Effects of devulcanization temperatures on the properties of ground waste tire modified asphalt

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ABSTRACT: Utilizing waste rubber in asphalt extends the lifespan of pavements and fosters the sustainable reuse of materials. This research explored how devulcanizing ground tire rubber (GTR) affects the qualities of rubber-modified asphalt. The study assessed their impact on flexibility, high-temperature and low-temperature performance, and storage stability by integrating devulcanized rubber at various temperatures and concentrations. Findings indicate that while devulcanization improves the compatibility of rubber with asphalt, it might diminish its performance at higher temperatures. Modifying the conditions of devulcanization could enhance the performance and stability of the binder.

1 INTRODUCTION

Addressing the effective recycling of waste tires is a significant environmental issue for numerous countries (Sienkiewicz et al., 2012). Each year, the disposal of tires exceeds approximately 1.5 billion, leading to environmental degradation, increased fire hazards, and heightened health risks (Hong et al., 2023). Around 40% of these tires are incinerated for energy recovery, while merely 5.5% are repurposed for civil engineering applications (Shu and Huang, 2014). Recycling waste ground tire rubber (GTR) as a modifier in asphalt pavement materials can substantially improve road performance, lower construction expenses, and mitigate environmental impact (Ma et al., 2022).

Rubber-modified asphalt is recognized for its enhanced resistance to rutting and cracking. However, the swelling effect of rubber significantly increases the viscosity of the asphalt if the rubber is used in wet process, presenting considerable challenges during handling, pumping, and compaction processes (Huang et al., 2017, Zhang et al., 2023). Additionally, the existence of insoluble rubber particles in the binder, which have different chemical and physical properties, exacerbates compatibility issues (Ma et al., 2021b). Therefore, it is essential to develop rubberized asphalt binders that are low in viscosity, homogeneous, and exhibit superior performance.

Devulcanization can promote the integration of rubber and asphalt. The degraded rubber hydrocarbons dissolve into the asphalt blender, resulting in an improved viscosity and compatibility of the binder. However, the devulcanization of the GTR elastomer leads to a loss of elastic properties and a sacrifice in the high-temperature performance (Meng et al., 2023). Effectively managing the devulcanization degree is a critical factor in obtaining a binder that exhibits desirable solubility, compatibility, and mechanical performance.

This research investigates the impact of varying levels of devulcanization on the characteristics of asphalt binders utilizing devulcanized GTR under different concentrations and conditions. By assessing the performance of asphalt, emphasizing the balance between enhanced low-temperature flexibility and the potential reduction in high-temperature stability, this investigation aims to improve application methods and increase the understanding of devulcanized rubber in road construction, ultimately contributing to the development of more durable and cost-effective solutions.

2 METHODOLOGY AND MATERIALS

2.1 *Rubber devulcanization*

GTR devulcanization was conducted using a twin-screw extruder, with temperatures strategically set as 240 °C, 260 °C, and 280 °C to break sulfur bonds.

2.2 *Characterization of devulcanized GTR*

In GTR, its composition includes natural rubber, synthetic rubber, carbon black, zinc oxide, sulfur, lubricating oils (acetone soluble), and fillers. To qualify the devulcanization degree of rubber, the Soxhlet extraction method separates the sol from the insoluble. After extraction, the compositions of the GTR and the sol fraction were determined using thermal gravimetric analysis (TGA).

Attenuated Total Reflection Fourier Transform Infrared (ATR-FTIR) spectroscopy was used to investigate the changes in the functional groups within the rubber during the devulcanization.

2.3 *Preparation of modified asphalt*

A high-speed shearing mixer was utilized to prepare the rubber-modified asphalt. Various parameters were set to investigate their effects on the properties of the asphalt, including different GTR contents (12%, 18%, 24%), and degrees of devulcanization of the GTR. PG 64-22 base asphalt binder was heated to 190 °C to ensure it became fluid. Adding the original and devulcanized GTR into the asphalt to make rubber-modified asphalt samples. In the following results, the original GTR-modified asphalt was named as ORP.

2.4 *Storage Stability of modified Asphalt*

The storage stability and phase separation of the modified asphalt were characterized according to ASTM D-7173. Dynamic Shear Rheometer (DSR) (ASTM D7175) test was applied for this purpose (Kim and Lee, 2013, Ma et al., 2021a).

2.5 *Brookfield viscosity*

The viscosity should be under 3000 cP at 135 °C, according to Typical Asphalt-Rubber Binder Specifications (Way, 2012). The viscosity asphalt binder samples were measured in accordance with AASHTO T-316.

2.6 *Aging simulation*

Short-term aging of the asphalt blends was simulated using the Rolling Thin-Film Oven (RTFO) according to AASHTO T-240. Long-term aging was simulated using the Pressure Aging Vessel (PAV) test, in accordance with AASHTO R28.

2.7 *High-temperature performance*

The oscillatory temperature sweep conducted using DSR in accordance with AASHTO T-315.

