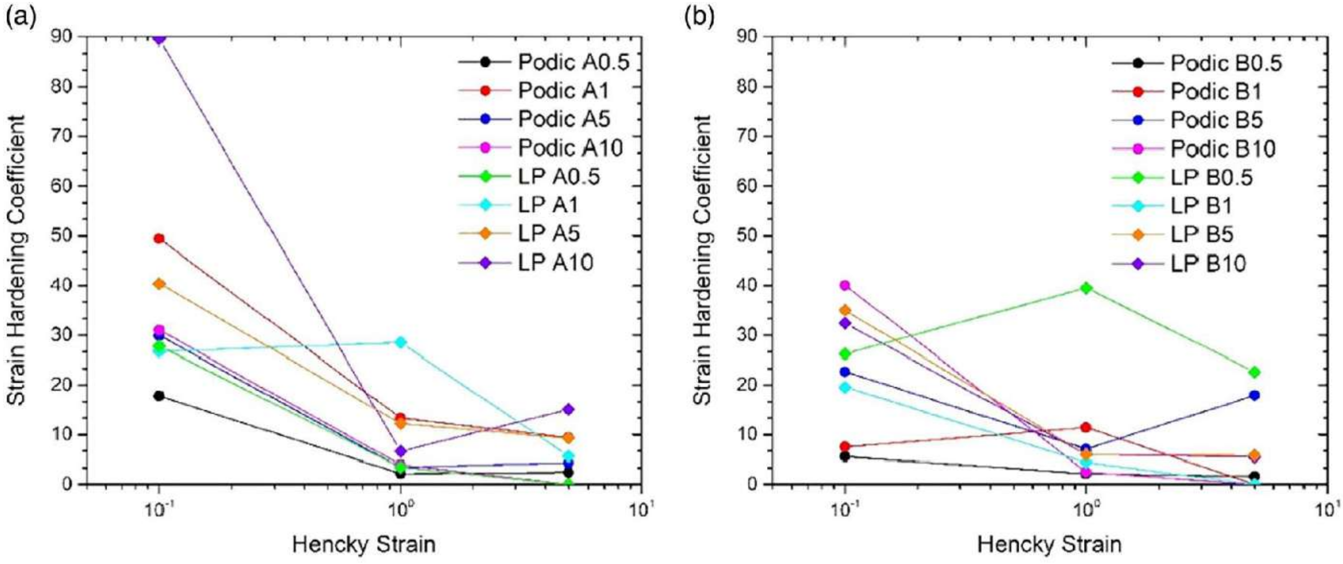

FIGURE 10 Strain hardening coefficient at different strain rates (0.1; 1; 5); for (a) the first extrusion step at 180°C and (b) the second extrusion step at 240°C [Color figure can be viewed at wileyonlinelibrary.com]

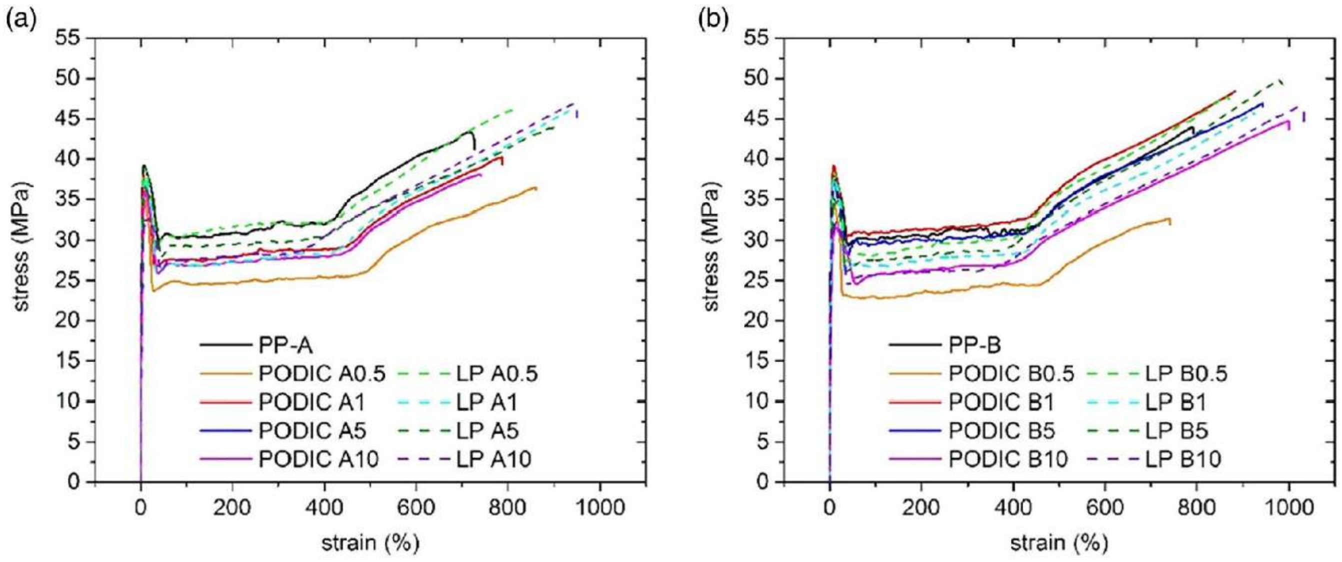

FIGURE 11 Stress strain curves of the unmodified and modified samples after the (a) first extrusion step at 180°C and (b) second extrusion step at 240°C [Color figure can be viewed at wileyonlinelibrary.com]

increased compared to the unmodified PP. In contrast, the modification with dilauroyl peroxide displays a nearly constant level for the sample of LP A0.5 in comparison to the unmodified PP but with higher concentrations of this peroxide the values could be increased very significantly. The sample LP A1 and LP A10 present an increase of 25% and therefore the highest values of elongation at break compared to the unmodified PP. After the second extrusion at 240°C a more clearly tendency could be observed for both peroxides.

The elongation at break values of each modified samples are depending on the peroxide content. With a higher concentration of peroxide, a higher value could be achieved compared to the unmodified PP. The samples, which contain peroxydicarbonate show a gradual increase and thereby the sample PODIC B0.5 presents a constant level compared to the unmodified PP, whereby the other PODIC samples present a growth by 15 up to about 30%. Also the modification with dilauroyl peroxide was successfully performed for the second extrusion step at 240°C and the values of elongation at break reflect this explicitly. In comparison to the unmodified PP the modified samples with dilauroyl peroxide show a consistently growth, which corresponds to an increase from about

TABLE 4 Tensile modulus (E_t), tensile strength (σ_M) and elongation at break (ε_B) of the unmodified and modified samples after the first extrusion step at 180°C and the second extrusion step at 240°C

Sample	E_t (MPa)	σ_M (MPa)	ε_B (%)
PP-A	2007 ± 99	39.1 ± 0.3	765 ± 17.3
PODIC A0.5	1729 ± 36	37.3 ± 2.1	860 ± 41.8
PODIC A1	1953 ± 287	37.0 ± 1.1	774 ± 49.6
PODIC A5	1721 ± 132	36.8 ± 0.5	738 ± 62.9
PODIC A10	1537 ± 106	32.7 ± 0.7	775 ± 49.8
LP A0.5	2072 ± 205	39.8 ± 0.9	703 ± 158.6
LP A1	1935 ± 144	37.1 ± 0.7	958 ± 98.5
LP A5	1718 ± 64	36.7 ± 0.6	891 ± 32.8
LP A10	1424 ± 36	31.8 ± 0.3	955 ± 33.4
PP-B	1916 ± 164	38.1 ± 0.6	753 ± 32.6
PODIC B0.5	2082 ± 269	35.3 ± 0.4	759 ± 69.5
PODIC B1	1847 ± 137	38.7 ± 0.6	876 ± 41.8
PODIC B5	1702 ± 146	37.0 ± 0.2	942 ± 17.1
PODIC B10	1478 ± 77	32.0 ± 0.2	999 ± 10.6
LP B0.5	1852 ± 118	38.4 ± 0.2	856 ± 34.6
LP B1	1711 ± 96	37.0 ± 0.5	917 ± 40.8
LP B5	1562 ± 136	35.1 ± 0.4	984 ± 30.9
LP B10	1262 ± 33	32.8 ± 0.4	1039 ± 22.9

Abbreviations: PODIC, peroxydicarbonates; PP, polypropylene.

10% for the sample with the lowest concentration of dilauroyl peroxide (LP B0.5) until nearly 40% for the sample with the highest concentration of dilauroyl peroxide (LP B10). In addition, the results of the impact tensile test are demonstrated in Figure 12.

As can be seen in Figure 12(a), the addition of peroxide improved the impact strength of each modified samples compared to the unmodified PP. In the case of peroxydicarbonate a percentage growth from 10% until 40% could be observed, whereby the sample with the highest concentration presents the lowest value of all PODIC C126 modified samples at an extrusion temperature of 180°C. Also the samples with dilauroyl peroxide have an improvement in the impact strength and the samples LP A0.5 and LP A1 display a similar behavior, which corresponded a growth about 40%. A significantly increase of the impact strength and therefore the highest value of all modified samples shows the sample with the highest concentration of dilauroyl peroxide (LP A10). Nearly a double improvement could be observed for this sample compared to the unmodified PP. Furthermore, the samples after the second extrusion step with a temperature of 240°C represent nearly the same behavior of the impact strength values. In general, all samples after the modification can achieve an improvement of the impact strength. The percentage growth amounts for the samples with peroxydicarbonate by 10% up to 45% and

TABLE 5 Calculation of Mw and Mw/Mn of the unmodified and modified samples

Sample	log ω_C (rad/s)	log Mw (kg/mol)	Mw (kg/mol)	1/Gc (kPa)	Mw/Mn	Comment
PP-A	1.56	5.59	390	0.0418	5.93	
PODIC A0.5	1.58	5.59	386	0.0418	5.93	MW ↓, MMD ~
PODIC A1	1.68	5.55	358	0.0427	6.11	MW ↓, MMD ↑
PODIC A5	2.02	5.45	284	0.0418	5.93	MW ↓, MMD ~
PODIC A10	1.89	5.50	315	0.0478	7.11	MW ↓, MMD ↑
LP A0.5	1.72	5.54	348	0.0426	6.07	MW ↓, MMD ↑
LP A1	1.92	5.48	303	0.0391	5.38	MW ↓, MMD ↓
LP A5	1.95	5.47	297	0.0578	9.06	MW ↓, MMD ↑
LP A10	1.88	5.49	311	0.0746	12.36	MW ↓, MMD ↑
PP-B	1.60	5.58	380	0.0391	5.38	
PODIC B0.5	1.64	5.57	370	0.0389	5.36	MW ↓, MMD ↓
PODIC B1	1.69	5.55	357	0.0424	6.03	MW ↓, MMD ↑
PODIC B5	1.86	5.50	317	0.0422	6.40	MW ↓, MMD ↑
PODIC B10	1.87	5.50	313	0.04545	6.64	MW ↓, MMD ↑
LP B0.5	1.79	5.52	332	0.04202	5.97	MW ↓, MMD ↑
LP B1	1.88	5.49	312	0.0377	5.13	MW ↓, MMD ↓
LP B5	2.10	5.43	267	0.0800	13.41	MW ↓, MMD ↑
LP B10	2.12	5.42	265	0.0613	9.75	MW ↓, MMD ↑

Abbreviations: MMD, molar mass distribution; MM, molar mass; PODIC, peroxydicarbonates; PP, polypropylene.

