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Production of Rubberized Bitumen by oxidation of black oil

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ABSTRACT: In the paper, production process of Rubberized Bitumen (RB)-based Rubber Crumb (RC) from worn tires was investigated. During the experiment, the heavy oil vacuum residue (black oil) was oxidized with an amount of 0.3 and 0.5 wt.% of catalyst ($FeCl_3 \cdot 6H_2O$) at 240 °C. As a result it was observed, with increasing content of rubber from 10 wt.% to 20 wt.% in bitumen, the penetration and ductility of rubberized bitumen were decreased. Otherwise softening point of RB was increased in any content of rubber. Physical and mechanical characteristics of rubberized bitumen are established by standard methods. The structure of rubberized bitumen was characterized by optical microscopy and Scanning Electron Microscopy (SEM).

1 INTRODUCTION

1.1 *Scrap tire and rubber crumb*

Crumb Rubber (CR) is the recycled rubber obtained by mechanical shearing or grinding of scrap tires into small particles. Scrap tires are valuable secondary raw materials containing 65–70% rubber, 15–25% technical-grade carbon, and 10–15% high-quality metal. During the recycling process steel and fluff are removed, leaving tire rubber with a granular consistency. Eng. Vasco Pampulim, et al. offered the model of typical tire rubber mix (Fig. 1). Thus, the efficient processing of scrap tires makes it possible not only to solve environmental problems but also to perform economically rational utilization processes [1–4].

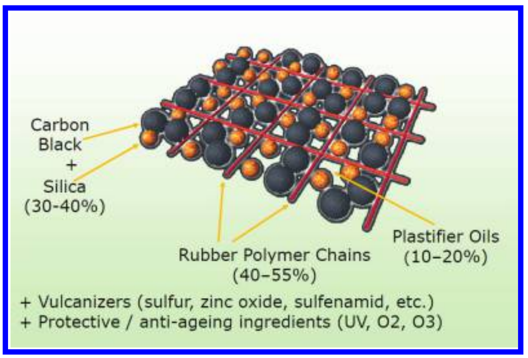


Figure 1. Model of typical tire rubber mix [4].

1.2 *Using rubber crumb and rubberized bitumen*

In the world, scientists have been offered a variety of ways to recycle and utilize the rubber crumb from worn tires. A well-known method is to burn the rubber waste to produce energy while producing cement [5]. Crumb rubber is often used in astroturf for cushioning, where it is sometimes referred to as astro-dirt. CR was used to remove ethylbenzene, toluene and xylene from aqueous solutions [6]. Rubber crumb also goes into the manufacturing of several auto parts and small percentages of crumb rubber go into manufacturing of new tires. A revolutionary nanotechnology process was developed to produce wood-replacement products paper-replacement materials from used tires [7]. Cut tires are used for the manufacture of drainage tubes, tapes for the protection of cables and pipelines, and soundproof walls. The combustion of tires generates energy and pyrolysis under conditions of relatively low temperatures. In addition, the processing of tires to obtain rubber crumbs for the manufacture of rubber bitumen compounds and asphalt-rubber compositions for insulating and roofing materials [3, 8–9].

There are many modification processes and additives that are currently used in bitumen modifications, such as Styrene Butadiene Styrene (SBS), styrene-butadiene rubber, ethylene vinyl acetate, and Crumb Rubber Modifier (CRM) [10].

Researches and applications of CRM and other modifications in the world showed that the bitumen binder has many advantages characteristics like improved resistance to rutting due to high viscosity, high softening point and better resilience, improved resistance to surface initiated, reduce fatigue/reflection cracking, reduce temperature susceptibility, reduce noise, resistance to fissure propagation, improved resistance to ultra-violet, improved resistance to oxygen or ozone, improved durability and lower pavement maintenance costs, and saving in energy and natural resource by using waste products [4, 11–12]. Asphalt concrete prepared with rubber-bitumen compounds exhibits high performance, enhanced wear and heat resistance, and resistance to aging [1, 13–14].

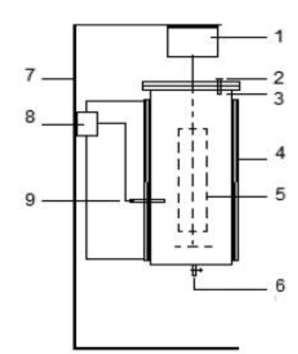
2 MATERIALS AND METHODS

2.1 *Production method of rubberized bitumen*

Experiments were performed to obtain rubber-bitumen compounds by mixing black oil (heavy oil residue) and rubber crumb. Mixing black oil with rubber crumb in an amount up to 20 wt.% at a temperature of 240 °C for 90 minutes and the stirring rate was 40/min. Oxidation processes of black oil in the presence of a catalyst in an amount of 0.3 and 0.5 wt% of $FeCl_3 \cdot 6H_2O$ were conducted. Air flow rate was 2.4 l/min. Then, oxidation products were stirred with a variety contents of (10; 15; 20 wt.%) rubber crumb for 60 minutes. Process was carried out at special apparatus, which was presented in Figure 2.

