

EVALUATION OF CRUMB RUBBER PROPERTIES TERM OF USE AS MODIFIER FOR ASPHALT

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Abstract

This work presents a study on evaluation of properties of crumb rubber by selected methods. The aim of this study was verify suitability of crumb rubber as modifier for asphalt. The sieving analyze were obtain overview about distribution of grain size of crumb rubber. After sieving analyze were obtain fractions of crumb rubber with narrower distribution of grain size. These narrower fractions were subjected to selected evaluation methods. The important criterion for verification of suitability of crumb rubber was differential scanning calorimetry. This method validated that crumb rubber retain their elastic properties even than marked low temperatures. Evaluation of crumb rubber with selected methods validated, that crumb rubber is suitable additive on modified asphalt.

Keywords: crumb rubber; modifier; differential scanning calorimetry.

1. Introduction

Increasing number of vehicles on roads generates millions of used tires every year. These tires are greater and problematic sources of waste due to the large volume produced and their durability. Many countries have relied on land filling but the capacity is limited. This is reason why millions of used tires are dumped or stockpiled [1]. Scrap tires are still a serious environmental and financial problem for many countries in the world [2]. European member states according to Directive 2008/98/EC of the European Parliament, must take the necessary measures to increase their recycling processes. In particular by 2020 must be increased to a minimum of 70 % by weight. Directive contains recycling and recovery of materials, re-use. In this context, efforts to increase the use of recycled materials at the same time develop and promote high performance and durable materials that are suitable for further re-use [3].

Scrap tires consist of rubber, steel, fibers and carbon black. There are some strategies of recycling waste tires. The recycling scrap tires have a good trend. One of the approaches of recycling scrap tires is use to crumb rubber as a component in asphalts mixtures. The crumb rubber in asphalt mixture improves the properties of asphalt pavements. Asphalt mixture by crumb rubber can minimize environmental impact and maximize the conservation of natural resources. Crumb rubber is a material commonly used in asphalt mixtures due to gives a higher viscosity, greater resistance of fatigue cracking and rutting performance of mixtures [4]. The ability of crumb rubber to improve the asphalt mixture properties depends on many factors such as: source of asphalt, reaction time between crumb rubber and asphalt, mixing methods, origin of the rubber, size and concentration of the crumb rubber particles [2].

Crumb rubber is made by mechanical shredding scrap tires, which is a particular material free of fiber and steel. There exist two techniques to produce crumb rubber as ambient grinding and cryogenic process [5]. Differences between these processes are in technique of grinding and in the different surface characteristics. Ambient process use room temperature, suitable machinery for cutting and grinding rubber. The particles from ambient process have irregular shape and rough surface. This grinding also gives crumb rubber a much higher specific surface area, twice that cryogenic grinding. Cryogenic process use liquid nitrogen for

freeze the rubber before cutting and grinding it in order to reduce its dimensions. Cryogenic process has regular shape and smooth surface which resembling shattered glass. These differences have significant effect on the adhesion between crumb rubber and asphalt matrix [4,6]. Crumb rubber is measured or described by the mesh or mm. Crumb rubber size can be classified into four groups as coarse (9.5 – 6.3 mm or 3-2 mesh), medium size (2 – 0.600 mm or 10 - 30 mesh), fine (0.425 – 0.180 mm or 40 - 80 mesh) and superfine (0.150 – 0.075 mm or 100 - 200 mesh) [7].

Knowledge of the specific surface values indicates the importance to modify and activate the surface of the crumb rubber. This allows not only assessing the resilience of the crumb rubber to solvents as well as estimation of potential of crumb rubber as asphalt modifier. For some of rubber products (e.g. gaskets, hoses, insulation and the like.) are significant poor interactions with solvents and liquids [8]. Conversely interaction, swelling is an important episodes of the use of crumb rubber as a modifier of asphalt. For the interaction of crumb rubber with the asphalt are dominant maltenes structures that cause swelling of the crumb rubber. Activation of crumb rubber is not new and has been used also in other industries. The crumb rubber activation by different substances is known [9]. Some of these technologies include the use of furfural [10], hot water activation [10-11], peroxides activation [12], used oils [13], grafting of acrylic acid and the use of a reacted and activated elastomers [14]. Information about properties of crumb rubber is important for the selection of conditions of addition of asphalt with crumb rubber.

