

DEVULCANIZED CRUMB RUBBER AS BITUMEN MODIFIER

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ABSTRACT. The dispersion of crumb rubber in road bitumen is essential for enhancing the elasticity of asphalt coatings. However, elastomer cross-linking through vulcanization can reduce the colloidal stability of bitumen. This study aims to enhance compatibility by partially devulcanizing crumb rubber using a pulverulent catalyst, specifically phosphomolybdic acid, in a batch reactor at 270°C. The use of a molybdenum-based catalyst is preferred due to its effectiveness in catalyzing the devulcanization process. Additionally, further conditioning of the catalyst through grinding optimizes contact with crumb rubber, enhancing catalyst activity and improving overall compatibility with road bitumen.

Keywords: *crumb rubber, desulfurization, molybdenum catalysts*

INTRODUCTION

With the significant increase in the number of private vehicles, an estimated 17 million tons of waste tires are discarded worldwide each year, creating serious environmental problems due to difficulty in disassembly [1]. Generally, tires are made of rubber, carbon black, steel wire, sulfur compounds and synthetic fibers.

Technical experience has shown that rubber and fibers can improve the paving performance of asphalt mixtures in the road construction industry [2]. Traditional asphalt pavements struggle to achieve their planned service life

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under increased traffic volumes and high loads [3]. Therefore, there is an increasing trend to improve conventional asphalt to resist rutting, fatigue and other road deterioration. Modifying bitumen with crumb rubber (CR) is a concern for developed countries aiming to resolve the environmental problems associated with the improper disposal of used tires [4].

The process of modifying bitumen with CR was initially introduced in the 1960s. Since then, this technique has undergone substantial development and is now widely implemented across various regions. Several countries have even established their specifications for crumb rubber-modified bitumen (CRMB). It is widely accepted that CRMB has improved resistance to rutting and cracking compared to conventional bitumen [5].

One of the most widely used metals for devulcanization so far is ZnO, which has been extensively used in rubber vulcanization processes [6]. However, it is currently believed to be toxic in large quantities, especially to aquatic environments. Therefore, another metal that has taken its place is magnesium oxide, for which the exact mode of action and desulfurization are not yet fully understood [7]. In addition to these oxides, transition metal oxides such as NiO₂, MoO₃, V₂O₅, TiO₂, WO₃, MnO₂, CeO₂, and FeO have received significant attention [8-9]. Molybdenum-based catalysts are extensively studied due to their high activity involving multivalent metal transitions (Mo⁵⁺/Mo⁶⁺). However, these catalysts exhibit drawbacks like reduced activity with repeated use and loss of active components. Improvements in catalyst activity and stability are essential and can be achieved through modifications in loading mode, synthesis methods or incorporation of other elements [10].

The devulcanization process involves a series of steps, which can be outlined as follows: (i) shredding tires into small rubber particles; (ii) utilizing appropriate separators to remove fibers and steel; and (iii) further grinding the rubber to achieve a finer size, followed by mixing with various reclaiming agents [11-12]. The extensively researched devulcanization strategies encompass mechanical, chemical, physical, biological, microwave and ultrasonic processes [13-19].

The rubber can pass through industrial devulcanization either before its incorporation into asphalt mixtures (pre-devulcanized) or during the production of CRMB. The devulcanization and depolymerization of crumb rubber particles can occur within the binder at elevated temperatures and under high-shear mixing conditions [20]. The effectiveness of devulcanization and depolymerization tends to be greater when the binder is abundant in aromatic compounds [21].

Despite the advantages of CR bitumen modification, the process is still underutilized. There are studies that demonstrate the ecological sustainability of using CR in asphalt pavements, reducing the costs of managing end-of-life

tire waste and improving asphalt properties [22-24]. Unfortunately, in many countries, the adoption of CR modification was obstructed by the absence of standards and laws that support it.

This paper focuses on employing molybdenum-based catalysts for the devulcanization of CR, aiming to improve rubber compatibility with road bitumen. Molybdenum-based catalysts are chosen due to their unique properties, which contribute to their high catalytic activity. Additionally, these catalysts offer the potential to facilitate the desulfurization process of CR, enhancing its performance as a modifier for road bitumen. The study aims to explore the effectiveness of molybdenum-based catalysts in optimizing the properties of CR for use in asphalt applications, addressing key challenges related to rubber-bitumen compatibility.

RESULTS AND DISCUSSION

The results of the thermogravimetric analysis of crumb rubber powder are shown in Table 1 and Figure 1. The mass losses in the first temperature range, starting from room temperature (R.T.) up to 125°C, are probably due to the presence of water in the rubber powder. Mass losses in the next range, up to 270°C, are the result of the evaporation of organic additives in the rubber such as mineral oils.