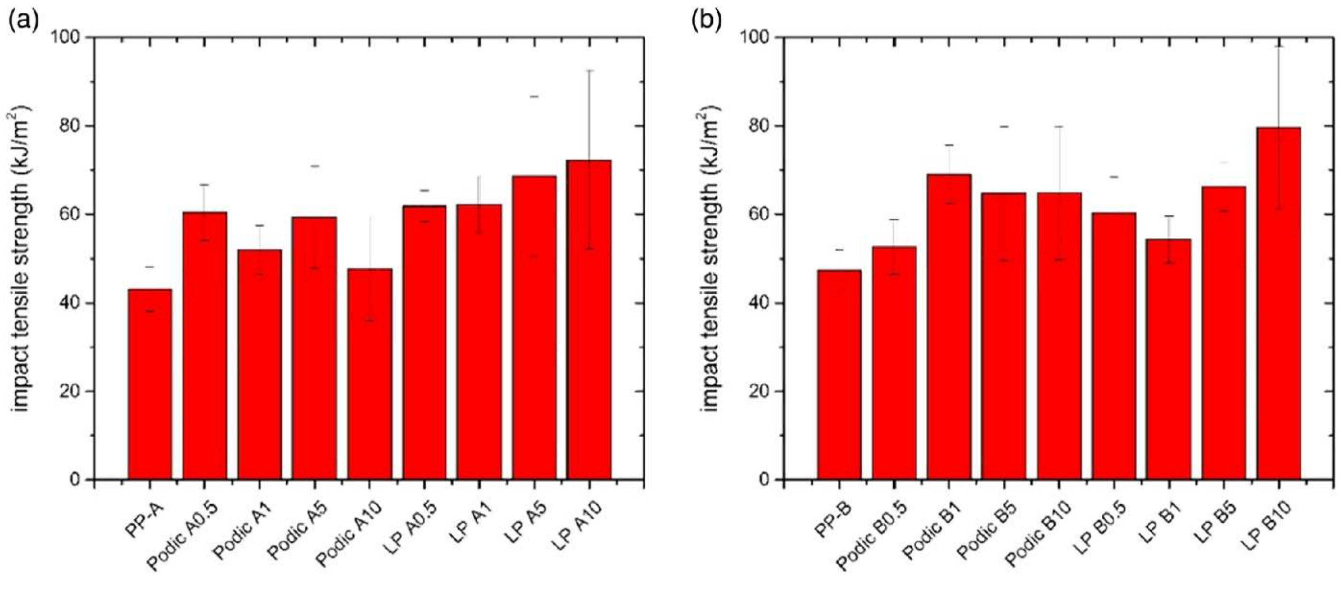

FIGURE 12 Results of the tensile test, especially the impact tensile strength for all samples at (a) the first extrusion step at 180°C and (b) the second extrusion step at 240°C [Color figure can be viewed at wileyonlinelibrary.com]

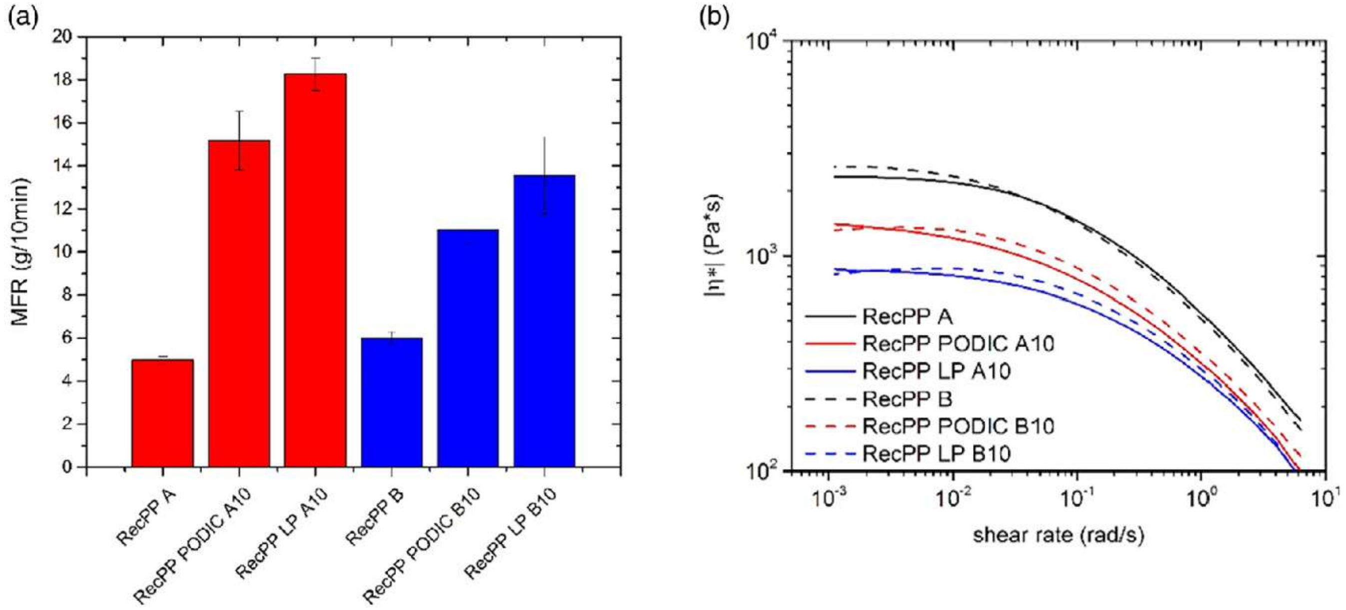

FIGURE 13 Melt flow rate (MFR) measurements at 230°C with 2.16 kg and complex viscosity versus shear rate of the unmodified and modified RecPP samples for the first extrusion at 180°C (a) and for the second extrusion step at 240°C (b) [Color figure can be viewed at wileyonlinelibrary.com]

for the samples of dilauroyl peroxide from nearly 30% until 70%, which show also nearly a double improvement for the sample with the highest concentration of dilauroyl peroxide (LP B10). In consideration of all results of the impact tensile test all modified samples for both extrusion steps present an improvement of impact strength. It can be assumed that the long chain branching reaction dominate compared to the degradation reaction or chain scission, because the impact strength depends on molecular weight directly.[112]

4 | UPCYCLING OF RECYLED PP

In order to further develop the already obtained results, which refer to PP virgin material, more application

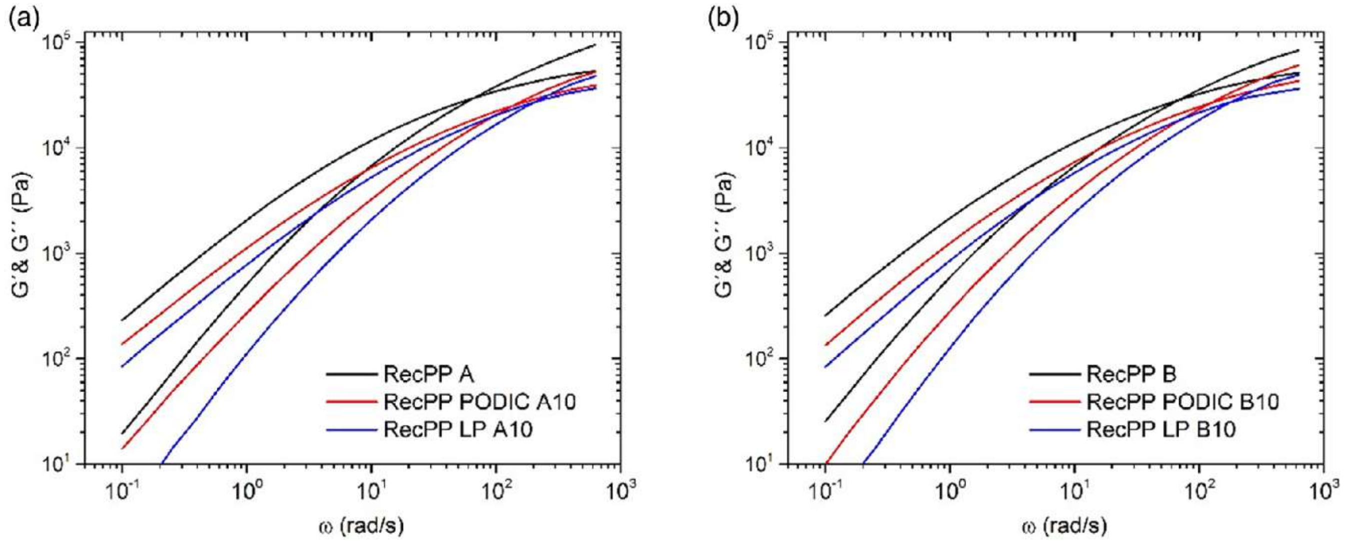

FIGURE 14 Storage and loss moduli as function of angular frequency for the first extrusion step at 180°C (a) and for the second extrusion step at 240°C (b); measured at 230°C [Color figure can be viewed at wileyonlinelibrary.com]

TABLE 6 Summary of rheological data from frequency sweep measured at 230°C

Sample	ω_C (rad/s)	G_C (kPa)	Comment	Sample	ω_C (rad/s)	G_C (kPa)	Comment
RecPP A	67.1	29.7		RecPP B	69.5	28.4	
RecPP PODIC A10	139.4	23.8	MW ↓, MMD ↑	RecPP PODIC B10	124.1	26.4	MW ↓, MMD ↑
Rec PP LP A10	207.9	27.2	MW ↓, MMD ↑	RecPP LP B10	180.5	27.0	MW ↓, MMD ↑

Abbreviations: MMD, molar mass distribution; MM, molar mass; PODIC, peroxydicarbonates; PP, polypropylene.

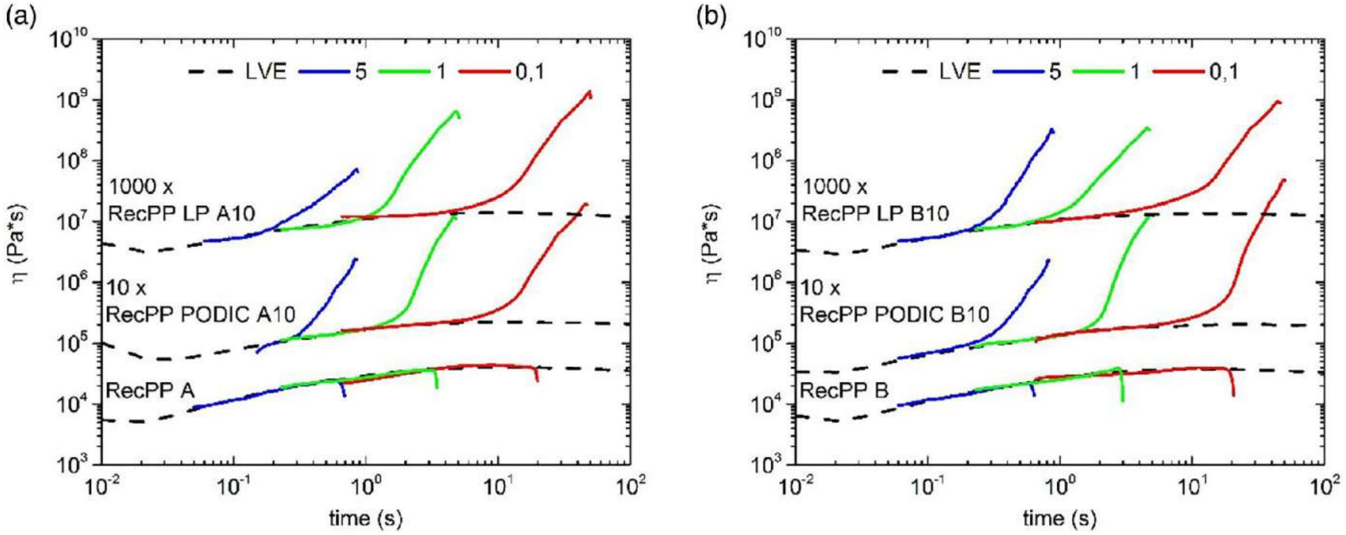

FIGURE 15 Extensional rheology od the unmodified and modified samples after the first extrusion step at 180°C (a) and after the second extrusion step at 240°C (b); measured at 180°C [Color figure can be viewed at wileyonlinelibrary.com]

specific with regard to recycling or upcycling, a recycled PP was additionally used instead of virgin PP for the final study. Considering the previous results using the highest peroxide concentration (200 mmol) of PODIC C126 and PEROXAN LP was assessed as the best option. The respective measurements of the rheological as well as the mechanical properties were carried out with the same conditions as for the modification of the virgin PP.