The aim of this study was characterization of crumb rubber by selected analytics methods and verifies suitability of using crumb rubber as modifier for asphalts. The aim was also using of these data for planning conditions at devulcanization of crumb rubber in asphalt. The properties of crumb rubber are important information for choosing conditions for addition of asphalt by crumb rubber. Methods used for evaluation of crumb rubber properties were: sieving analysis, determination of specific surface, scanning electron microscopy, differential scanning calorimetry and swelling of crumb rubber.

2. Experimental design

This section includes crumb rubber characterization by test methods such as sieving and elementary analyses, scanning electron microscopy (SEM), specific surface area (BET), differential scanning calorimetry (DSC) and swelling in solvents.

The crumb rubber (CR) was obtained from the firm V.O.D.S., a.s., Košice, Slovak Republic. The technology of the company starts with processing by feeding of used tires into crusher (coarse crushing). Elimination of metal and textile fractions of tires follows after first crushing in magnetic and air separators. After next crushing the crumb rubber is separated to the various grain sizes fractions. The company produces fractions of three various grain sizes: coarse – medium grain size (2 mm > and \geq 0.5mm), medium – fine grain size (\leq 1mm) and fine grain size (\leq 0.5mm). With each type of V.O.D.S crumb rubber fraction was carried out the sieving analyze. For getting narrower fractions of crumb rubber grain size were following sieve openings used: 2.50 mm, 1.40 mm, 1.00 mm, 0.80 mm, 0.63 mm, 0.355 mm, 0.20 mm, 0.16 mm, 0.09 mm, 0.05 mm and bottom. The upper bolter 300 g of the fraction was dosed. Sieving was realized using sieve shaker machine at laboratory temperature during 50 minutes. Four representative fractions (1.40 mm, 1.00 mm, 0.63 mm and 0.20 mm) retrieved from the sieving process were using for next tests.

Elementary analyze was measured on commercial micro-analyzer FlashAE 1112 fy THERMO FINNIGAN, based on chromatograph determination of oxidative burning fumes and their next reduction. Relative accuracy of results of elemental analysis was 4 %. Determination of ash was carried out according to standard method EN ISO 3451-1 [15].

Structure characterization of the CR samples was performed by a Tesla BS300 scanning electron microscope (SEM) with the acceleration tension of 20 kV. Samples of the CR were placed on a double-sided tape glued onto aluminum targets of 15 mm in diameter. The samples were coated by gold in an argon atmosphere using the Balzers equipment. The coated

samples were monitored by SEM. The microscope was equipped with a TESCAN electronic scanning component. The image was scanned into the BMP format and processed using the WinTip 3.1 software.

Surface characteristics were measured by physical adsorption of nitrogen at -196 C using ASAP-2400 (Micromeritics). On measuring was used large-volume burette (30 ml), which was special prepare for detection textural properties of samples with very low surface. The crumb rubber sample was processed 12 hours at 70°C under vacuum 2 Pa.

Differential scanning calorimetry (DSC) measurement was performed on PerkinElmer DSC8500 (Norwalk, CT, USA) equipped with an intercooler. Sample of 12 mg (grain size of CR was 0.63 mm) was placed into sealed aluminum pans. Sample was initially cooled from 30°C to -75°C at gradient $-10^\circ\text{C min}^{-1}$ and subsequently reheated by gradient $10^\circ\text{C min}^{-1}$. The sample was measured in heating regime only and nitrogen was used as the purge gas at flow 30 mL min^{-1} . The glass transition temperatures were calculated by three methods which are included in the standard EN ISO 11357-2 [16].

The thermogravimetric analyze (TG) was also realized to complement the DSC measurement. The derivation of thermogravimetric data (dTG) was used for identification of the temperature at which the maximal rate of crumb rubber degradation was reached. TG measurement was performed on simultaneous TG/DTA apparatus Seiko Exstar 6300 (SII, Tokyo, Japan). Sample of approx. 7 mg was placed into an open alumina pan; nitrogen at 150 mL min^{-1} was used as a purge gas. Sample was heated from 30°C to 1000°C at 5°C/min .

