# Devulcanized Rubber for Bitumen Modification


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*Partial devulcanization of rubber crumb spent was performed in the presence of oxide nanoparticles. Nanoparticles on the basis of CaO and ZnO were prepared by dry grinding in a laboratory planetary mill and nanoparticles on the basis of $Fe_3O_4$ were obtained by precipitation. The distribution of particle sizes based calcium, zinc and iron were measured by dynamic light scattering. Devulcanization of the rubber crumb was carried out in a batch system at a temperature of 200°C and the sulfur content of rubber decreased more than 15 times after devulcanization. Homogeneity of bitumen, determined by fluorescence microscopy, was superior in case of modification with devulcanized rubber compared to the case of modification of bitumen with vulcanized rubber. Adhesiveness of bitumen road increases significantly after modification with desulfurized rubber compared to the case of bitumen modified with vulcanized rubber.*



*Keywoords: waste, desulfurized rubber, bitumen modification, nanoparticles*


An increasing amount of waste is generated every year. From economic and environmental reasons it is necessary that such waste must be recycled instead of being stored. The scientific literature published several papers in which is approached waste recycling [1-7]. Waste rubber is a substantial part of the solid waste, most of which being used tires for cars and trucks. With the increased production of cars and trucks and because of limited life of the tire, the amount of waste tires increases annually. Some of these tires are used for recycling and the rest is stored or deposited, creating environmental problems. An EU Directive prohibits the storage of such waste which has intensified the research for its recycling.

In order to use rubber from used tires, obtained through a grinding process (CR) to obtain asphalt were performed rheological and adhesion evaluations. Such modified bitumen with crumb rubber was characterized with a rotating viscometer, with a dynamic shear rheometer and then by conventional binding tests. Hot asphalt mixtures that include modified bitumen with crumb rubber were evaluated by determining fatigue, permanent characteristics and rigidity modulus. The bitumen and asphalt mixtures properties modified with the crumb rubber were compared with modified bitumen with different contents of styrene-butadiene-styrene (SBS) and asphalt mixtures based SBS. Tests have shown that to achieve the same performance as in the case of the SBS-modified, CR content to be used must be more than SBS, exactly 8%. [8]

Adding crumb rubber in asphalt can be achieved in two ways. In the first version, bitumen was mixed with rubber at a rate of 5-22% and applied on roads using the wet process. In the second variant of asphalting process, crumb rubber products was used as part of the mineral aggregates, replacing some solid fractions [9]. Navarro et al. investigated the rheological behaviour of the bitumen modified with 9% wt. crumb rubber obtained by grinding tires. It was observed that the addition of rubber used in bitumen increases the linear viscoelastic modulus and the viscosity at high temperatures. It is recommended to use the rubber particles smaller than 0.35 mm [10].

Addition of crumb rubber in asphalt mixture improves strength and reduces their cracking at low temperatures. It was also observed that the addition of recycled rubber from tires in asphalt mixtures using a dry process can improve the properties of these asphalt mixtures, and rubber content has a significant effect on the resistance to permanent deformation and on the cracking. However the dry process is a much less usual method for the production of modified asphalt with crumb rubber probably due to compatibility issues of mixtures. In a related study of the size pieces of rubber effect, it was concluded that by using 10% CR to bitumen in wet processes, the modified mixtures with pieces of rubber of 0.15 mm shows the best effect for asphalt mixtures dense, while modified mixtures with crumb rubber of 0.60 mm shows a good effect of porous asphalt mixtures [11].

Bernardo Celauro et al demonstrated that improving road bitumen performance can be achieved by modifying bitumen with crumb rubber from used tires using the wet process [12]. Experimental attempts were made for optimizing the asphalt-rubber ratio and mixing times, to adjust the manufacturing temperature during the production process (the study was conducted with a Brookfield rotary viscometer). After the process optimization was made a comparison between the conventional and the rheological properties of rubber-asphalt mixture with those of modified bitumen with commercially available polymer (synthetic rubber styrene-butadiene-styrene). This comparison allowed to highlight obtaining a rubber-asphalt mixture with improved performance. By reusing adequate tires grinded is possible to obtain an improved bitumen with high recycled content corresponding to the specific needs of regions with warm climates.

Davide Lo Presti revealed the benefits of using modified asphalt with used rubber in civil engineering applications, in arrangement of sports and recreation areas and in other areas where it is necessary to use rubber modified asphalt [13]. For example, he demonstrated the quality of this asphalt mixtures by evaluating the behaviour in time of built roads in the last 40 years with rubberized asphalt obtained by ''wet process''. It is particularly beneficial the use of rubber obtained by grinding tires for road construction. Thus, by changing the asphalt mixtures properties, it improves bonding and mechanical properties.