TABLE 7 Strain hardening coefficient at different strain rates of the modified RecPP samples

Strain rate (s^{-1})	RecPP PODIC A10	RecPP LP A10	RecPP PODIC B10	RecPP LP B10
5	15	7	17	32
1	56	47	70	26
0.1	88	106	245	72

Abbreviations: PODIC, peroxydicarbonates; PP, polypropylene.

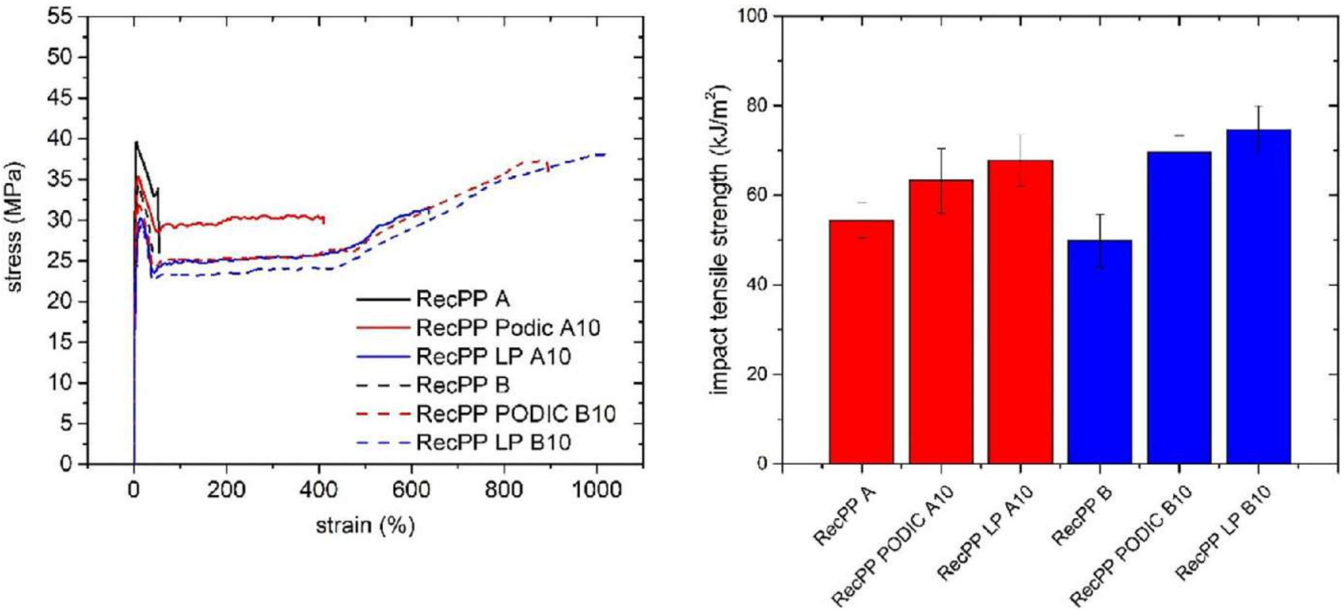

FIGURE 16 Stress–strain curves and results of impact tensile test of the unmodified and modified RecPP samples after the first extrusion step at 180°C and after the second extrusion step at 240°C [Color figure can be viewed at wileyonlinelibrary.com]

As can be seen in Figure 13, the MFR value increases very sharply after the first extrusion step at an extrusion temperature of 180°C due to the addition of peroxides. Comparing the two peroxides with each other shows that the degradation behavior of RecPP is slightly more pronounced with the use of PEROXAN LP. However, after the second extrusion at an extrusion temperature of 240°C and the addition of 0.5 wt% Irganox 1010 as stabilizer, the same phenomenon is reflected as in the modification of the pure PP. It can be clearly seen that the MFR values of the modified samples have decreased compared to the once extruded samples. For a better comparison, the viscosity curves of the individual samples, which resulted from the dynamic rheology measurements at 230°C, are shown. Here it can be seen that the pairs of curves of once and twice extruded samples are very close to each other. However, the trend shows that the second extrusion at 240°C and the use of Irganox 1010 has a stabilizing effect on the modified RecPP samples. This allows the assumption, as stated in the study with the pure material, that the stabilizer used is possibly incorporated as a long-chain compound during reactive extrusion.

As already mentioned, dynamic rheology provides information about the influence on the molecular structure and the viscoelastic properties in the polymer melt. The following figures show the curves of G′and G″. A clear shift of the curves modified by the addition of peroxide to higher frequencies can be seen for both of the samples that were extruded once at 180°C and for the samples that underwent the additional extrusion step at 240°C. The following table summarizes the values of the respective crossover points for all samples (Figure 14).

The dynamic rheology results from the RecPP showed the same trend as those for the pure PP. It is clearly shown that the molecular weight decreases by using the peroxides and the crossover point shifts to higher frequencies. Furthermore, it was also shown by the reduction of the Gc values compared to the starting material, in this case the RecPP, that the molecular weight distribution for the modified samples increases (Table 6).

As expected, no strain hardening could be determined for the starting material RecPP after the first as well as after the second extrusion. Contrary the modified samples showed a pronounced strain hardening. It can be clearly seen (Figure 15) that the modified samples show a

TABLE 8 Tensile modulus (E_t), tensile strength (σ_M) and elongation at break (ε_B) of the unmodified and modified RecPP samples after the first extrusion step at 180°C and the second extrusion step at 240°C

Sample	E_t (MPa)	σ_M (MPa)	ε_B (%)
RecPP A	2309 ± 51	39.6 ± 0.2	51 ± 3.8
RecPP PODIC A10	1551 ± 62	33.4 ± 1.1	415 ± 45.5
RecPP LP A10	1232 ± 24	30.4 ± 0.6	623 ± 26.3
RecPP B	1635 ± 135	33.7 ± 1.1	51 ± 2.6
RecPP PODIC B10	1530 ± 79	31.9 ± 0.6	887 ± 44.9
RecPP LP B10	1147 ± 26	28.9 ± 0.4	1017 ± 9.6

Abbreviations: PODIC, peroxydicarbonates; PP, polypropylene.

steep increase in viscosity at all strain rates and thus the long-chain branching could be realized very successfully by means of the peroxides used.

For better comparison and quantification of the long chain branching and the resulting strain hardening effects strain hardening coefficients were calculated for all samples and are listed in the following table (Table 7).

In addition to the rheological properties, the mechanical properties were also investigated for the RecPP. On the one hand the tensile properties and on the other the impact strength. The results of the tensile properties of the individual samples showed a huge increase in elongation at break and a decrease in the modulus of elasticity due to the use of peroxides for both single and double extrusion. Figure 16 shows the stress strain curves for the respective samples. It can be clearly seen that the elongation at break increases strongly due to the modification of the respective peroxides after the first but also after the second extrusion. Whereas the tensile strength decreases. The results of the individual measurements are listed in the following table for a better overview. It can also be observed that the modulus of elasticity decreases sharply due to the addition of the peroxides after the first as well as the second extrusion step, which is a result of the reduced crystallinity induced by long-chain branching (Table 8).

In addition to the results of the tensile test already mentioned, the results of the impact tensile test (notched impact strength) of the individual samples are also shown in Figure 16. Looking at the results after the first extrusion, it can be seen that the modification with PODIC C126 and PEROXAN LP increased the impact strength between 15 and 25%. This means that successful modification and long-chain branching can be assumed after the first extrusion step. After the second extrusion step, the increase between the starting material (RecPP B) and the modified samples is even greater and an increase of 40% for PODIC C126 and 50% for PEROXAN LP could be achieved. Comparing the values of the modified samples after the first and second extrusion step, a slight increase can be seen. All in all, a successful modification can be assumed as besides the melt properties the mechanical properties could be clearly increased by the introduction of long chain branching using PODIC C126 and PEROXAN LP.

5 | CONCLUSIONS

In this work, LCB-PP were prepared by modifying linear PP with a diverse amount of two different peroxides, peroxydicarbonate and dilauroyl peroxide (PODIC C126 and PEROXAN LP), by using reactive extrusion at a temperature of 180°C. These modified samples subsequently were extruded a second time at 240°C in a single screw extruder at 70 rpm by adding an antioxidant. On the one hand, the effects of the different peroxide concentrations (0.5 wt% to 10 wt%) and their effects on the unmodified PP were studied and, on the other hand, the effect of double extrusion was examined with regard to a possible recycling simulation process. For the characterization of these modified samples the DSC measurements, MFR, rheological and the mechanical properties were studied to differentiate them from the linear or unmodified PP.

All in all, it could be concluded that the modification of PP with peroxydicarbonate and dilauroyl peroxide (PODIC C126 and PEROXAN LP) for both extrusion steps are very good possibilities to generate PP-LCB and a further processing step does not deteriorate the modified samples. This effect is very promising regarding recycling options. With regard to peroxide concentration it can be said that, through the application of a higher amount of peroxydicarbonate or dilauroyl peroxide (100 or 200 mmol) the degradation reaction in these samples is more pronounced in comparison to the unmodified samples and the samples with a lower peroxide concentration (10 or 20 mmol). Nevertheless, the long chain branching reaction during the reactive extrusion at 180°C increased more for the samples with higher amount of peroxide. Especially for the formulation of dilauroyl peroxide the extensional rheology, which represent the LCB behavior of the modified samples, remains constant and is present after a further extrusion step at 240°C.

Although the modulus of elasticity decreases with increasing concentration of peroxide in both cases (PODIC C126 and PEROXAN LP) an improvement of their mechanical properties could be achieved, such as higher elongation at break values and higher impact tensile strength. It was also noted that these properties could be increased continuously with more and more peroxide. In particular, the formulations with 200 mmol dilauroyl peroxide (LP B10) present after the second extrusion step the highest values of elongation at break and impact tensile strength.

For the study on the RecPP, the same trend could be identified as already observed for the pure materials with the highest peroxide concentration of PODIC C126 and PEROXAN LP. Above all, the elongation rheological properties and thus the strain hardening could be increased compared to the original material. But also the mechanical properties, especially the elongation at break and the impact strength could be drastically increased by modification with the peroxides. All in all, a real upcycling could be successfully carried out at RecPP through the introduction of long-chain branching.

Summarizing, the results of this study are very promising in view of possible "up-cycling" options and in view of a possibility to create a long chain branched master batch, which is used for the further processing of various PP materials.

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Article

Improving Rheological and Mechanical Properties of Various Virgin and Recycled Polypropylenes by Blending with Long-Chain Branched Polypropylene

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Abstract: Blends of two long-chain branched polypropylenes (LCB-PP) and five linear polypropylenes (L-PP) were prepared in a single screw extruder at 240 °C. The two LCB-PPs were self-created via reactive extrusion at 180 °C by using dimyristyl peroxydicarbonate (PODIC C126) and dilauroyl peroxide (LP) as peroxides. For blending two virgin and three recycled PPs like coffee caps, yoghurt cups and buckets with different melt flow rate (MFR) values were used. The influence of using blends was assessed by investigating the rheological (dynamic and extensional rheology) and mechanical properties (tensile test and impact tensile test). The dynamic rheology indicated that the molecular weight as well as the molecular weight distribution could be increased or broadened. Also the melt strength behavior could be improved by using the two peroxide modified LCB-PP blends on the basis of PODIC C126 or PEROXAN LP (dilauroyl peroxide). In addition, the mechanical properties were consistently enhanced or at least kept constant compared to the original material. In particular, the impact tensile strength but also the elongation at break could be increased considerably. This study showed that the blending of LCB-PP can increase the investigated properties and represents a promising option, especially when using recycled PP, which demonstrates a real "up-cycling" process.

Keywords: reactive extrusion; long-chain branching; recycled polypropylene; blends; upcycling; rheology; mechanical properties

1. Introduction

The worldwide production of plastics has experienced great growth in the last decades and therefore the consumption of plastics has also increased more and more. As such, plastics and their products are already being promoted as the material of the 21st century. The three largest areas in which plastic products play an important role are the packaging industry with 40%, building and construction with 20%, and the automotive industry with 10%. For these and other application segments, the plastics that are used can be divided into different polymers. These include polypropylene (PP), polyethylene (PE), polyvinyl carbonate (PVC), polystyrene (PS), polyethylene terephthalate (PET) and others [1].