Evaluation of crumb rubber swelling was done according the modified standard method ASTM D3616-95 [17]. Impact of time to equilibrium saturation by the solvent was verified by measuring of the crumb rubber swelling in tetrahydronaphthalene. Swelling of crumb rubber was monitored in six solvents: hexadecane (HD), 1,3-dimethylcyclohexane (DMCH), isopropylcyclohexane (IPCH), tetrahydronaphthalene (THN), decahydronaphthalene (DHN) and 1-methylnaphthalene (MN). On swelling were used 1 g of each fraction of CR, swelling time was 24 h. Swelled crumb rubber was filtered and washed by pentane to remove excess of the solvent from the rubber surface. Pentane was from rubber surface at slight heating in air flow removed. Swelling indexes SI were calculated according equation (1), where m_1 is weight of sample before swelling and m_2 is weight of sample after swelling. Influence of time on achieve saturation of CR by solvent was determination with swelling CR in THN.

$$SI = (m_2 - m_1) / (m_1 * 100) \quad (1)$$

3. Result and discussion

The used methods for evaluation of crumb rubber were selected especially with the view of physical properties. The only data which represents chemical composition of crumb rubber are results given by elementary analysis. The physical properties of crumb rubber in context with modification of asphalts are therefore mainly discussed.

3.1. Elementary analyses

The elemental analysis was chosen as basic information of crumb rubber qualitative parameter. Table I presents elementary composition of used crumb rubber. The content of ash is important not only at energetic utilization of crumb rubber, but also in knowing about content of inorganic solids present in the rubber.

Table I. Elementary composition of crumb rubber

x (wt. %)				
N	C	H	S	Ash
0.48	80.64	7.29	0.15	11.44

The results of elemental analysis can be used as auxiliary information; they do not reflect only the elements in the polymer itself. Thus, the content of individual elements fits not only

the presence of a rubber polymer but also the quantity and composition of ingredients. The carbon content increases the presence of carbon black. The content of hydrogen with respect to the content of elemental hydrogen in the polymer is affected by the presence of curatives, particular by zinc stearate). Similarly with the other elements and ashes, their content depends on the amount of ingredients in rubber.

3.2. Sieving analyze

The three type of fractions V.O.D.S. crumb rubber (coarse – medium size, medium – fine size and fine size) have excessively wide grain size distributions. The grain size distributions of three fractions are shown on Figure 1. The sieve analyses of these crumb rubber fractions allowed not only obtaining the grain size distributions, but also gave samples of crumb rubber with narrower grain size distribution.

After sieving of V.O.D.S. crumb rubber samples were selected four representative fractions for next characterization. The fraction of coarse grain sizes was captured on sieve 1.40 mm, the fraction of medium grain sizes was captured on sieve 1.00 mm, the fraction with fine grains was captured on sieve 0.63 mm and the fraction with very fine grain was captured on sieve 0.20 mm.