The apparatus were heated electrically (4), and the temperature of reactor was fixed by thermoregulator (8). Top to reactor connected stirrer (1 and 5), which allows for mechanical mixing of raw materials for process intensification.

1 - motor stirrer, 2 - pipe for gas outlet, 3 - a cylindri-



cal reactor, 4 - electric oven, 5 - agitator, 6 - a branch pipe for the withdrawal of products, 7 - Cabinet, 8 - thermo regulator, 9 - thermocouple.

Figure 2. Scheme of apparatus for preparing RB.

2.2 *Determination of physical and mechanical characteristics of bitumen materials*

Penetration involves the determination of the extent to which a standard needle penetrates a properly prepared sample of bitumen under specified conditions of temperature, load, and time. The unit of penetration is 0.1 mm, which is generally omitted in favor of reporting just the measured number. It was determined by apparatus Penetrometer PNB-03 in accordance with standard 11501-78.

Softening temperature—The temperature at which the bitumen goes from a relatively solid state into a liquid state. The softening point was determined by the method of "ring and ball" according to standard 11506-73.

The penetration index characterizes the degree of penetration of colloidal bitumen or rejection of his status from a purely viscous form. It is determined by empirical formula:

Ductility test gives a measure of adhesive property of bitumen and its ability to stretch. Tensile properties were determined by the apparatus Ductilometer CDB-974 N according to standard 11505-75.

3 RESULTS AND DISCUSSION

3.1 *Producing rubber modified bitumen*

Standard accordance of rubber modified bitumen was determined according to "Recommendation on the application of crumb rubber in road construction R RK 218-76-2008". Physical and mechanical characteristics of rubberized bitumen produced from heavy oil with rubber crumb (in same content of catalyst) are given in Table 2.

As seen from Table 1, with increasing content of rubber from 10 wt.% to 20 wt.% in bitumen, the penetration of rubberized bitumen decreased. Otherwise softening point of RB increases in any content of rubber. It was shown that the ductility

Table 1. Physical and mechanical characteristics of rubberized bitumen materials.

Objects	Indicators	Samples 1	Samples 2	Samples 3
Content of adding	Catalyst, %	0.3	0.3	0.3
	Rubber crumb, %	10	15	20
Bitumen characteristics	Penetration, 0.1 mm	75	64	62
	Softening point, °Ñ	39	47	50
	Ductility, cm	16	10	8
	Penetration index	0.9	1.0	1.3

Table 2. The influence of catalysts' content in the bitumen production.

Content of addition		Characteristics of bitumen		
Catalyst, %	Rubber crumb, %	Penetration, 0.1 mm	Softening point, °Ñ	Dutility, cm
0.3	15	64	50	10
0.5	15	56	52	7.4

Table 3. Group composition of black oil and bitumen products.

Hydrocarbon materials	Group composition of hydrocarbons		
	Asphaltene	Oil	Tar
Black oil	5.5	24.6	69.9
Oxidized bitumen	9.2	31.8	59.0

of RB is decreasing depending to the increase in content of modifier in bitumen. This is due to the action of rubber particles as stress concentrators. It means that the viscosity of bitumen compounds increases and starts to harden. These bitumen composition functions as a liquid or pseudo-thermoplastic matrix, the rubber particles provide resilient power frame in the amount of binder. The influence of catalysts' content in the bitumen production process is presented in the Table 2.

According to tabulated date, the adding content of catalyst increases (in same content of rubber crumb), and the physical and mechanical characteristics of products changed to highly viscous and harden. In the process rule, the catalyst content was impacted to increase its oxidation process. Group composition of hydrocarbon materials before and after oxidation process with catalysts were studied (Table 3) experimentally.

According to the results, asphaltene content was increased after oxidation of hydrocarbon. It is an infusible solid material with a density slightly more than 1 g/cm^3, which was contained in the bitumen in an amount of 10–25%. Asphaltene determines the structure formation processes, temperature resistance and increase in the viscosity of the bitumen.