Isotactic polypropylene (PP) is one of the most popular and most universally applicable plastics worldwide with one of the largest share in global plastic production next to polyethylene (PE) [1]. PP is used in a wide range of applications from plastic pipes to various packaging applications and injection molding. Due to its excellent properties, such as good mechanical properties, high melting temperature, high chemical resistance or low density, PP is used in the aforementioned applications [2]. In general, the recycling of plastics and thus also of PP is becoming increasingly important due to the enormous production and consumption of plastics. In the literature there are different approaches for the solution of plastic waste such as mechanical recycling, energy recovery and landfill [3,4]. In particular, mechanical recycling is environmentally friendly and represents an economically viable practice, where theoretically a saving of 20–50% of the market price is achieved compared to the virgin material [5–8]. Various methods have been tried out in the literature to promote the quality of the recycled plastic. The basic idea is to add other material during the melting process such as virgin polymers, fillers, fibers, compatibilizers etc. [9–21].

However, the use of linear PP (L-PP) is limited because it has a relatively low melt strength and shows no strain hardening, which is particularly important in processes such as thermoforming, foaming and blow molding [22–24]. According to the literature, the introduction of long chain branching improves the properties of L-PP like a more pronounced shear-thinning effect or strain hardening, which leads to the effect that the melt strength increases significantly [25–30]. There are different methods to produce long-chain branched PP (LCB-PP) such as direct synthesis using metallocene catalysis [31,32], electron beam irradiation [33–35] or reactive extrusion [36–40]. Reactive extrusion is the most popular method because it requires no solvents, allows short reaction times and involves relatively low infrastructure costs [41,42]. In addition to the introduction of long-chain branching, various concurrent reactions take place in the case of polypropylene during reactive extrusion. Mainly, chain scission (β-scission) is expected in the case of PP, which leads to the formation of unsaturated short chain segments as a result [43,44]. Due to the use of peroxides, this phenomenon tends to become more common and is known as controlled rheology PP (CR-PP). This leads to a reduction in viscosity and to a reduction in molecular weight as well as a narrowing of the molecular weight distribution [45,46]. The use of peroxides can lead to further side reactions during reactive extrusion such as recombination disproportionation of peroxide radicals. The temperature used also plays an important role in reactive extrusion in the case of PP. Higher temperatures lead to β-scission and disproportionation being favored to some extent, thus negatively affecting the introduction of LCB. For this reason, reactive extrusion is mostly carried out at a temperature of 180 °C, whereas higher temperatures are used in industry and the balance shifts in the direction of chain scission.

Nonetheless, not only can the production of LCB-PP lead to an increase in melt strength. In order to achieve a higher melt strength also the blending with L-PP and LCB-PP is possible to obtain a significant increase of strain hardening. According to Stange et al. [47], a small amount of LCB-PP influences the rheological properties significantly, especially the elongation behavior. The same behavior was concluded by Fang et al. [48], which reported that adding LCB-PP into L-PP improved the melt strength resulting in a strain-hardening behavior. In addition to the rheological properties of L-PP/LCB-PP blends, according to McCallum et al. [49] not only could the melt strength be increased but also the mechanical properties as well. These studies have been carried out mainly with virgin PP materials.

The aim of this work is to investigate the rheological and mechanical properties of blends consisting of PP respective recycled PP and 10 wt.% LCB-PP blended at an extrusion temperature of 240 °C to simulate industry-related processes. The novel LCB-PPs (based on dimyristyl peroxydicarbonate (PODIC C126) and dilauroyl peroxide (PEROXAN LP)), which were produced by reactive extrusion in a previous study in the research group and investigated for their mechanical and rheological properties, were used as blend material in this work [50]. In order to investigate the blend properties of these two LCB-PP materials as potential masterbatch material, a virgin linear PP but also a commercial available high melt strength polypropylene (HMS-PP) with a content of 10 wt.% were additionally used in this work for better comparison. For the experiments in this study, two different virgin PPs were used, which covered a melt flow rate (MFR) range between 8–21 g/10 min. Besides the virgin material, three different recyclates consisting of flakes from yoghurt cups, coffee caps and buckets were blended with the respective LCB-PPs. To the best of our knowledge, no papers have been published in which recycled PP and their blends with LCB-PP were analyzed.

2. Materials and Methods

2.1. Materials

Two different isotactic PP homopolymers were used for the study, which were supplied by Borealis (Vienna, Austria). The type of HD 601CF (PP3; MFR value of 8 g/10 min at 230 °C and 2.16 kg) is normally used as film resin for chill roll processes and the second virgin PP, HF 700SA (PP4; MFR value of 21 g/10 min) can be used for different injection molding applications. Additionally, three different PP were collected from household post-consumer waste, which consisting of flakes from coffee caps (MFR = 14.3 g/10 min), which was supplied by Walter Kunststoffe GmbH (Wels, Austria), flakes of yoghurt cups (thermoformed PP; MFR = 5.3 g/10 min) and flakes of buckets (injection-molded PP; MFR = 31.9 g/10 min). The yoghurt cups and buckets were self-collected.

The LCB-PPs, which were used for the blends, were based on HC 600TF (PP2) appropriated for thermoforming applications, which was also supplied by Borealis (Vienna, Austria), and the peroxides PODIC C126 (dimyristyl peroxydicarbonate; 10 h half-life time at 48 °C) or PEROXAN LP (dilauroyl peroxide; 10 h half-life time at 61 °C) from Pergan GmbH (Bocholt, Germany). The choice of peroxide content was investigated on the basis of a preliminary study, which examined different concentrations from 10 to 200 mmol/kg PP of the respective peroxides on virgin material. An increase in melt stiffness as well as an increase in mechanical properties, tensile strength and impact strength, could be observed [50]. These two modified materials have an MFR value of 7.7 g/10 min for PODIC C126 and an MFR value 6.0 g/10 min for PEROXAN LP at 230 °C and 2.16 kg weight. In general, the PP2 with an MFR value of 2.8 g/10 min was used as blend material in this study to get a better comparison between the blends with L-PP and LCB-PP. In addition, the Daploy™ WB140HMS from the company Borealis (Vienna, Austria) with an MFR value of 2.1 g/10 min served as a comparison material of a high melt strength polypropylene (HMS-PP).

2.2. Sample Preparation

The two LCB-PPs were produced using a three-zone single-screw extruder, Extron 18–26−1.5, with a screw diameter of 18 mm and a ratio L/D = 25:1 (Extron Engineering, Ltd., Akaa, Finland). The rotational speed was 70 rpm and the temperature profile for the three independent temperature zones (feeding zone/extrusion zone/die zone) was 165/180/220 °C. The pure material (PP2) and the respective peroxide (PODIC C126 or PEROXAN LP) with a quantity of 10 wt.% were mixed directly and added to the extruder.

For this study and the production of the blend, the respective pure materials and the investigated mixing ratios are shown schematically in Figure 1.

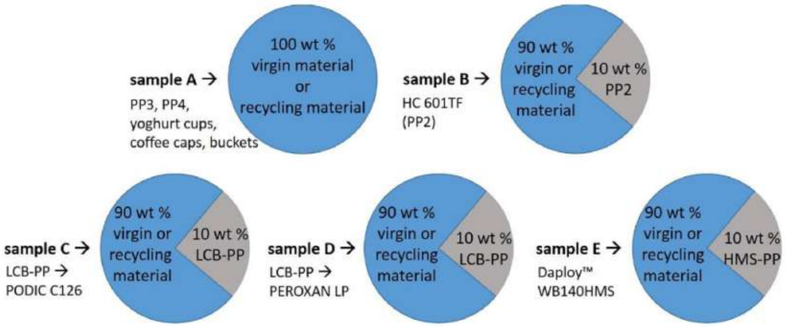


Figure 1. Schematic blend composition and specification of all series.

For better mixing during extrusion (blend production), the three post-consumer waste materials and both LCB-PPs were shredded before use with a universal cutting mill, Pulverisette 19 (Fritsch, Idar-Oberstein, Germany), equipped with a 4 mm sieve insert. The extrusion or blending of these samples were performed at a temperature profile of

165/240/240 °C and also a screw rotation of 70 rpm. The polymer strands produced were then ground again with the Pulverisette 19 for further production steps.

2.3. Melt Flow Rate (MFR)

With a manual testing device from Karg Industritechnik (Krailling, Germany), Melt-Flow basic, the MFR measurements were performed in accordance with DIN EN ISO 1133 method A under a load of 2.16 kg and a temperature of 230 °C [51].

2.4. Differential Scanning Caloremtry (DSC)

The thermal behaviour of all materials (virgin/recycling materials and their blends) after extrusion at 240 °C was investigated by using TA Q2000 differential scanning calorimeter (DSC) from TA-Instruments (Newcastle, DE, USA). We inserted 5–10 mg of each sample in aluminium pans and the measurements were carried out under a nitrogen atmosphere. The samples were heated from room temperature to 200 °C at a rate of 10 K/min, cooled to room temperature and heated a second time also at a rate of 10 K/min to 200 °C. The analysis software TA Universal Analysis was used to determine the crystallisation temperature (T_c) and from the second heating the melting temperature (T_m) as well as the enthalpy of fusion (ΔH_m). From the enthalpy of fusion the degree of cristallinity Xc was calculated using 207 J/g as the enthalpy of a fully crystalline PP.

2.5. Fourier Transform Infared (FTIR) Measurements

The Fourier transform infrared (FTIR) spectroscopy measurements were carried out at room temperature with a spectrometer (Tensor 27) of the company Brucker (Billerica, MA, USA), which is equipped with an ATR diamond (DuraSample IR II) with single reflection. The measurement covered with a number of 16 scans and a wave number range of 600–4000 cm^{-1} with a 4 cm^{-1} resolution.

2.6. Rheology Properties

The characterisation of the polymer melt and its rheological properties was carried out by using dynamic rheology and extensional rheology measurements. The specimens for the dynamic rheology measurements were made by compression molding (Collin P 200 P, Maitenbeth, Germany) at a temperature of 240 °C and a pressure of 30 bar. The dimensions for the round samples were 25 mm in diameter and 1.2 mm thick. For the extensional rheology measurement stripes with dimensions of 20 × 8 mm were necessary, which in form of squares were produced by compression molding with dimensions of 60 × 60 × 0.8 mm.

The dynamic rheology respectively the frequency sweep test was done on a plate-plate system with a diameter of 25 mm via Anton Paar (Graz, Austria) MCR 302 rheometer, which was equipped with a CTD 450 heating chamber, under nitrogen at 230 °C. The frequency range was selected from 628 to 0.01 rad/s, the deformation rate increased logarithmically over the selected range from 1% to 2%, and the gap size of the plate-plate system was 1 mm. Also the extensional rheology measurements were done at the Anton Paar MCR 302 rheometer, which was equipped with a Sentmanat Extensional Rheometer (SER-HPV 1, Xpansion instruments, Tallmadge, OH, USA). Three different strain rates ($\dot{\varepsilon}$ = 5; 1; 0.1 s^{-1}) were used at a temperature of 180 °C and additionally the corresponding start up curves were measured with a plate-plate system with a diameter of 25 mm at 0.001 and 0.1 s^{-1} shear rates.

2.7. Mechanical Properties

Tensile and tensile impact strength tests were used for the determination of the mechanical properties. The required test specimens were produced using Haake Mini Lab II (Thermo Fisher, Waltham, MA, USA), a twin screw extruder, in combination with Haake Mini Jet II injection molding equipment from Thermo Fisher Scientific (Waltham, MA, USA). The extrusion was carried out at a temperature of 240 °C and a screw rotation of 100 rpm. For the injection molding process, the mold temperature was set at 90 °C, the pressure was 350 bar with an injection time of 10 s.

The test machine for the tensile test (Zwick 050, ZwickRoell GmbH and Co. KG, Ulm, Germany) was used with a test speed of 10 mm/min and was equipped with a 1 kN load cell and an extensometer. The test specimens for these measurements corresponded to the standard ISO 527-2-5A [52].