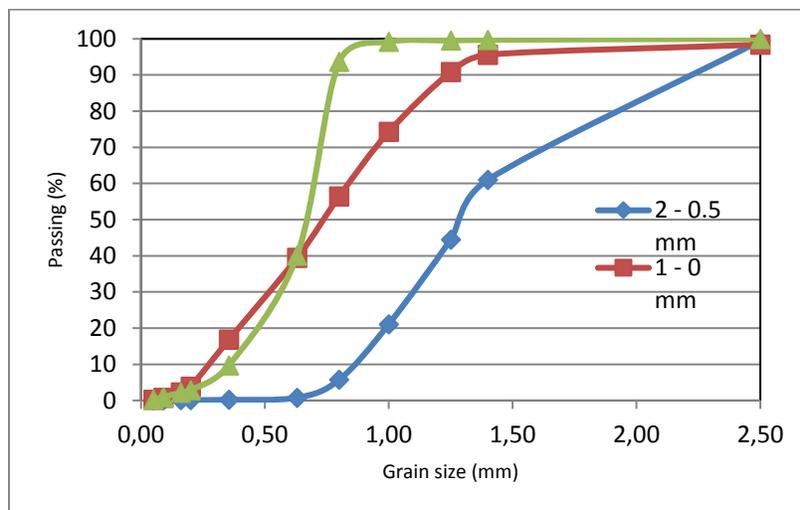


Figure 1. Grain size distributions of crumb rubber

3.3. Scanning electron microscopy (SEM) results

Scanning electron microscopy showed the morphology of the surface of the crumb rubber particles. On the surface of the particles were observed different types of asperity as a result of grinding the raw material rubber. Small irregularities in the surface were observed on the particle with grain size 1.4 mm (Figure 2 A). The relatively smooth surface, similar to fracture brittle material particles showed images of the grain size of 1.00 mm (Figure 2 B). The rugged surfaces were observed on the surface of particles of grain size 0.63 mm and 0.20 mm (Figure 2 C, D). Records scanning electron microscopy indicated a greater diversity of the surface of crushed finer crumb rubber particles.

3.4. Determination of specific surface area of crumb rubber

Measurement of crumb rubber surface by adsorption of nitrogen at temperature of nitrogen boiling point was performed at entirety relative pressure in full range of the BET isotherm validity ($p/p_0 = 0.05-0.3$). In consideration of the significant variance of measurement points (correlation coefficient = 0.88) was the specific surface area (S_{BET}) calculated using the one point BET-isotherm and with the value of the volume adsorbed at a relative pressure $p/p_0 = 0.30$. According this calculation the specific surface of the crumb rubber was equal $0.017 \pm 0.003 \text{ m}^2/\text{g}$. The value of the total pore volume V_p was also determined from adsorption data

at relative pressure $p/p_0 = 0.30$. Based on the result was CR surface very low. The differences between crumb rubber fractions of various grain sizes were negligible because the results were within experimental error.