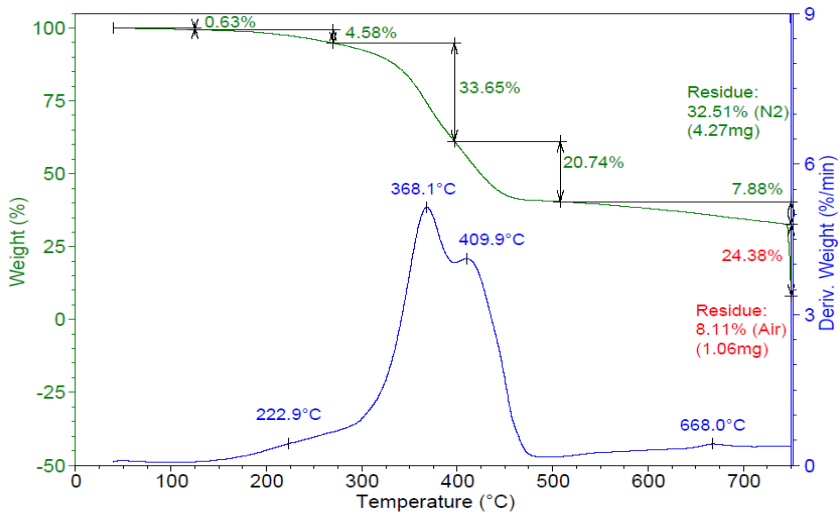


Figure 1. Thermogravimetric analysis (TGA) of crumb rubber powder

At temperatures above 270°C the pyrolysis reaction of the polyisoprene starts, which also occurs at higher temperatures (508°C). In the temperature range of 508 - 750°C thermal decomposition reactions of the carbonaceous materials from the previous steps as well as decomposition of inorganic rubber materials occur. The remaining residue represents 32.51% of the initial mass of the crumb rubber. The inert gas was changed to synthetic air at 750°C to highlight the type of residue left in the crucible. For 5 min at 750°C in the air (burning) the carbon black and other resulting carbonaceous materials were burned, leaving 8.11% residue. This ash consists of inorganic materials, probably silica which is used in the rubber industry together with carbon black for reinforcement.

Table 1. Results of thermogravimetric analysis of crumb rubber powder

Domain, °C	Wt. loss, %	Tmax, °C
R.T. - 125°C	0.63	-
125 - 270°C	4.58	222.9
270 - 397°C	33.65	368.1
397 - 508°C	20.74	409.9
508 - 750°C	7.88	668.0

The characteristics of the crumb rubber powder used in the experimental program are shown in Table 2.

Table 2. The characteristics of crumb rubber powder

No.	Characteristics	Value
1.	Particle sizes, mm	1...2
2.	Density, kg/m ³	441
3.	Total sulfur content (Grote combustion method), % wt.	2.34

A nanopowder of phosphomolybdic acid catalyst (sample code PMo) obtained by grinding in a planetary ball mill was used for the catalytic desulphurization of crumb rubber powder. Size distribution analysis of the catalyst dispersed in toluene was carried out using the Dynamic Light Scattering (DLS) method. An average particle size of 79.26 nm and a narrow nanoparticle size distribution were observed, as shown in Figure 2.

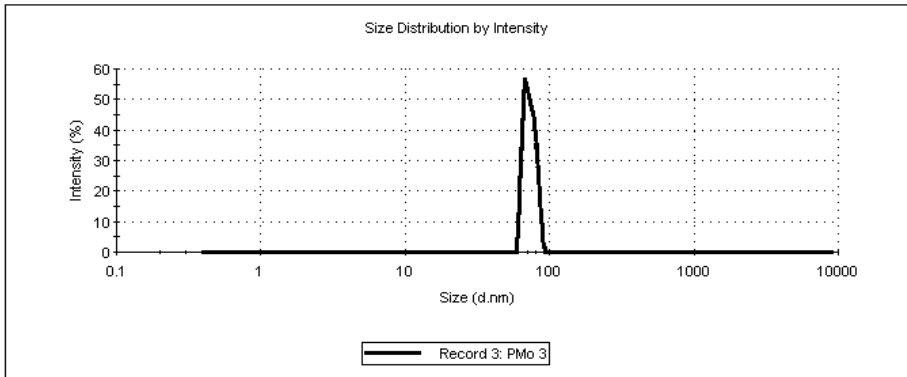


Figure 2. Particle size analysis (DLS) of ground PMo catalyst

Acid strength and distribution of acid sites on the PMo catalyst were characterized using diethylamine thermodesorption. The diethylamine thermodesorption curve, shown in Figure 3, provided insights into the acid strength profiles – weak, medium and strong centers. Table 3 presents the concentrations of acid sites with varying strengths and temperature ranges, as determined from the thermodesorption analysis of diethylamine.