For the tensile impact strength test the specimens were notched on both sides with a Notch-Vis from Ceast and tested according to ISO 8256/1A [53] on an Instron Ceast 9050 (2 J hammer; cross head mass = 15 g, Instron, Darmstadt, Germany).

2.8. Scanning Electron Microscopy (SEM)

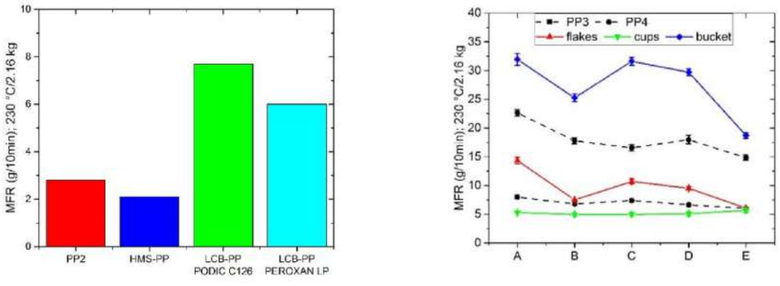
For the morphological investigation of the respective samples, the fracture surfaces of the impact tensile test samples were analyzed using scanning electron microscopy (FEI Philips XL30, Hillsboro, OR, USA). The individual samples were coated with gold prior to imaging (Agar Sputter Coater B7340, Stansted, UK).

3. Results

3.1. Melt Flow Rate

In general, the MFR value gives a first good approximation of melt behavior and the process ability of polymer blends. It is generally known that the MFR value, especially for PP, can increase very strongly as a result of β-scission and the associated increase in chain mobility, but can also be reduced by long chain branching or cross-linking [54–56].

Figure 2a shows the MFR values of the blending materials, which amounted for PP2 = 2.8 g/10 min, LCB-PP modified by PODIC C126 = 7.7 g/10 min, LCB-PP modified by PEROXAN LP = 6.0 g/10 min. Figure 2b represents the MFR values of all materials after the extrusion temperature of 240 °C. It can be clearly seen that the use of blends reduces the MFR values. In particular, for the starting materials with a high MFR value such as PP4 (virgin granulate) but also for the flakes or bucket a reduction is visible. For the two materials with a lower MFR value (PP3 and cups) a slight reduction or at least keeping the values constant can be observed. However, as these values do not increase due to the addition of LCB-PP, which show a higher MFR than cups, it can be assumed that the mixing rule is not the reason for the reduction of the MFR values.

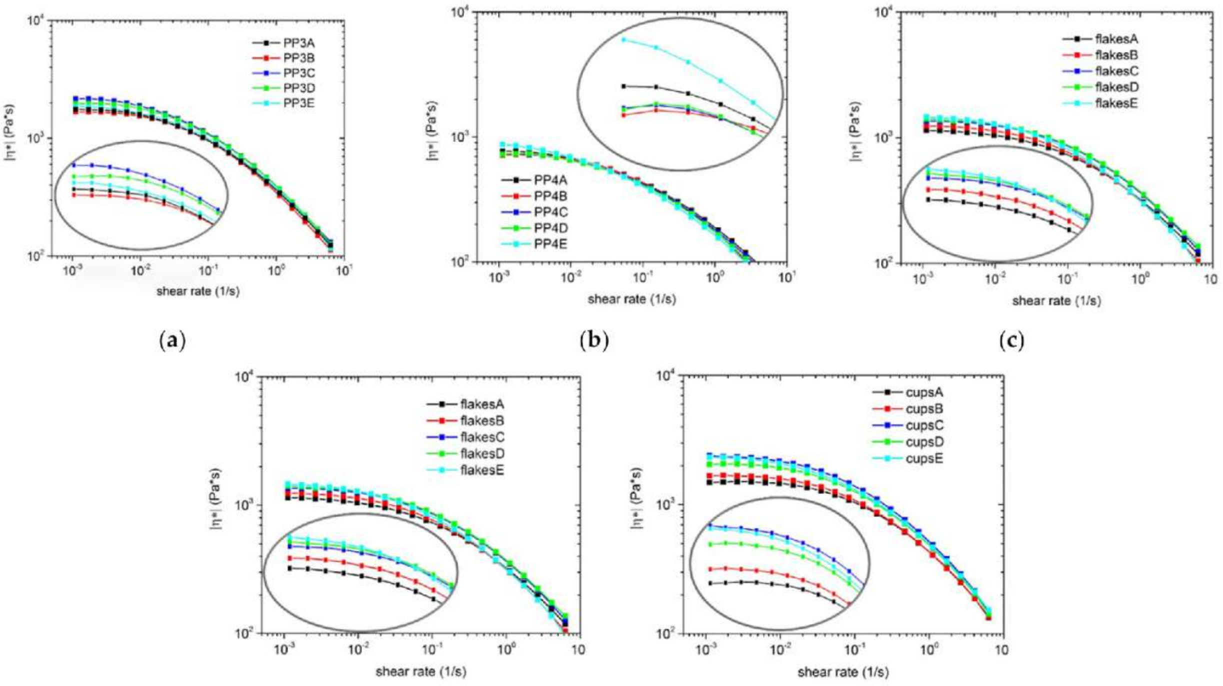


(**a**) (**b**)

Figure 2. Melt flow rate (MFR) values of the materials, which was used for blending (**a**) as well as all starting materials and their blend series (**b**); measured at 230 °C with 2.16 kg.

3.2. Dynamic Rheology Properties

Rheology measurements have been shown in literature to be a good tool of identifying molecular structures and to be very sensitive to changes in them [36,57–64]. Several studies have investigated the rheological behavior of blends with linear PP and branched PP or PE and have shown that these blends have a higher shear thinning effect or strain hardening compared to linear PP [47–49,65]. The Figure 3 show the viscosity curves, which were measured at 230 °C to achieve better comparability with the MFR values, of the respective virgin materials and the blends. The viscosity curves of the respective materials are very close to each other, so these curves were additionally plotted larger in the low shear range in order to get a better overview. For the series with lower MFR (PP3, flakes and cups) it was found that the use of LCB-PPs or HMS-PP resulted in a pronounced increase in viscosity. While the blends with L-PP only achieved a slight increase in viscosity for the recycled materials, the curve progression of virgin granules could only be kept constant. No clear trends could be observed for the two series with higher MFR (PP4 and buckets). On the one hand, no changes between the individual viscosity curves are clearly visible in the PP4 series blends and on the other hand, an opposite trend could be observed in the recycled bucket and its blends compared to the other recyclates. In this case, the blend with L-PP shows an increase in the viscosity curve, whereas the blends with LCB-PPs and HMS-PP show a small reduction.

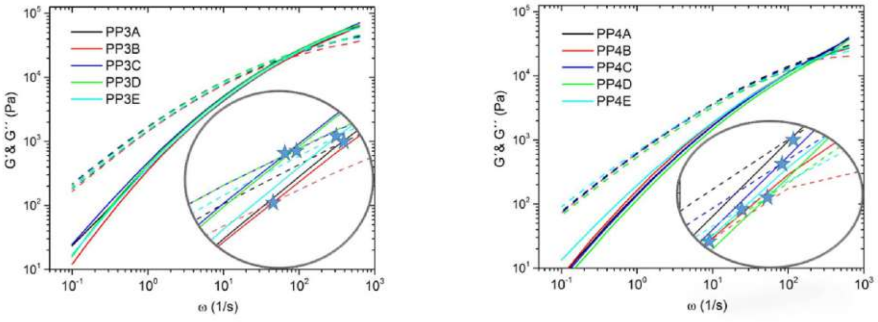


(a) (b) (c)

(d) (e)

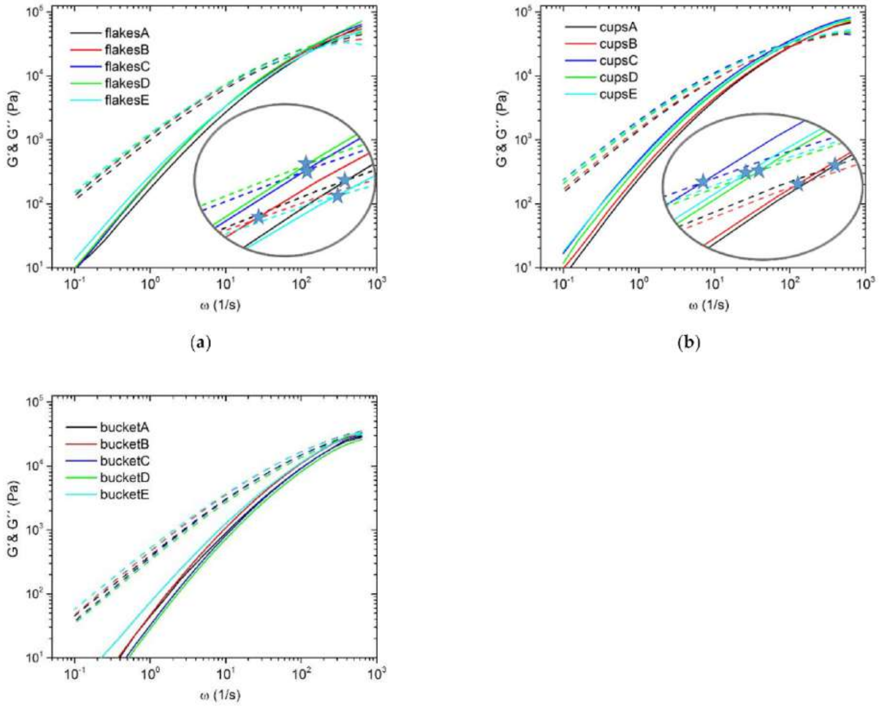
Figure 3. Complex viscosity of all samples (polypropylenes PP3 (**a**) and PP4 (**b**), flakes (**c**), cups (**d**), bucket (**e**)) and their blends; measured at 230 °C.

In addition to the complex viscosity, the storage modulus (G') and the loss modulus (G'') are important parameters in dynamic rheology, which provide information about viscous or elastic effects depending on the shear rate [66,67]. In Figures 4 and 5 the respective curves of the associated series are shown. For a better representation of the crossover points, this area of the curves was displayed larger and additionally the intersection points were marked with a star for each graph. Figure 4 shows the curves of the two virgin materials PP3 (a) and PP4 (b) and their blends. If both pictures are compared, it becomes clear that the curves and the cross points of G' and G'' are shifted from PP4 to higher frequencies, which is attributable to the high MFR values. As the curves are so close to each other in nearly all cases and the crossing point of G' and G'' partly overlap, the respective values are given in Table 1.



(**a**) (**b**)

Figure 4. Storage modulus (G') lines and loss modulus (G'') dashed lines of the series PP3 (**a**) and PP4 (**b**) and their blends; the stars represent the crossover point of the two curves (G' and G'') of the respective blend series; measured at 230 °C.



(**a**) (**b**)

(**c**)

Figure 5. Storage modulus (G') lines and loss modulus (G'') dashed lines of the flakes (**a**), cups (**b**), bucket (**c**) and their blends; the stars represent the crossover point of the two curves (G' and G'') of the respective blend series; measured at 230 °C.

Figure 5 additionally shows the series of recyclates (flakes (a), cups (b) and bucket (c)). Comparing the different recyclates with each other, the difference between the crossing points of G' and G'' is even more pronounced. It can be seen that with increasing MFR value the crossing point shifts to higher frequencies. This is most pronounced with the bucket. Here no intersection point could be determined under the given measurement conditions because it was outside the measurement range. However, the values of the crossing points of the other two series (flakes and cups) are also listed additionally in Table 1.

Table 1. Results of crossover point (G′ = G″) from dynamic rheological measurements at 230 °C.