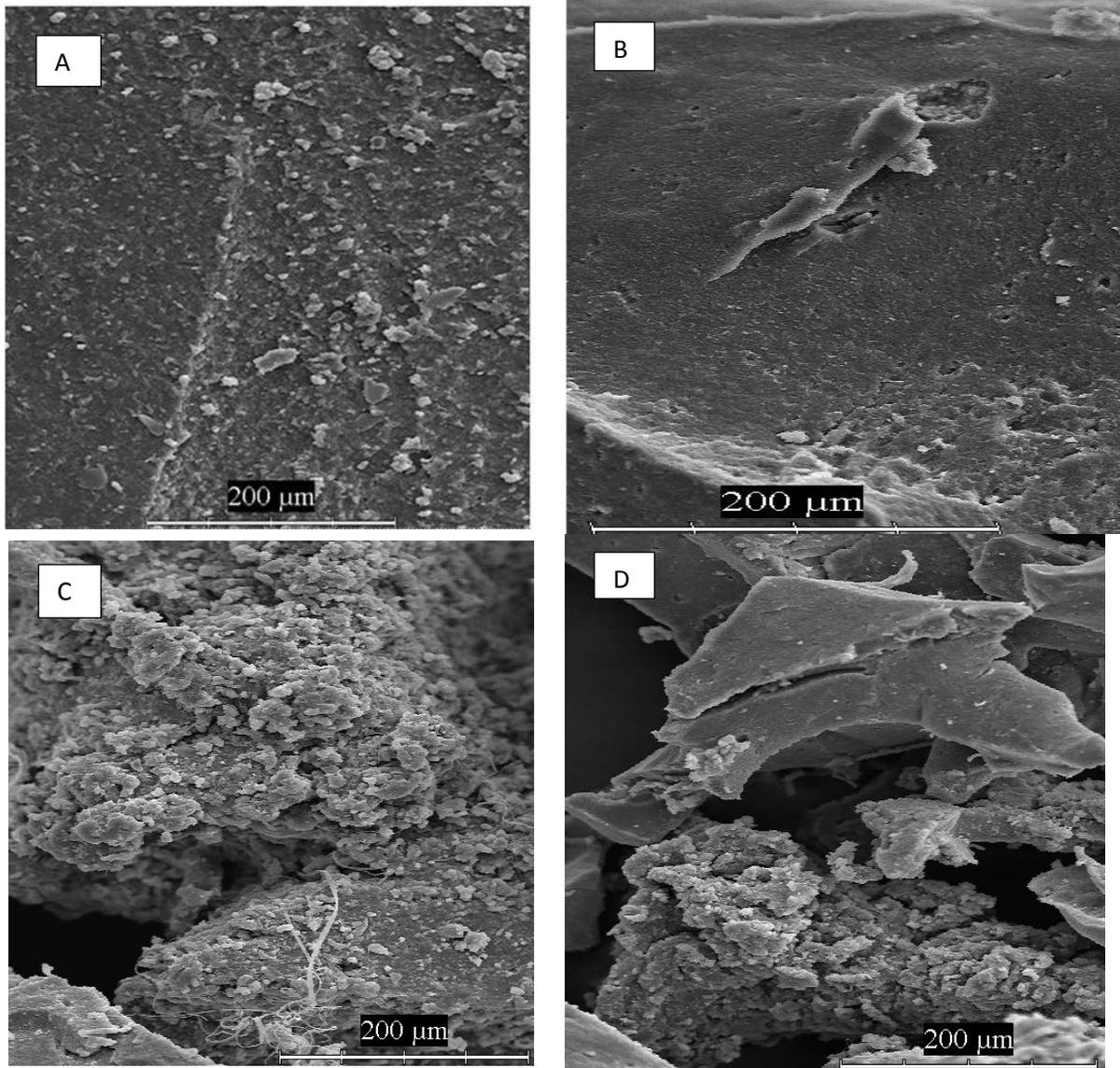


Figure 2. SEM pictures for various sizes of CR particles: A) 1.40 mm, B) 1.00 mm, C) 0.63 mm, D) 0.20 mm

3.5. Differential scanning calorimetry results

The crumb rubber was examined at low temperatures in order to know the glass transition temperature. The glass transition temperatures were calculated according to the procedures in the international standard [16]. Determination of the glass transition temperature in the DSC experiment was carried out in the range from -76 to 0°C . There have been selected three calculation method, and thus obtained results of the glass transition temperature were compared.

Figure 3 illustrates three methods of determining the glass transition temperature. The dependence of the normalized heat flow at the temperature within the range from -75 to -50°C showed over the course of the characteristic inflection point. The method of determining the inflection point (-57.6°C ; 0.2119 W/g) gave the highest value of the glass transition temperature. Determining the point of defining equal segments on the curve and tangents

gave the lowest glass transition temperature (-59.4°C; 0.2065 W/g). The glass transition temperature determined by a point equidistant from the tangents have a value close to the average of the two already used methods (-58.4°C; 0.2095 W/g). The average glass transition temperature of the crumb rubber calculated from the obtained results was $-58.5 \pm 1^\circ\text{C}$. Since the CR retains elastic properties at low temperatures it is suitable as a modifier for asphalt. Given that a very low glass transition temperatures maintain crumb rubber elastic properties at low temperatures, and is suitable as a modifier for asphalt.