2.8 *Permanent deformation resistance*

The non-recoverable creep compliance (J_{nr}) and average percent recovery (R) were calculated following AASHTO T-350 based on Multiple Stress Creep Recovery (MSCR).

3 RESULTS AND DISCUSSION

3.1 *Determination of rubber devulcanization degree*

Table 1. Effects of extrusion temperature on sol fraction

Pretreatment Temperature (°C)	Devulcanization Degree (%)		
	Rubber	Natural Rubber	Synthetic Rubber
Untreated	5.054	6.460	2.086
240	15.950	16.085	13.159
260	20.970	25.521	17.380
280	27.524	31.432	26.615

The sol fraction of both natural and synthetic rubber increased with temperature. Notably, natural rubber consistently exhibited a higher sol fraction than synthetic rubber.

3.2 *Characterization of chemical modification by ATR-FTIR*

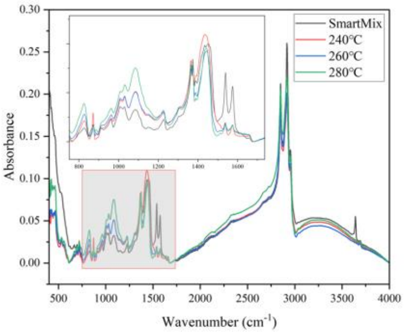


Figure 1. FTIR spectra of the devulcanized samples

With the increase of devulcanization temperature, the intensity ratio of S-S to S-O shows a trend of first slightly increasing and then decreasing, while the intensity ratio of C-S decreases slightly. The degree of bonding depends on the exposure of the sample to the devulcanization temperature, and the energy required to break each sulfur bond. The bond energies of S-S, S-O, and C-S are 268 kJ/mol, 226 kJ/mol, and 285 kJ/mol (Rooj et al., 2011). These results confirm that the devulcanization of GTR does occur at high temperatures and under the action of vacuum and that there may be non-uniform breaking and formation of different types of sulfur bonds.

3.3 *Compatibility test*

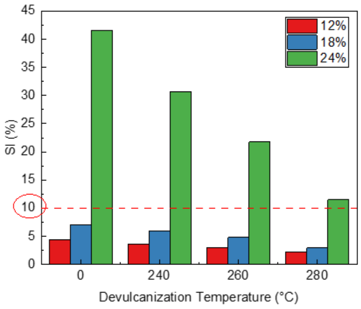


Figure 2. Separation Index (*SI*) of samples

The *SI* values of rubber-modified asphalt samples containing 12% GTR and 18% GTR are lower than 10%, which means that they can meet the ASTM requirements. As the GTR content increased from

12% to 24%, the SI also rose significantly, indicating reduced storage stability.

3.4 *Brookfield viscosity*

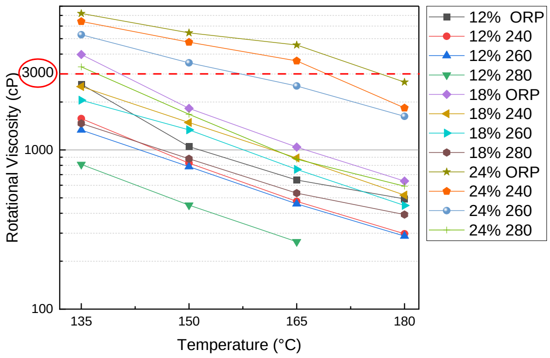
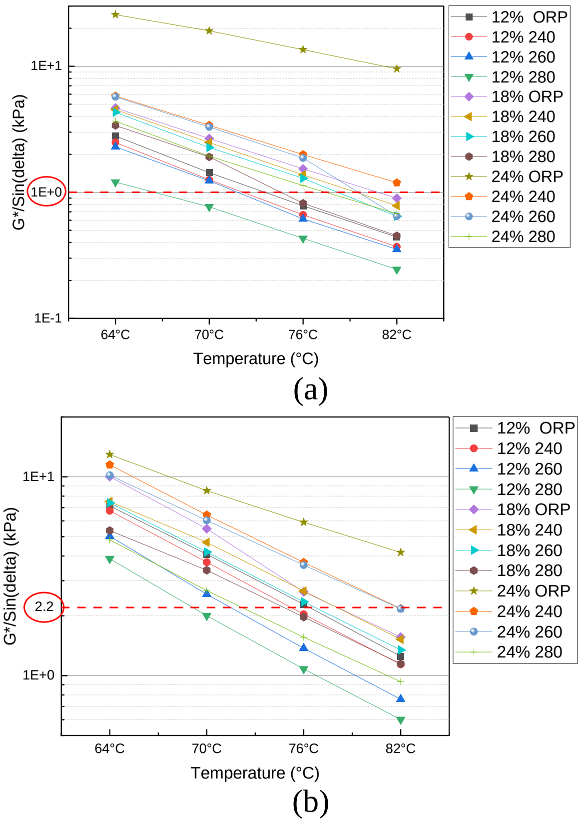


Figure 3. Brookfield viscosity profiles for various rubber-modified asphalt samples

At 12% rubber content, all asphalt binders have suitable processing viscosity. At 18% rubber content, the asphalt containing 18% untreated GTR exceeds the viscosity threshold at 135°C. At 24% rubber content, viscosities frequently approach or exceed the 3000 cP limit.