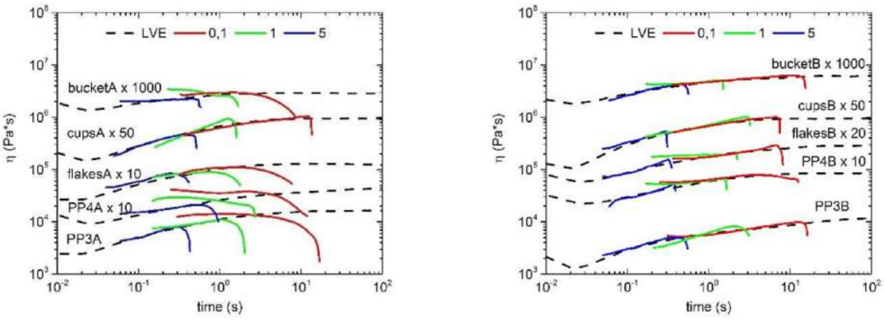
Sample	ω_C (rad/s)	G_C (kPa)	*M*w/MMD
PP3A	102	24.52	
PP3B	78	20.26	*M*w ↑, MMD ↑
PP3C	80	23.51	*M*w ↑, MMD ↑
PP3D	81	22.96	*M*w ↑, MMD ↑
PP3E	100	24.09	*M*w ↑, MMD ↑
PP4A	255	21.18	
PP4B	170	15.29	*M*w ↑, MMD ↑
PP4C	238	19.37	*M*w ↑, MMD ↑
PP4D	232	18.87	*M*w ↑, MMD ↑
PP4E	201	16.96	*M*w ↑, MMD ↑
FlakesA	177	32.47	
FlakesB	124	25.02	*M*w ↑, MMD ↑
FlakesC	150	30.16	*M*w ↑, MMD ↑
FlakesD	152	31.01	*M*w ↑, MMD ↑
FlakesE	170	27.47	*M*w ↑, MMD ↑
cupsA	123	31.86	
cupsB	106	29.61	*M*w ↑, MMD ↑
cupsC	76	30.00	*M*w ↑, MMD ↑
cupsD	93	31.22	*M*w ↑, MMD ↑
cupsE	90	31.14	*M*w ↑, MMD ↑

The position or change of the crossover point can be used to determine the change in molecular weight (M_W) or molecular weight distribution (MMD) [68–73]. If the crossover point shifts to lower frequencies, this represents the presence of branched molecules with longer relaxation time. In contrast, the vertical shift of the crossover point to lower G values results from a broadening of the MMD. The values of the crossover frequency ω_C and crossover modulus G_C are given in Table 1. By comparing the individual series and their blends with each other, it can be seen that both the ω_C values and the G_C values are lower than the virgin/recycled material used. All in all, this could mean that the use of blends, which have been applied in this work, can increase the molecular weight and broaden the molecular weight distribution compared to the respective starting materials.

3.3. Extensional Rheology

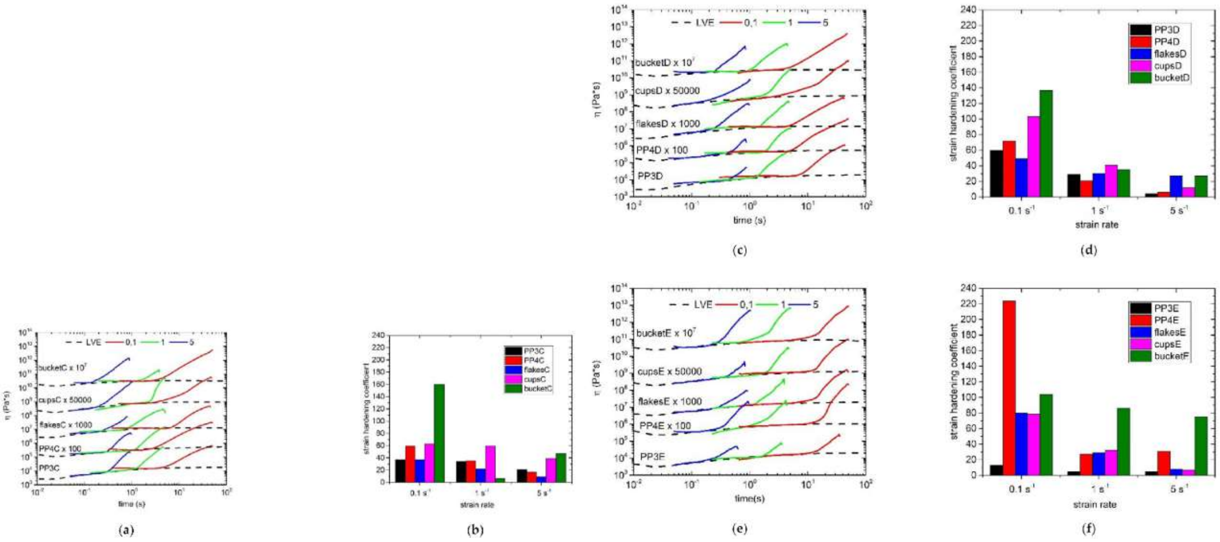
It is known that extensional rheology plays an important role in the detection of long-chain branching and the associated changes in molecular structure [74–77]. It has been shown in various studies that the melt strength, which is also referred to as strain hardening, can be increased compared to linear PP [78–82]. The increased melt strength of materials is very important and desired for many manufacturing processes such as thermoforming, film casting, film blowing, foaming, and so on [83,84].

The following figures show the starting materials and the respective blends using PP2, the two LCB-PPs and HMS-PP. The dashed lines correspond to the linear viscoelastic start-up curve (LVE), which was measured by shear rheology and multiplied by the Trouton factor to obtain the extensional viscosity [85]. The presence or absence of melt strength (strain hardening) of all materials were measured with three different Hencky strain rates ($\dot{\varepsilon}$ = 5; 1; 0.1 s^{-1}). As expected, the virgin materials showed no deviation of the respective strain curves from the LVE and thus no strain hardening could be determined in all cases (Figure 6a). The same result was reflected in the blends with a content of 10 wt.% PP2, which is represented in Figure 6b. Again, no deviation and thus no strain hardening could be achieved. In contrast, the two blends with the respective LCB-PPs and HMS-PP showed a significant deviation from the LVE curve for all three different strain rates. In these cases, a significant strain hardening and associated increased melt strength behavior can be seen for the LCB-PP with PODIC C126 in Figure 7a, for LCB-PP with PEROXAN LP in Figure 7c and for HMS-PP in Figure 7e.



(a) (b)

Figure 6. Extensional rheology of all curves for the virgin materials (**a**) and with the PP2 blends series (**b**).



(a) (b) (c) (d) (e) (f)

Figure 7. Extensional rheology curves of all samples with the blend series of long-chain branched polypropylene (LCB-PP) dimyristyl peroxydicarbonate (PODIC C 126) (**a**), with LCB-PP dilauroyl peroxide (PEROXAN LP) (**c**) and HMS-PP (**e**); Strain Hardening Coefficient of all samples with the blend series of LCB-PP PODIC C 126 (**b**), with LCB-PP PEROXAN LP (**d**) and HMS-PP (**f**).

In order to make a better statement or distinction about the strain hardening behavior and thus the melt strength of the blends with the two LCB-PPs and HMS-PP, the strain hardening coefficient (SH) of the respective blends was determined. This represents the maximum strain viscosity η(t) at the strain hardening rate in relation to the strain viscosity of the LVE curve $\eta_0(t)$. The results are represented in Figure 7b,d,f. It can generally be seen that with increasing strain rate, the strain hardening coefficient continuously decreases for both blended sets. Comparing the two blend sets with each other, no general statement can be made about the results with PODIC C126 or PEROXAN LP. However, this is clear evidence that the use of LCB-PPs produced by ourselves in laboratory scale as blends can successfully increase melt strength (Figure 7b). Especially with recycled materials, a significant increase in melt strength was observed when using PEROXAN LP LCB-PP (Figure 7d). Here the strain hardening coefficient tends to be higher than the values of the virgin material (PP3 and PP4). In order to be able to make a better statement about the two LCB-PPs, the melt strength of the blends with HMS-PP and their strain hardening coefficients were also investigated (Figure 7f). On the one hand, the same trend was observed again, that the melt strength of the respective series decreased with increasing strain rate and, on the other hand, that the blends with LCB-PPs, with the exception of PP4 and a strain rate of 0.1 s^{-1}, can keep up with the blends with HMS-PP in terms of melt stiffness.

All in all, the melt strength properties of the relevant samples, especially those of the recycled materials, can be increased and thus new areas of application can be found.

3.4. Thermal Characterization

All materials, including the complete mixtures of the different blends, exhibit single melting and crystallization peaks. The temperature of melting (Tm) and crystallization (Tc) as well as the crystallinity of all blends and their virgin material are listed in the Table 2. To determine the crystallinity, the melting curves were integrated from 80 °C to the temperature of return to baseline after melting (The diagrams of the second heating are presented in Figure S1 in the Supplementary Material). Except for the buckets which consist of a PP copolymer and has a much broader melting peak with lower peak temperature. In that case the integration starts at 50 °C. Regarding the crystallization temperature there is no clear trend visible, in most cases there is no strong shift by the addition of PP2 and the LCB-PPs. The same behavior was reported from Tabatabaei et al. [86] for blends containing 10 wt.% LCB-PP and more. Adding of HMS-PP results in every series in the highest crystallization temperature, which indicates a nucleating effect. This is also visible by a slight increase in crystallinity for the mixtures of PP3, PP4, flakes and cups with HMS-PP. The blends from the buckets show a different behavior, there occurred a notable increase of the crystallization temperature if the second components are added. This is not unlikely if primarily homopolymer type PP is added to a PP copolymer. Interestingly, the blends of the bucket with the LCB-PPs show a 10% increase of crystallinity. It should be respected that the melting curves of PP3C, PP4A-D and flakesC and E contain a small shoulder at a temperature between 149–152 °C, which it the typical melting temperature of the β—phase of PP. In principle this should be considered if someone calculates the crystallinity from melting curves because a superposition of melting of the β—phase and recrystallization to the α—phase takes place. But this shoulder is really small and the calculated crystallinities do not show outliers, so it can be neglected.

Table 2. Crystallization temperature (T_c), melting temperature and crystallinity (2nd heating) of all samples obtained from differential scanning calorimetry (DSC) measurements; mechanical properties (tensile modulus, elongation at break and tensile strength) obtained from tensile test.

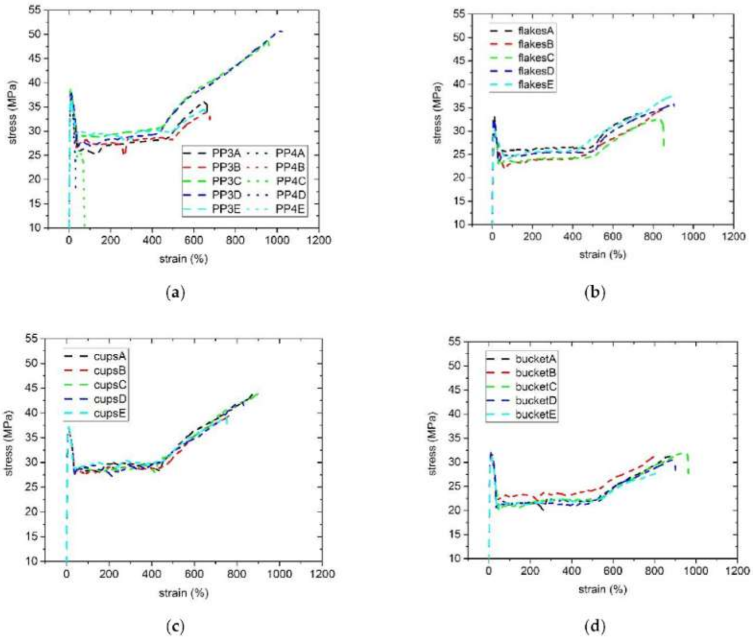
Sample	T_c (°C)	T_m (°C)	X_C (%)	E_t (MPa)	ε_B (%)	σ_m (MPa)
PP3A	115	167	50	2039 ± 139	689 ± 65	38.7 ± 0.5
PP3B	119	169	49	1848 ± 115	650 ± 105	36.5 ± 0.7
PP3C	121	167	50	2181 ± 140	921 ± 77	38.9 ± 0.3
PP3D	115	165	50	1904 ± 108	1008 ± 34	38.1 ± 0.5
PP3E	129	168	53	2037 ± 81	681 ± 57	36.9 ± 0.3
PP4A	118	164	50	1960 ± 18	23 ± 4	37.1 ± 0.5
PP4B	118	164	48	1898 ± 151	35 ± 4	37.0 ± 0.5
PP4C	120	165	50	1980 ± 164	77 ± 25	36.9 ± 0.3
PP4D	117	165	50	1950 ± 125	26 ± 6	36.7 ± 0.7
PP4E	128	167	50	1966 ± 53	43 ± 5	36.8 ± 0.4
FlakesA	121	167	42	1864 ± 55	748 ± 85	32.8 ± 0.6
FlakesB	121	165	43	1436 ± 35	863 ± 48	29.8 ± 0.4
FlakesC	122	165	44	1717 ± 51	917 ± 38	31.7 ± 0.2
FlakesD	121	165	44	1733 ± 66	916 ± 49	32.2 ± 0.3
FlakesE	125	166	45	1502 ± 123	912 ± 21	30.5 ± 0.4
cupsA	129	167	51	1794 ± 143	859 ± 39	37.1 ± 0.3
cupsB	129	167	50	1913 ± 188	758 ± 35	37.5 ± 0.4
cupsC	129	167	50	1708 ± 123	913 ± 32	36.9 ± 0.4
cupsD	129	167	51	1818 ± 114	826 ± 29	37.1 ± 0.2
cupsE	130	167	52	1976 ± 188	757 ± 48	37.9 ± 0.3