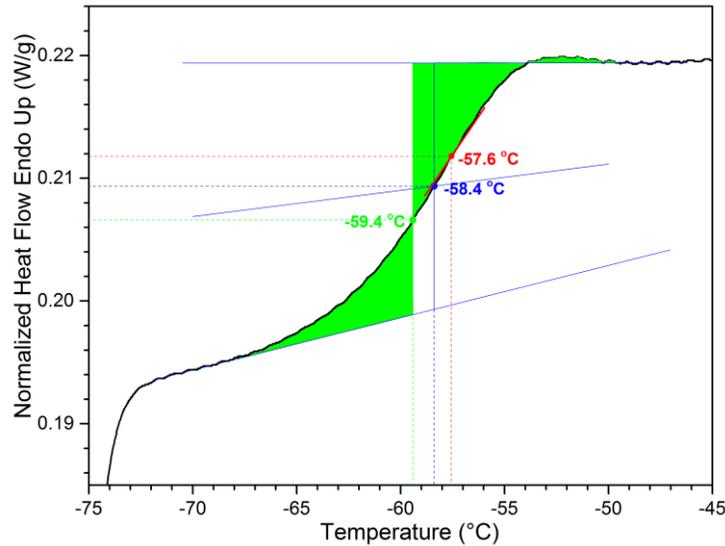


Figure 3. Determination of the glass transition temperature by DSC

Crumb rubber was also analysed by thermogravimetric (TG) method. Weight changes were monitored as function of temperature during of crumb rubber heating from 30°C to 1000°C. Figure 4 shows the course of the change in weight in the range 50°C-800°C. In the temperature range 30°C - 50°C and 800°C - 1000°C there has been no significant change in weight. The disintegration of CR starts at about 200° C and finishes at 500°C. Using derivation of thermogravimetric dependence were two significant minima observed (Figure 4). The points belong to temperatures 364°C and 409°C. The minima correspond to the inflection points on the gravimetric curve. Round about these points are the largest sample weight changes.

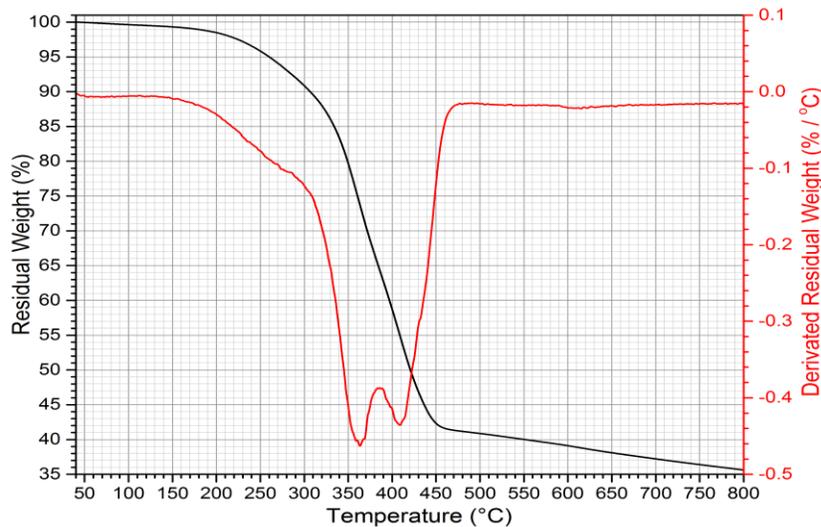


Figure 4. Curve of thermogravimetric analyses and its derivation curve

3.6. Activation – swelling of crumb rubber

Swelling of crumb rubber was monitored in non-polar solvents. Hydrocarbon solvents were used: hexadecane (HD), isopropyl cyclohexane (IPCH), 1, 3 - dimethyl cyclohexane (DMCH), decaline (DHN), tetraline (THN), and 1-methylnaphthalene (MN). The swelling time was set at 24 hours. Verification of the steady state of saturation of crumb rubber by solvent is reviewed between 1 and 8 hours at $20 \pm 2^\circ\text{C}$. Swelling index was calculated at gradually increasing time interaction of solvent with crumb rubber. The values of swelling index on Figure 5 documents the steady-saturation of CR after 8 hours of contact THN.