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Also the modified bitumen with crumb rubber can be used in the construction of insulating layers, retaining walls road culverts, noise barriers etc. Using of these wastes to build embankments, has improved freezing resistance but also has increased the resistance to biological degradation. The softening point, penetration and viscosity index increased and the elasticity increased from 5-10% to about 75%. So, using rubber in asphalt, result in increased resistance to permanent deformation, increased fatigue durability, the viscoelastic properties and resistance to aging. Based on these studies it was observed that the best aging resistance improvement can be obtained by a wet method using modified bitumen with rubber at a rate of over 15%. It was noted that the crumb rubber modified asphalt mixtures have a fatigue resistance of 15-20 times higher than in the case of asphalt mixtures with binder unchanged.

Gawe et al revealed shortcomings of pyrolysis of tire rubber, processes occurring in special reactors at temperatures between 300 and 800°C. In addition to valuable products are obtained solid subproducts (oil, soot) and gaseous. Thus eliminating waste tire by pyrolysis is a very costly and requires the use of additional devices to prevent environmental contamination [14]. Due to its viscoelastic properties over a wide temperature range, bitumen modified with rubber is used for sealing joints in pavement and other types of sealing in the road construction [15]. Thus, the mixture of filler with bitumen modified with rubber shows excellent adhesion to the surfaces of adjacent plates, traffic resistance to various weather conditions and high chemical resistance. Also, the pavement based on asphalt mixtures modified with rubber shows improved anti-slip properties, resistance to aging of asphalt, increased durability (resistance to weather conditions), increased durability at fatigue but small maintenance costs. Handling these mixtures is much easier, their frost resistance is higher, and the friction coefficient between tires and road surface is higher.

Although in most cases it was demonstrated the improvement of road pavement performance, modifying bitumen with crumb rubber presents some disadvantages. Interactions between rubber and bitumen affects binder performance. Such rubber-bitumen interaction is based by diffusion phenomenon: rubber particles absorbed aromatic components in the bitumen which are swelling. The swelling degree depends on the chemical nature and viscosity of bitumen, on the content and rubber particles size, on the temperature and mixing time and on the crosslinking degree of the polymer. A low swelling degree decreases the homogeneity of the bitumen and of the mixtures asphalt performance. Increasing the degree swelling is favored by a low crosslinking of the polymer, respectively. The vulcanization of the rubber used in the manufacture of tires is carried out by treating it with sulfur. The presence of sulfur in vulcanized rubber crosslinking and thus diminishes its degree of swelling in bitumen and diminishes the homogeneity of modified bitumen with polymer. In this paper we proposed the devulcanizing of rubber spent by treatment with various nanostructures and modification of road bitumen with this devulcanized rubber.

## Experimental part

Particles of metal oxides (CaO and ZnO) were prepared by dry grinding of zinc oxide and calcium oxide powder (reagents Sigma-Aldrich). The grinding process was done in a laboratory planetary mill Fritsch Pulverisette 6, fitted with a stainless steel grinding vessel with a capacity of 500 mL and with 10 stainless steel balls with a diameter 20 mm. Working conditions were: mass ratio balls / powder = 1/3, grinding duration 60 min. the speed of 500 rpm, the number of balls used is 10.

Iron-based nanoparticles were prepared by dosing under stirring (1000 rpm) of a 25% ammonia solution in a mixture of 0.1M aqueous solution of $FeCl_{23}$ and 0.1 M $FeCl_2$ aqueous solution at a volume ratio of 2: 1 (molar ratio $NH_{23}$ / $FeCl_{23}$, $FeCl_{22}$ 4: 1). Oxygen was removed from distilled water by bubbling of ultrapure nitrogen for 4 h. The particles thus obtained were separated in a magnetic field and washed three times with distilled water. To determine the size distribution of nanoparticles, they have been dispersed in water at the concentration of 0.1mg/ mL.

The distribution of particle sizes based calcium, zinc and iron was measured with a particle size measurement by dynamic light scattering (DLS). The instrument used for measuring is a Nano ZS (Red badge).

Desulfurization tests were conducted in a laboratory autoclave with a volume of 600 ml, fitted with mechanical stirrer, electric heating furnace, automatic temperature control panel, thermocouple, exhaust valves of the reaction products liquid or gaseous. The raw materials used were:

- crumb rubber size between 0.5-2 mm and a sulfur content of 5.21% (as determined by Grote);
- CaO, ZnO and $Fe_3O_4$ nanoparticles;
- ortho-xylene.