Table 2. *Cont.*

Sample	T_c (°C)	T_m (°C)	X_C (%)	E_t (MPa)	ε_B (%)	σ_m (MPa)
bucketA	114	151	42	1570 ± 94	892 ± 73	30.9 ± 1.3
bucketB	114	155	44	1537 ± 75	813 ± 129	32.8 ± 0.5
bucketC	114	154	54	1488 ± 81	880 ± 134	30.9 ± 1.1
bucketD	114	153	54	1560 ± 70	864 ± 67	30.4 ± 1.3
bucketE	124	157	45	1476 ± 50	817 ± 69	30.6 ± 1.4

3.5. Mechanical Properties

The determination of mechanical properties of each material consists of tensile and tensile impact strength test, whereby both tests are good methods to analyze the material properties in dynamic and quasi-static loading. In particular, the tensile test and its data like modulus of elasticity, elongation at break and tensile strength gives a good insight into the general deformation behavior of polymers and, therefore, allows general statements to be made about the influence of material modification [87–89]. Figure 8 illustrates the stress–strain curves for all materials, which were obtained from tensile test.



(**a**) (**b**)

(**c**) (**d**)

Figure 8. Stress-strain curves of all samples (PP3 and PP4 (**a**), flakes (**b**), cups (**c**), bucket (**d**)) obtained from tensile test.

Additionally, Table 2 displays the tensile properties, including the tensile modulus (E_t), the elongation at break (ε_B) and the tensile strength (σ_m). It could be observed, that the tensile strength, which is defined as first maximum of the stress–strain curve according ISO 527-1, was kept constant for all blends compared to their virgin materials [52]. Also, the observation of the tensile modulus did not show any significant change and the values are constant within a certain range. However, the elongation at break showed a change as a result of the use of blends. It was found that the sets of blends consisting LCB-PP had an increase and at least a constant level in comparison to the virgin materials. For example, the values of PP3 increased by 33% and 46%, respectively, through the blending with LCB-PP, but also a significant increase of 23% was achieved with the recycled flakes.

The results of the tensile impact strength test are shown in Figure 9. Here it can be clearly seen that the use of blends leads to an increase in impact tensile strength. An increase can be seen in the blending with a pure material (PP2), with the exception of PP3, as well as in the use of LCB-PP. In addition, it is evident that the addition of LCB-PP can further increase the results. This is especially the case for the materials of PP3, flakes and cups, whereby the LCB-PPs modified with PEROXAN LP are even more pronounced than the respective blends. The respective series with HMS-PP blends also showed an improvement in impact strength compared to the starting materials. However, if we compare the blends of the two LCB-PPs and the HMS-PP with each other, we see that the values are almost constant for the series with PP4 and bucket. However, for the materials with the lower MFR values (PP3, flakes and cups), the LCB-PPs show an increase compared to the HMS-PP. In particular, the blends with LCB-PP, which were modified with PEROXAN LP, are outstanding.

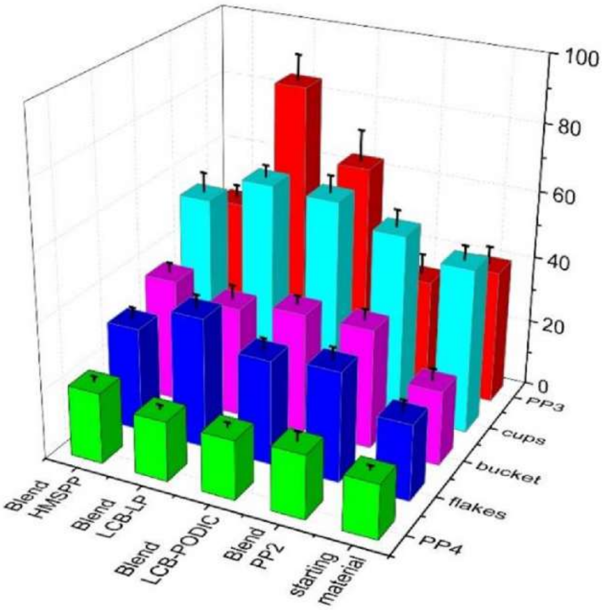


Figure 9. Tensile impact test of all samples.

3.6. Scanning Electron Microscopy (SEM)

In addition to the previous results, the mixing behavior of the respective starting materials and the corresponding blends was analyzed using scanning electron microscopy (SEM, Figure 10). For this purpose, the fracture surfaces of the specimens resulting from the impact tensile test were examined. The following pictures show examples of the virgin material PP3 and the blends with PP2, PP-LCB (PODIC C126 and PEROXAN LP) as well as HMS-PP and, for comparison, the recycled flakes of the coffee caps and their corresponding blends.

If a view is taken of the virgin material PP3A and its blends (PP3B-PP3E), no representative difference can be seen between the individual images of the respective morphology. Therefore, it can be assumed that the materials used for the blends in this quantity (10 wt.%) do not influence the morphological structure and thus the miscibility of the blend is guaranteed. This reflects the results of the DSC measurements which have already been described.

In addition, PP3 and the flakes of the recycled coffee caps have almost the same MFR value, which makes it possible to compare the two materials very well.

A morphological difference between the two starting materials PP3 and flakes of coffee caps can be seen clearly. It can be observed that the recycled post-consumer material (flakesA) already has some polymeric particles in the fracture surface. However, no changes could be detected through the blending process with L-PP (flakesB), LCB-PP on basis of PODIC C126 (flakesC), LCB-PP on basis of PEROXAN LP (flakesD) or HMS-PP (flakesE). This means that no additional particle formation in the morphological structure was recognizable and therefore the blends used did not play a role in the miscibility of the recycled material. This in turn means that there is no phase segregation at the 10 wt.% blend content used and it is, therefore, very easy to process.

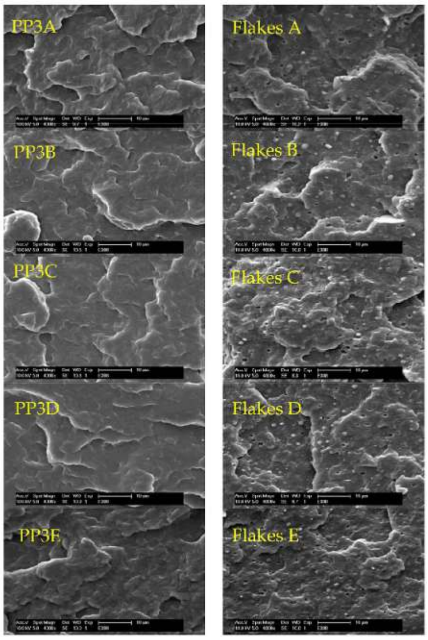


Figure 10. Scanning electron microscope (SEM) images of the virgin material of PP3 and the recycled flakes (**A**) and the blend series on basis of PP2 (**B**), LCB-PP with PODIC C126 (**C**), LCB-PP with PEROXAN LP (**D**), HMS-PP (**E**).

These results, which were just described for the two materials at PP3 as well as for the recycled flakes of the coffee caps, were also evident for the other materials. Although there was a large difference in the MFR values between PP4 or the flakes of the recycled buckets and the respective blended materials, no phase segregation was observed here either. These studies of the starting materials with pure PP4, recycled flakes of yoghurt cups and recycled flakes of the bucket and their different blends are shown in Figure A1.

3.7. *Characterization of Modified Polymers Long-Chain Branched Polypropylenes (LCB-PP)*

The branching mechanism of PODIC C126 and PEROXAN LP was examined by using FTIR. It is well known in the literature that the modification or branching with different components such as HDDA (1,6-hexanediol diacrylate) or MAH (maleic anhydride) by using FTIR can be demonstrated clearly [37,59,90,91]. Figure 11 shows the FTIR spectra of the unmodified PP and the two LCB-PPs each modified with 10 wt.% peroxide. The two modified PPs show an absorption band at 1743 cm^{-1} compared to the unmodified PP. This band describes the stretching vibration of a carbonyl group of an ester, which is generated by the introduction of long-chain branching and the use of peroxides [25,92,93].

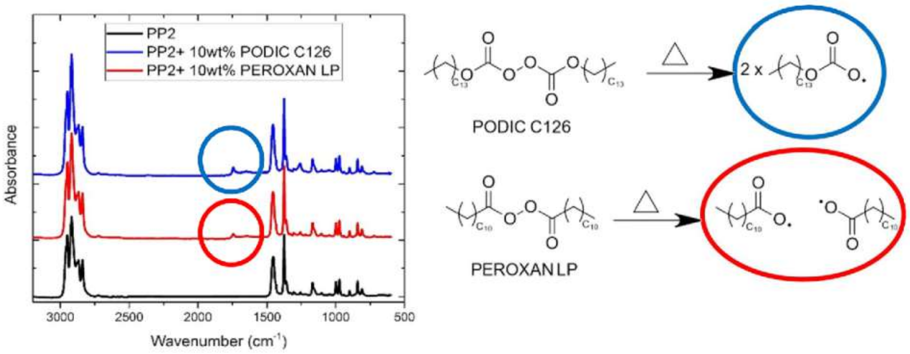
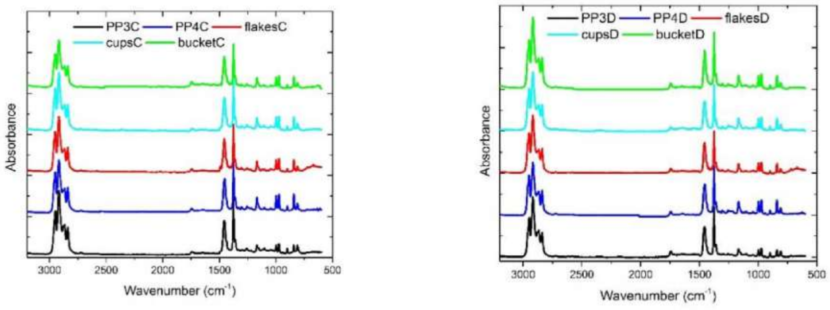


Figure 11. Fourier transform infrared (FTIR) spectra of the unmodified PP and the two LCB-PPs.