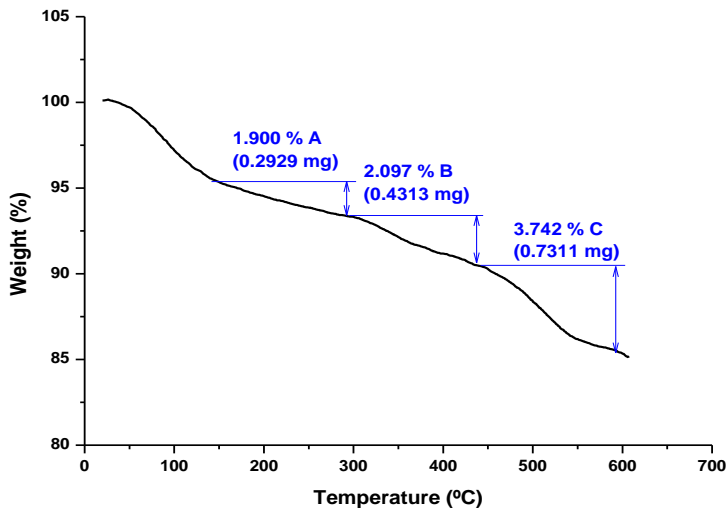


Figure 3. Thermodesorption curve for calculating the acid strength of PMo catalyst

Table 3. The proportion of acid centers of the PMo catalyst

Acid centers	Temperature range, °C	Value, mEq/ g analyzed sample
Weak	160 – 300	0.2598
Medium	300 – 440	0.2867
Strong	440 - 580	0.5116

A high proportion of strong acid centers is observed (48.4%), with the proportion of weak and medium acid centers being smaller and approximately equal.

The temperature selected for desulfurization of the crumb rubber was 270°C. From the thermogravimetric curve (Figure 1) it can be seen that at higher temperatures the pyrolysis of the elastomer starts, with a negative influence on the elastic characteristics of the bitumen modified with it.

The total sulfur content of crumb rubber after the catalytic desulfurization process in a batch system at 270°C for 3 hours was 1.08% wt and the calculated conversion with equation (1) was higher with ground phosphomolybdenic acid 47.06 % compared with non-ground catalyst (Table 4).

Table 4. Performance of the catalytic desulfurization process of crumb rubber powder in batch system

Catalyst	Catalyst conc., % wt.	Time, h	Temperature, °C	Conversion, %
Phosphomolybdenic acid	1.05	3	270	36.89
Ground phospho-molybdenic acid	1.05	3	270	47.06

The homogeneity of the CRMB was evaluated by determining the composition after short-term storage in a narrow tube, and by determining the asphaltene and elastomer content in the upper and lower zones of the tube. The values obtained are shown in Table 5.

Table 5. Asphaltene content of modified road bitumen sample

Sample	Asphaltene content, %	
	Upper zone	Lower zone
Sample 1	19.35	19.47

The asphaltene content of road bitumen modified with devulcanized crumb rubber in the two areas of the bitumen sample is close, the observed differences being of the order of the error of the determination method.

CONCLUSIONS

In conclusion, the desulfurization of crumb rubber was effectively facilitated by a nanostructured phosphomolybdenic acid catalyst. Thermogravimetric analysis of crumb rubber derived from used tires revealed its limited thermal stability above 280°C. Grinding the phosphomolybdenic acid produced a nanopowder with a narrow, monomodal particle size distribution, averaging 79.26 nm in diameter, and an acid strength exceeding 1 mEq/g. Using this catalyst, the desulfurization of crumb rubber dispersed in catalytic cracking oil at 270°C for 3 hours achieved a conversion rate of 47.06%. The resulting bitumen modified with devulcanized crumb rubber demonstrated high homogeneity, evidenced by consistent asphaltene content across different bitumen layers.

EXPERIMENTAL SECTION

Materials

Crumb rubber powder results from ground rubber from used tire waste, with a particle size in the range of 1-3 mm, a density of 441 kg/m³, with a sulfur content of 2.34%, determined by the Grote combustion method. In the experimental program were used catalytic cracking oil and bitumen type D20/30 (Romp petrol), phosphomolybdenic acid, diethylamine (Merck), Pluronic® P123 (Sigma-Aldrich), toluene, heptane (Chimopar S.A), hydrogen peroxide solution 3%, sodium carbonate (Chimreactiv SRL).

The main characteristics of the road bitumen and catalytic cracking oil used in the experimental program are shown in Tables 6 and 7.