The mass ratio of crumb rubber / metal oxide was 5/1 and the concentration of the crumb to the solvent was 5 wt%. The temperature was 200°C, stirrer speed of 500 rpm and the duration of the 8 h. Removal of the solid was performed by decantation-filtration and the recovery of the desulfurized rubber was carried out by evaporation of the solvent at 120 ° C in an oven provided with air flow, until the constant weight. The sulfur content of desulfurized rubber was determined by the method Grote. Desulfurized rubber was dispersed in bitumen at a concentration of 4 wt%. in an autoclave equipped with stirring at a speed of 1800 rpm and a temperature of 180°C, for a period of 8 h. The properties of road bitumen used are shown in table 1.

The homogeneity of the modified bitumen was determined by fluorescence microscopy (Zeiss device) and the binding characteristics by determining of anti-stripping properties to the mineral aggregates according to SR EN 10969-2007.

## Results and discussions

The particle size distribution of metal oxides used in the devulcanizare is shown in figure 1-3.

From DLS analysis it results that the average particle size of calcium oxide obtained by milling is 641.3 nm and the size distribution is between approx. 300 and 900 nm.

**Table 1**
MAIN CHARACTERISTICS OF BITUMEN

| The characteristic | The method | Value |
|---|---|---|
| Penetration at 25°C, 1/10 mm | SR-EN 1426 | 60 |
| Ring and ball softening point, °C | SR-EN 1427 | 47 |
| Ductility at 25°C, cm | SR 61-97 | 150 |
| Breaking point Fraass, °C | SR EN 12593-07 | -13 |
| Flammability, °C | STAS 5489-80 | 260 |
| Density at 15°C, g/cm3 | SR ISO 3838-04 | 1.034 |

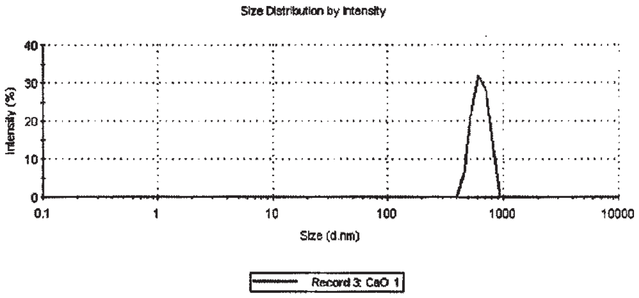


Fig.1 CaO particle size distribution

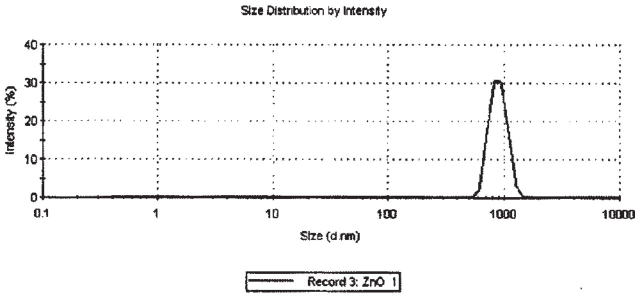


Fig.2. ZnO particle size distribution

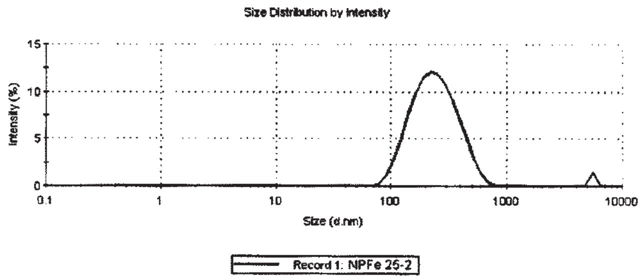


Fig.3. $Fe_3O_4$ particle size distribution

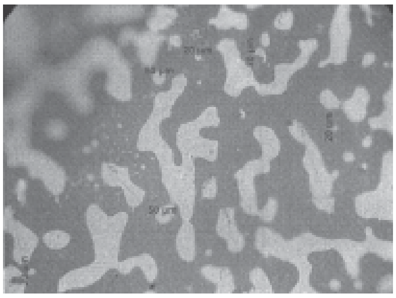

Fig.4. Fluorescence microscopy analysis of the bitumen modified with crumb vulcanised rubber

From figure 2 it is observed that the average particle size of ZnO obtained by milling is 905.4 nm and the size distribution is between approx. 400 and 1050 nm.

From figure 3 we see that the average particle size is 257.8 nm, the minimum size is 70 nm and the size distribution is very wide.

Sulfur content of devulcanized rubber in the presence of the three metal oxides is presented in table 2.

Analysis of sulfur content of rubber spent after devulcanization shows a decrease of almost 15 times for CaO compared to the initial crumb, nearly 35 times for $Fe_3O_4$ and nearly 44 times for ZnO.