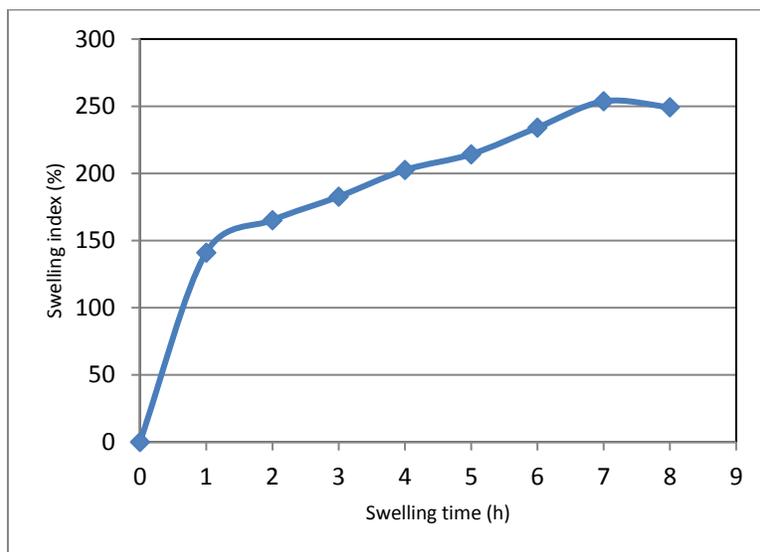


Figure 5. Dependence of swelling CR in THN on contact time

The crumb rubber particles saturated by solvents were evaluated also visually. After 7 hours was visible volume increase of the particles in comparison with state after 1 hour. There was also observed increased sticking of crumb rubber particles. Figure 6 shows the particle of CR after the first and after seven o'clock in contact with THN.

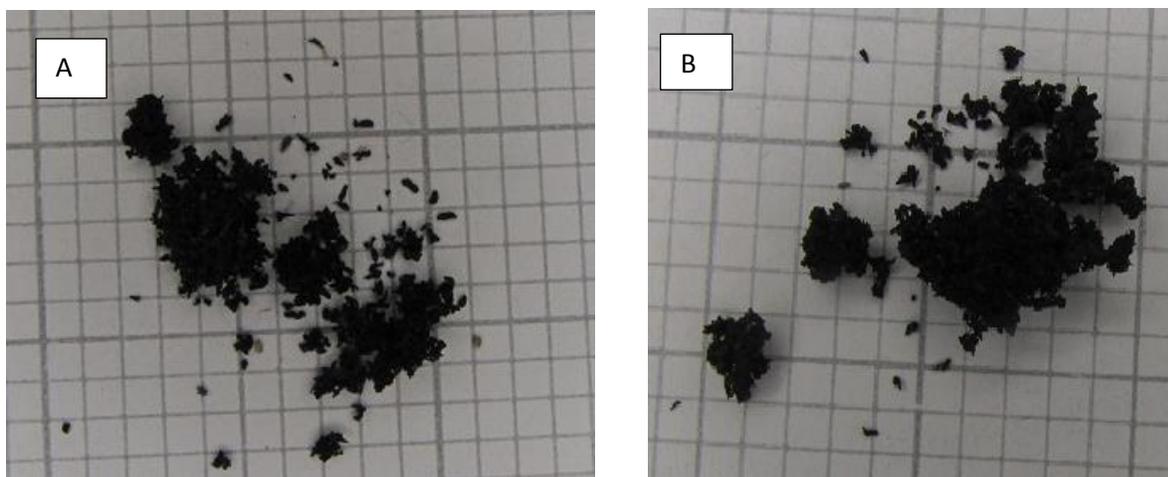


Figure 6 The crumb rubber (particle size 0. 20 mm) saturated by THN, A) after 1 h, B) after 7 h

Figure 7 shows swelling indexes of crumb rubber saturated with various hydrocarbon solvents. The results allow evaluating the swelling of the crumb rubber at different hydrocarbons and comparing the swelling of particles of different sizes. Higher swelling index in all solvents was clearly reached by reduction in particle size CR.