Oil content was increased in bitumen after oxidation, too. It is liquid hydrocarbon at normal temperature with a density less than 1 g/cm^3. Usually, their content in bitumen is 40–60%. Oil determines the mobility and fluidity of the bitumen.

Tar content was decreased through oxidation. It is fusible visco-plastic material, solid or semi-solid at ordinary temperature with a density of about 1 g/cm^3. Tar contained in the bitumen is found in an amount of 20–40%, which determines the elasticity and extensibility of the binder [15].

3.2 *Microscopic study of rubber-bitumen compounds*

Surface structure of bitumen compound materials was studied using a microscopic technique. They describe interaction between bitumen and rubber crumb in rubberized bitumen. Optical microscopic images of rubber modified bitumen with 5 wt.% catalyst are presenting at Figure 3.

From the Figure 3 it is shown that the appearance of original bitumen is very smooth. The bitumen appearance becomes uneven after addition of rubber crumb and the rubber crumb becomes sticky after mixing it with base bitumen. During the preparation of rubber and bitumen, the bitumen aggregation almost covered the swelled rubber crumb while heating and stirring the mixture. The reason may be that rubber powder swelled by absorbing some light components or more liquid part of bitumen [16]. As the rubber crumb has

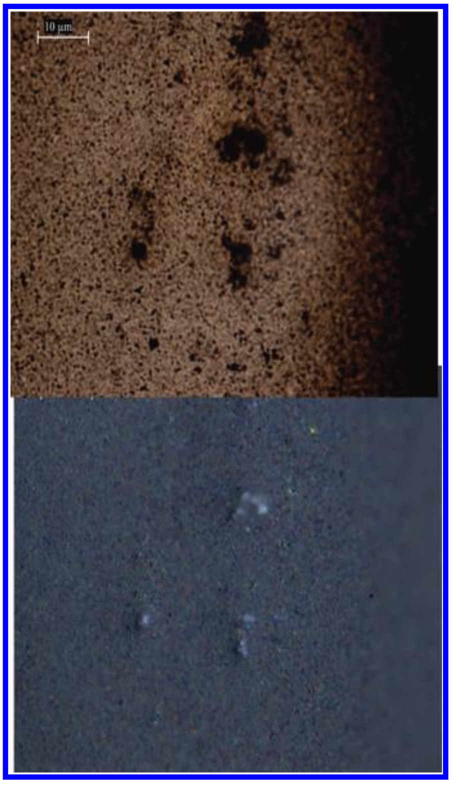


Figure 3. Optical microscopic image of rubberized bitumen.

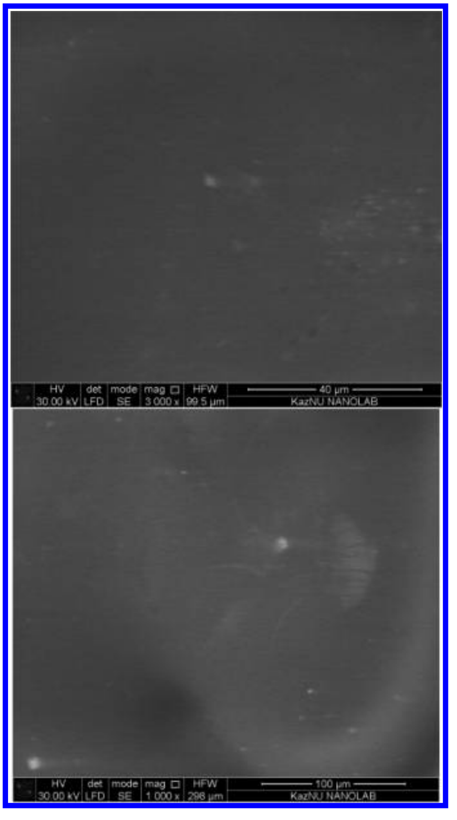


Figure 4. Scanning electron microscopic image of rubberized bitumen.

1.474 m^2/g of surface area, 0.300 nm is of medium pore size. It is important for rubber crumb to react with bitumen.

By electron microscopy images (Fig. 4) can approve that it is possible, these particles are particles of ferric chloride, which were catalysts for the oxidation of tar. In general, examples of rubber-binders are homogeneous mixtures with fully distributed components in the dispersed bitumen environment.

4 CONCLUSION

Thus, in the paper the possibility of producing rubberized bitumen from heavy oil residue with modification and catalyst. Due to the action of rubber particles as stress concentrators, the viscosity of bitumen compounds increases and starts to harden. These bitumen composition functions as a liquid or pseudo-thermoplastic matrix, the rubber particles provides resilient power frame in the amount of binder.

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