In figures 4-7 are presented the analysis by fluorescence microscopy of bitumen modified with crumb rubber vulcanized and modified with the three samples of rubber desulfurized with nanostructured metal oxides.

From figure 4 is seen a low dispersion vulcanized crumb rubber in asphalt, rubber particle size ranging between 20 and 150 μm.

**Table 2**
SULFUR CONTENT OF DEVULCANIZED RUBBER

| Nr. crt. | The metal oxide used in the devulcanizing | Sulfur content, % |
|---|---|---|
| 1. | CaO | 0.35 |
| 2. | ZnO | 0.12 |
| 3. | $Fe_3O_4$ | 0.15 |

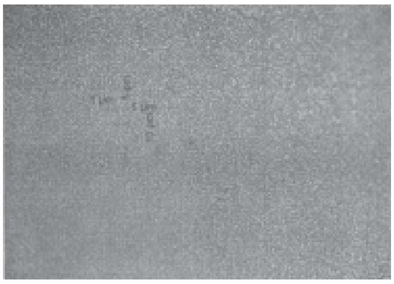

Fig.5. Fluorescence microscopy analysis of the modified bitumen with devulcanized rubber in the presence of CaO

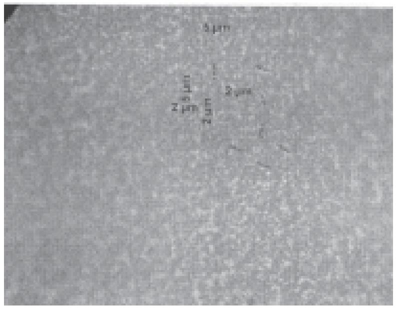

Fig.6. Fluorescence microscopy analysis of the modified bitumen with devulcanized rubber in the presence of ZnO

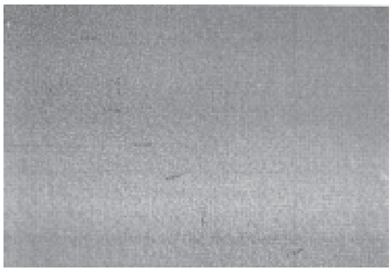

Fig.7. Fluorescence microscopy analysis of the modified bitumen with devulcanized rubber in the presence of $Fe_3O_4$

Figure 5 shows a high dispersion of devulcanized rubber in the presence of CaO in bitumen, rubber particle size ranging between 5 and 13 μm.

Figure 6 shows a high dispersion of devulcanized rubber in the presence of ZnO in bitumen, rubber particle size ranging between 2 and 9 μm.

Figure 7 shows a high dispersion of devulcanized rubber in the presence of $Fe_3O_4$ in bitumen, rubber particle size ranging between 2 and 11 μm.

Table 3 shows the results of adhesiveness tests carried out with mineral aggregates standard and bitumen modified with the desulfurized rubber.

From table 3 we see that the adhesiveness of road bitumen increases after modification with rubber desulfurized, the increase being more pronounced in case of modification with ZnO nanoparticles.

| crt. | aggregate | | devulcanized rubber, % | |
|---|---|---|---|---|
| 1 | Chileni; sort 5-8 | - | 0 | 94.53 |
| 2 | Chileni; sort 5-8 | CaO | 4 | 96.12 |
| 3 | Chileni; sort 5-8 | ZnO | 4 | 98.36 |
| 4 | Chileni; sort 5-8 | $Fe_3O_4$ | 4 | 97.29 |

**Table 3**
ADHESIVENESS OF MODIFIED BITUMEN

## Conclusions

Partial devulcanization of rubber crumb spent was performed in the presence of oxide nanoparticles type Ca, Zn and Fe in the same operating conditions.

Nanoparticles on the basis of CaO and ZnO were prepared by dry grinding in a laboratory planetary mill and nanoparticles on the basis of $Fe_3O_4$ was obtained by precipitation.

The distribution of particle sizes based calcium, zinc and iron was measured with a particle size measurement by dynamic light scattering.

The process of devulcanization of the rubber crumb was carried out in a batch system at a temperature of 200 °C, the mass ratio of crumb rubber / metal oxide is 5/1 and the concentration of the crumb to solvent was 5 wt%.

The sulfur content of rubber decreased more than 15 times after devulcanization, the lowest sulfur content was obtained if devulcanization was carried out in the presence of ZnO particles.

Homogeneity of bitumen, determined by fluorescence microscopy, was superior in case of modification with devulcanised rubber compared to the case of modification of bitumen with vulcanized rubber.

Adhesiveness of bitumen road increases significantly after modification with desulfurized rubber compared to the case of bitumen modified with vulcanized rubber.

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