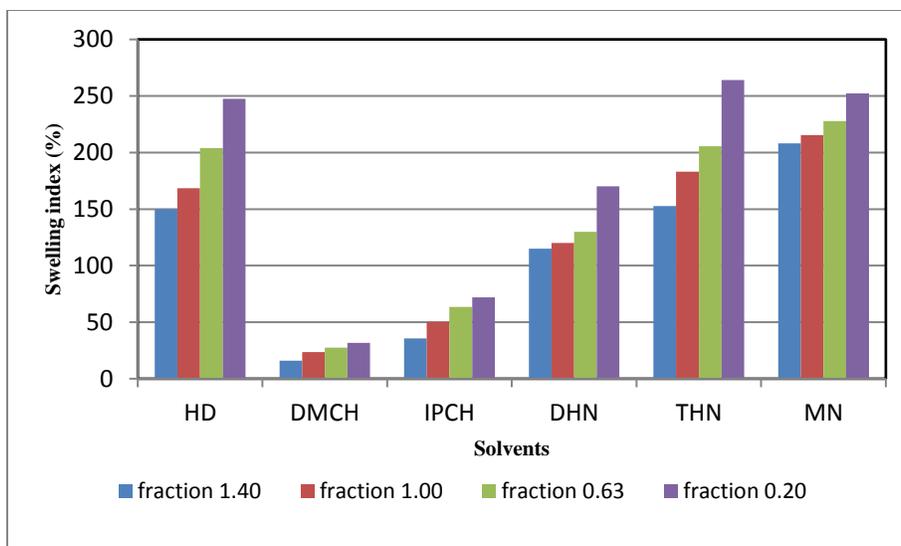


Figure 7. Swelling indexes of different fractions of CR in solvents

The interactions of various types of hydrocarbon with crumb rubber have demonstrated their affinity to butadiene and styrene polymer structures which are present in rubber. Saturated hydrocarbons have a structure closer to butylene than styrene structures. Alkanes dissolve maltenes, but coagulate asphaltenes present in asphalt. This can cause a breakdown of the gel structure in the asphalt mixture with GD. The relatively high swelling index in hexadecane can be attributed to the similarity with structures subsistent in polybutadiene rubber. Saturated cyclic compounds showed the lowest indices swelling. The di-cyclic saturated hydrocarbon DHN had higher swelling index than alkylated monocyclic hydrocarbons. The interaction THN and its high swelling index were reflected in the saturated cyclic structure and aromatic part of the compound, which is similar to polystyrene structures. High swelling indices were expected in aromatic solvents as it was observed at MN. Swelling indices indicates that among hydrocarbons are aromatic hydrocarbons most suitable activators for crumb rubber. These hydrocarbons are structurally closest to polystyrene and polybutadiene rubber structures. Aromatics are also good solvents maltenes and asphaltenes present in the asphalt. The knowledge of swelling properties gives good information on the quality of crumb rubber and is suitable for examination of addition of asphalt with crumb rubber.

4. Conclusion

Evaluation of crumb rubber properties is important for its further use. By the choice of the tests for evaluation of CR was an effort to prove their suitability in connection with its use of CR in asphalt mixtures. Knowing these characteristics can help in the planning of laboratory experiments and in practice.

Sieve analysis and SEM provide information on the distribution, size and shape of the particles. By the BET method was confirmed that the specific surface of CR is very small. Therefore, the attempt to use activators of crumb rubber and apply the particles of lower grain sizes.

Differential scanning calorimetry and thermogravimetric provide relevant information about the elastic properties and thermal stability of rubber. By DSC was determined the glass transition temperature. The value of t_g was identified in range $-58.5 \pm 1^\circ\text{C}$. Based on this test it is clear that CR lose elasticity up to very low temperatures. The thermogravimetric method confirmed that the decomposition of the crumb rubber at 200°C runs through only slightly. This is the temperature at which it is possible to manipulate with the CR without changing their properties. Facts about the relatively good thermal stability of the rubber up to about 200°C are significant. In the preparation of the asphalt mixtures is recommended maximal temperature of 180°C . This is required in particular in accordance with the thermal stability of

additives. The same temperature condition at preparation of asphalt mixtures is prescribed in European standard. If it is degradation desired, the mixing of CR with asphalt must operate at temperatures above 250°C. Therefore, it is requirement to reduce the crumb rubber devulcanization temperature by using catalysed systems adequate.

Investigation of swelling properties showed different interaction of crumb rubber with hydrocarbon solvents. The swelling of crumb rubber in the paraffin hydrocarbon has demonstrated a relatively high index as compared to cyclic saturated hydrocarbons. The high swelling index was found in solvents having an aromatic ring in the molecule. These hydrocarbons are closest to the styrene and or butylene structures, therefore, may be useful activators of crumb rubber.

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