Table 6. Specification of bitumen grade D20/30*

No.	Specification	Unit	Value	Method
1.	Penetration (25°C),	1/10 mm	27	SR EN 1426:2015
2.	Softening Point (Ring & Ball)	°C	59	SR EN 1427:2015
3.	Ductility (25°C)	cm	110	SR EN 13589:2015
4.	Fraass point	°C	-12	SR EN 12593:2015

*from the technical sheet of the product

Table 7. The characteristics of the catalytic cracking medium oil fraction*

No.	Specification	Unit	Value
1.	Appearance	-	viscous liquid, reddish brown
2.	Relative density at 20°C	g/cm ³	0.882
3.	Boiling range	°C	400-450
4.	Flashpoint (closed cup)	°C	78
5.	Dynamic viscosity at 20°C	mPa·s	40.8

* from the technical sheet of the product

Characterization Methods

Thermogravimetric analysis (TGA) of crumb rubber was performed with a Q5000IR (TA Instruments, USA), with the following parameters - 100 μ L platinum crucible, 1-nitrogen purge gas (99.999%) with a flow rate of 50 mL/min, 2- synthetic air purge gas (99.999%) with a flow rate of 50 mL/min. Working method: 1) heating rate 10°C/min up to 750°C; 2) exchange gas 1 (nitrogen) with gas 2 (synthetic air); 3) isotherm for 5min.

Dynamic light scattering (DLS) was employed to analyze the particle size and particle size distribution of PMo using a NanoZS Zetasizer device from Malvern Instruments, UK. The sample was prepared by dispersing 0.005g ground phosphomolybdic acid in 25 mL of toluene

Acid strength and acid strength distribution of PMo was carried out by thermal desorption of diethylamine [25] using a DuPont Instruments apparatus. Before analysis, the test sample was placed in a vacuum oven at 120°C for 12 hours to remove moisture.

Laboratory experiments

Preparation of phosphomolybdic acid catalyst

Phosphomolybdic acid was dry ground using a laboratory planetary mill in the presence of an anti-caking additive at 1% concentration (Pluronic-P123) for the preparation of the nanoparticle catalyst. A planetary ball mill (Fritsch Pulverisette 6) equipped with a 500 mL stainless steel bowl and 10 stainless steel balls (ϕ 20 mm) was used for the laboratory experiments

Catalytic devulcanization of crumb rubber powder

The experiments were carried out in a 1L stainless steel autoclave Parr 4520 series, with thermostatic electric heating, at a temperature of 270°C, with stirring at 160 rpm, in an inert gas atmosphere (nitrogen 5.0), and a crumb rubber/aromatic solvent mass ratio of 1/10 for 3 hours.

The conversion in the desulfurization process of crumb rubber with the phosphomolybdic acid was calculated by determining the total sulfur content by the Grote combustion method before and after experiments with equation (1):

$$\text{Conversion, \%} = \frac{TSC_i - TSC_f}{TSC_i} \cdot 100 \quad (1)$$

TSC_i = initial total sulfur content of the crumb rubber sample;

TSC_f = final total sulfur content of the crumb rubber sample after the desulfurisation.

The modification of road bitumen type D20/30 was done in a glass autoclave with a volume of 1 liter equipped with a thermostatic electric jacket and stirring. Working parameters were: temperature 160°C, stirrer speed 180 rpm, reaction time 5 hours, the concentration of the crumb rubber conditioned in aromatic oil 3%, and the mass ratio bitumen/ dispersion of 4/1.

The stability of the modified bitumen with devulcanized crumb rubber was assessed by determining its composition after short-term storage in a narrow tube for 24 hours. After preparation of the modified bitumen and cooling to 80°C, it was placed in a cardboard tube, fixed in an upright position, and closed at the bottom. After storage for 24 hours in an oven at 80°C, followed by cooling to room temperature, samples of modified bitumen (approx. 5 g) were taken from the area of the two ends of the tube to evaluate homogeneity. The homogeneity test of the modified bitumen was carried out by determining the asphaltene plus rubber content by the precipitation method in the presence of heptane. After adding about 5 g of modified bitumen to 50 ml of heptane and stirring, the mixture was left in the dark for 24 hours. The mixture was filtered and asphaltenes and non-dispersed rubber (insoluble in heptane) remained on the filter paper. The filter paper was brought to constant mass and weighed, thus calculating the asphaltene and polymer content of the modified bitumen sample analyzed.

ACKNOWLEDGMENTS

This work was supported by a grant of the Ministry of Research, Innovation and Digitization, CCCDI - UEFISCDI, project number PN-III-P2-2.1-PTE-2021-0552, within PNCDI III.

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