3.5 *Oscillation temperature sweep test*



(a)

(b)

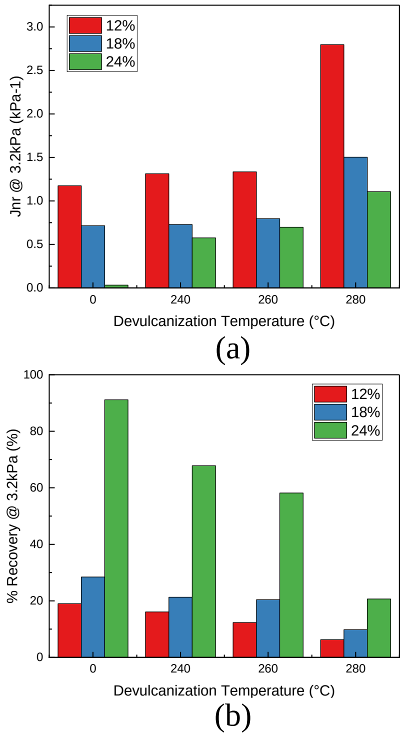
Figure 4. Results of Oscillation Temperature Sweep test: (a) original asphalt samples, (b) RTFO residues.

Figure 4 (a) reveals that most samples initially meet the minimum high-temperature performance standard of 1.0 kPa at 64 °C and 70 °C. As temperatures rise, particularly at higher devulcanization temperatures, the values drop below this threshold, showing decreased effectiveness in rutting resistance with increased temperature.

In Figure 4 (b), samples with 12% rubber content at lower devulcanization temperatures show better high-temperature performance than the base asphalt. At a devulcanization temperature of 280 °C, performance under 70 °C does not meet the required standards. Increasing the rubber content enhances the $|G^*|/\sin\delta$ value, potentially raising the PG grade to 76 °C for 18% rubber and above 82 °C for 24% rubber when using original GTR. If devulcanization temperatures range from 240 °C to 260 °C with 18% or 24% rubber, the PG grade improves to 76 °C. At 280 °C, despite a slight increase in value, the grade remains unchanged.

3.6 *Multiple stress creep recovery test*

For rubber-modified asphalt, a stress level of 3.2 kPa is required to accurately simulate real traffic loads.



(a)

(b)

Figure 5. (a) Non-recoverable creep compliance, (b) Percent recovery.

Both $J_{\text{nr, 3.2}}$ and $R_{3.2}$ results indicate that increasing the GTR dosage improves the elasticity and deformation resistance of the asphalt. The devulcanization process also plays a critical role in enhancing these properties. By breaking down the sulfur crosslinks in rubber, devulcanization improves the compatibility between rubber and asphalt, but increased the susceptibility of asphalt to permanent deformation and reduced the elasticity.

3.7 *Bending Beam Rheometer Test*

Table 2. BBR test results of rubber-modified asphalt samples

Sample	12% ORP	12% 240	12% 260	12% 280
S at -12 °C (MPa)	82.8	89.3	86.7	91.55
m-value at -12 °C	0.381	0.364	0.373	0.385
S at -18 °C (MPa)	187	189	194	189
m-value at -18 °C	0.330	0.334	0.314	0.331
Sample	18% ORP	18% 240	18% 260	18% 280
S at -12 °C (MPa)	54.4	63.6	55	58.3
m-value at -12 °C	0.387	0.381	0.393	0.372
S at -18 °C (MPa)	136	132	127	113
m-value at -18 °C	0.336	0.341	0.342	0.335
Sample	24% ORP	24% 240	24% 260	24% 280
S at -12 °C (MPa)	---	38.1	26.7	35.5
m-value at -12 °C	---	0.386	0.412	0.396
S at -18 °C (MPa)	62.9	76.6	56.8	91.3
m-value at -18 °C	0.346	0.340	0.366	0.371

The results show that both untreated and devulcanized GTR (at 240°C, 260°C, and 280°C) maintain the stiffness (*S*) values well below the 300 MPa threshold at -12°C and -18°C, with m-values consistently above 0.300 across all rubber contents (12%, 18%, and 24%). Notably, the S and m-values at 240°C and 260°C are similar, showing consistent performance, whereas at 280°C, a higher S hints at reduced flexibility at lower temperatures.

4 CONCLUSIONS

1. Changes of S-S, S=O, and C-S bonds confirmed the chemical degradation of sulfur cross-links due to devulcanization. Higher temperatures caused these bonds to break, making the rubber more reactive but less structurally sound.
2. The devulcanization procedure significantly improved the storage stability of asphalt binders by promoting a uniform distribution of rubber particles.
3. Incorporating rubber enhanced the rheological properties of asphalt, improving its resistance to deformations under cyclic loading. However, the devulcanization process tended to reduce the elastic response, which could potentially compromise the material's performance when subjected to stress.

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