To characterize whether the long-chain branches of the LCB-PPs based on PODIC C126 and PEROXAN LP are still present after blending at an extrusion temperature of 240 °C, the FTIR spectra of the respective materials (virgin/recycled materials) were additionally examined. The spectra of the blends with 10 wt.% LCB-PP are shown in the Figure 12. As shown in Figure 11, the characteristic band at 1743 cm^{-1} for the decomposition products of the peroxides could be detected by introducing the long chain branches. This band can be shown for LCB-PP based on PODIC C126 in Figure 12a and for LCB-PP based on PEROXAN LP in Figure 12b after blending with the respective virgin/recycled materials. This finally supports the statement that the LCB-PP blends can be processed very well at an extrusion temperature of 240 °C with virgin/recycled material, since on the one hand the long chain branching can be detected in the FTIR and on the other hand the LCB-PP blends, show no impurities at the molecular level as already indicated by the SEM results.



(**a**) (**b**)

Figure 12. FTIR spectra of the blend series with LCB-PP (**a**) on basis of PODIC C126 and (**b**) on the basis of PEROXAN LP.

4. Conclusions

In this study, the influence of blends on virgin PP (HD 601CF and HF 700SA) and recycled PP (flakes of yoghurt cups, coffee caps and buckets) was investigated. For this purpose, two LCB-PPs were used, which were produced and investigated in a previous work in the research group. The two LCB-PPs were prepared by reactive extrusion and by using 10 wt.% peroxides (PODIC C126 and PEROXAN LP) and served as masterbatches in this work. To investigate the influence of these a virgin blend material, a linear PP (HC 600TF) and a commercially available HMS-PP (Daploy™ WB140HMS) were also used as blend materials. The blends each contained 10 wt.% of the second component.

The starting materials that were investigated and blended had different initial MFR values ranging from 5 g/10 min to an MFR of 32 g/10 min, thus covering a wide range of different PPs. By using the respective second blend components, a reduction or at least a constant MFR value could be achieved. In general, the starting materials with higher MFR values, such as the recycled buckets or recycled flakes, but also the vrigin PP (HF 700SA), showed a greater reduction of the MFR value than the starting materials with lower MFR values.

The rheology measurements were carried out at 230 °C to obtain a better comparison of the complex viscosity versus the MFR values. The series, using virgin PPs, showed different curves of complex viscosity. In the case of HD 601CF, the addition of the two LCB PPs and the commercial HMS PP led to an increase in viscosity in the low-frequency range, whereas the linear PP as blending material led to a decrease. In the series, using HF 700 SA, the curves are so close together that no significant change in viscosity can be assumed. Also in the series with the different recycled materials, no uniform trend could be observed. For the series of the flakes of yoghurt cups and coffee caps the same trend was seen by the use of the different blend components. It led in both cases to an increase in viscosity compared to the starting materials. In the case of the flakes of the bucket, again, a different trend is shown and no increase in viscosity of the blends with the two LCB-PPs and the commercially available HMS-PP could be achieved.

In addition to the viscosity curves, the curves of the storage and loss moduli were also studied, as well as their crossover points. In principle, an increase in molecular weight as well as a broadening of the molecular weight distribution could be achieved by using the blend materials compared to the respective starting material. However, the flakes of the recycled bucket were an exception. In the specified measuring range an approximation between the storage modulus curve and the loss modulus curve can be recognized but no corssover point could be measured for this series and thus no statement could be made.

However, in order to determine whether strain hardening also occurs due to the use of the respective blending materials, the elongational rheology was also investigated in addition to the dynamic rheology. Here, a large difference was found between the linear PP as blend material compared to the two LCB-PPs and the commercially available HMS-PP. The starting materials as well as the series blended with the linear PP showed no strain hardening and thus no melt stiffness. However, the blend series with the two LCB-PPs and the commercial HMS-PP showed strain hardening throughout. Comparing the blends with each other and contrast the series with the linear PP with those of the LCB-PPs, the two blend series with the respective LCB-PPs have the advantage that a melt stiffness occurs with them and thus a significant strain-hardening effect occurs. If one compares these two series with the blend series of the commercial HMS-PP, these two can simply keep up in terms of elongation rheology.

In the case of the mechanical properties, especially elongation at break and tensile impact strength, different results could be achieved by using the respective blends, which were consistently better for all blends compared to the starting material. By using commercial PP and HMS-PP, the properties could be increased compared to the virgin materials. However, by blending with LCB-PP this could be increased even more in comparison to the blends with PP or HMS-PP. Finally, for the LCB-PP on the basis of PODIC C126 with the LCB-PP on the basis of PEROXAN LP, both are comparable.

For the thermal characterization, DSC measurements of the starting materials as well as the corresponding blends were performed. The use of the different blends did not result in any changes in the melting temperature compared to the starting material. When analyzing the crystallization temperature, only the blends with HMS-PP showed an increase, whereas the crystallization temperature of the other blends remained uneffected. The degree of crystallization was also not significantly affected by the blending of the individual materials. The only exceptions were the two blends with LCB-PP based on PODIC C126 or PEROXAN LP, which were added to the flakes of buckets. Here an increase in crystallinity could be detected.

The SEM measurements clearly showed the miscibility of the individual blends with the respective start materials. In particular, when comparing the SEM photos of the virgin/recycled material with the blend series, no influence of the blends could be detected and thus no particle contamination could be verified. In addition, by using FTIR measurements, it could be verified that the modified LCB-PPs used for blending showed the characteristic band for the carbonyl group of an ester at 1743 cm^{-1} for all virgin/recycled materials even after extrusion at 240 °C.

According to theses results, by using 10 wt.% LCB-PP based on PODIC C126 or PEROXAN LP, the properties of recyclates can be upgraded, leading to an actual upcycling of these materials. This makes it possible to specifically the use the recyclates in other areas of application where a higher melt strength is desired or required.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/polym13071137/s1, Figure S1: DSC curses of the second heating of the investigated materials; (a) PP3, (b) PP4, (c) flakes of coffee caps, (d) flakes of yoghurt cups, (e) flakes of buckets.

Author Contributions: Conceptualization, S.S.; methodology, S.S. and T.K.; validation, S.S., T.K. and V.-M.A.; formal analysis, S.S.; investigation, S.S.; resources, K.S.; writing—original draft preparation, S.S.; writing—review and editing, S.S., T.K. and V.-M.A.; visualization, S.S.; supervision, K.S., S.K. and V.-M.A.; project administration, S.S.; funding acquisition, V.-M.A. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflict of interest.

Appendix A

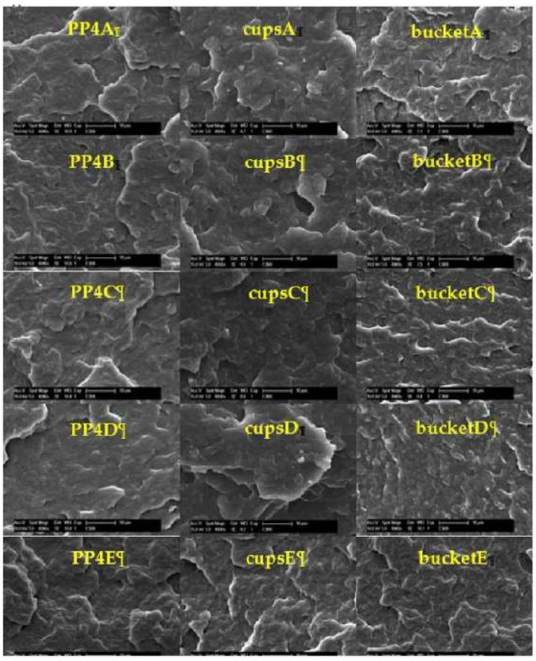

Figure A1. SEM images of the virgin material of PP4 and the recycled flakes of cups and bucket (**A**) and the blend series on basis of PP2 (**B**), LCB-PP with PODIC C126 (**C**), LCB-PP with PEROXAN LP (**D**), HMS-PP (**E**).

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PERSONAL DATA

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LANGUAGES

German	●●●●●
English	●●●○○

SOFT SKILLS

IT

MS Office	●●●●●
OriginPro	●●●○○
Chemistry software (RheoPlus, TA Universal Analysis, Chemdraw, etc.)	●●●●●

FURTHER EDUCATION

Rheology workshop Anton Paar
European Business License Level A
Paramedic training

HOBBYS

Triathlon, Fitness, Soccer, Travel

WORK EXPERIENCE

PHD STUDENT

Technical University, Vienna 02/2018 – 05/2021

- Upcycling or modification of polypropylene by reactive extrusion using various organic peroxides
- Analysis of mechanical properties (tensile test and impact tensile test)
- Thermal analysis using DSC, DMTA and TGA
- Investigation of rheological properties in melt and extensional rheology
- Supervision of Master and Bachelor students
- Maintenance of extruder, injection moulding and rheometer

TUTOR AT THE INSTITUTE OF APPLIED SYNTHETIC CHEMISTRY

Technical University, Vienna 10/2014 – 07/2015
10/2015 – 07/2016
09/2016 – 02/2017
10/2017 – 01/2018

- Mentoring the students in the lab and supporting them with their analyses
- Safety briefing of all lab participants

PARAMEDIC

Österreichisches Rotes Kreuz 08/2009 – 08/2011

- Ambulance transport
- Rescue mission

TRAINEE

Gorenje, d.d. (Si) 10 – 10/2007

- Installation and plant construction (welding, repairs of gearboxes, etc.)
- Basics of electrical circuit diagrams and electrical components (programming and connection of Siemens frequency controllers)

TRAINEE

Prinz GmbH - Kettensägetechnik 07 – 08/2007

- Metalworking (soldering, drilling, grinding)
- Paint shop (preparation work)
- Maintenance services

EDUCATION

MASTER DEGREE (Dipl.-Ing)

Technical University, Vienna 04/2016 – 01/2018

Master thesis: Highly filled hydrogels as biocomposites and Ceramicprecursor for 3D Printing

- Major: Synthetic chemistry
- Synthesis of water soluble vinyl ester
- Analysis of various water-soluble photoinitiators using photorheology and photo-DSC
- 3D printing of ceramic-filled hydrogels in cooperation with Lithoz GmbH

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LANGUAGES

German	●●●●●
English	●●●○○

SOFT SKILLS

IT

MS Office	●●●●●
OriginPro	●●●○○
Chemistry software (RheoPlus, TA Universal Analysis, Chemdraw, etc.)	●●●●●

FURTHER EDUCATION

Rheology workshop Anton Paar
European Business License Level A
Paramedic training

HOBBYS

Triathlon, Fitness, Soccer, Travel

BACHELOR DEGREE – TECHNICAL CHEMISTRY

Technical University, Vienna 10/2010 – 04/2016

Bachelor thesis: Radikal induzierte kationische Frontalpolymerisation

- Evaluation of different initiator concentrations and their influence on the radical induced cationic frontal polymerisation
- Test of storage stability
- Use of insulating fillers

A-LEVEL

HTL-St. Pölten (Mechanical engineering) 09/2005 – 06/2010

Main focus of studies: Automation technology
Thesis: Adaptation and commissioning of a linear transfer system

FOREIGN EXPERIENCE

LEONARDO DA VINCI - MOBILITÄTSPROGRAMM

Solski Center Velenje, Slowenien 09/2007 – 10/2007

- Processing of metal
- Surface treatment of metals (bronzing)
- Welding

PUBLICATIONS & CONFERENCES

- Improving Rheological and Mechanical Properties of Various Virgin and Recycled Polypropylenes by Blending with Long Chain Branched Polypropylene, Polymers, **2021**
- Long chain branching of polypropylene with various concentrations of peroxydicarbonate and dilauroyl peroxide and two processing steps (in view of recycling, Journal of Applied Polymer Science, **2021**
- Effect of different compatibilization systems on the rheological, mechanical and morphological properties of polypropylene/polystyrene blends; Polymers, **2020**
- Influence of Different Types of Peroxides on the Long-Chain Branching of PP vie Reactive Extrusion, Polymers, **2020**
- A highly efficient waterborne photoinitiator for visible-light-induced three-dimensional printing of hydrogels, Chemical Communications, **2018**

- International Symposium – Science to support circular economy, TU Wien **2018**, Wien, Poster,
- Danube Vltava Sava Polymer Meeting **2017** DVSPM, Wien, Poster
- Bypos Workshop **2017**, Zemplinska Sirava, Slowakai, Talk