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THE RELATIONSHIP BETWEEN THE STRUCTURE AND FRACTURE MECHANICAL CHARACTERISTICS OF RUBBERS

Thesis book of PhD dissertation

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1. INTRODUCTION

Rubber is a widely used structural material both in everyday applications and high-performance industrial products. Since it is so widely used, it has to adapt to numerous conditions. Due to its chemical resistance and tribological properties, rubber is an indispensable raw material for many industries. Because of their elasticity, rubber parts are most often subjected to cyclic loading, as a result of which microcracks can form on the surface or inside the material. The cracks can combine, facilitate the propagation of already existing ones, and can result in the failure of the product. All these processes together are called fatigue. The fatigue life span of rubbers is shorter under cyclic loading than could be estimated with conventional models from tensile properties, therefore performance tests under quasi-static loading are not enough to analyze life span. Since the failure of rubbers occurs through crack propagation, fracture mechanical methods can be used best to analyze it.

The material of a rubber part is usually very complex systems, usually composites. There are many methods to modify the properties of rubber; the most obvious is to vary the quality and quantity of fillers and reinforcements. In recent years many new rubber additives have been introduced, and in addition to the conventional spherical fillers (carbon black, silica), now plate-like (graphene, layered silicate, organophilic clay minerals) and needle-like (nanotubes, nanofibers) fillers are used, too.

Associating rubbers with these new nanoparticles is a new direction of research in the development of elastomers. They improve mechanical, thermal and physical properties of the material and are also effective in small amounts provided adhesion between the components and the dispersion of nanoparticles is adequate. If the filler can be dispersed well, the boundary phase between the particles and the matrix increases considerably, therefore the effectiveness of nanofillers is a great deal greater than that of conventional, not active fillers. Their effect is similar to the effect of active fillers, e.g. SiO₂ and carbon blacks.

Carbon nanotubes and graphenes stand out even from nanofillers. They have exceptional mechanical properties, and great thermal and electrical conductivity. As in the case of all nanofillers, achieving proper dispersion in the polymer matrix is a considerable challenge with conventional processing technologies. Composites reinforced with multi-walled carbon nanotubes (MWCNT) and graphene are much researched and numerous papers are available in this field. They mostly focus on the mechanical properties of rubbers, but fracture mechanical characteristics are not researched much.

The recycling of used tires is a huge problem all over the world. They are mostly used for energy production. From an environmental point of view, the recycling of rubber as a material would be far more advantageous, any pyrolysis can provide a solution to this problem. The gas and oil fractions obtained this way can be used to produce energy or fed back to production as fuel. The forming solid fraction (pCB carbon black) can complement or even substitute commercially available carbon blacks in rubber production, this way facilitating the value-added recycling of used tires. A problem can be the inferior quality of the carbon black obtained this way, which may be caused by the varying input material

(type and composition of tires) and uncertainties in the manufacturing technology. For this reason, nowadays pCB is also used for energy production instead of in the rubber industry. The goal of my dissertation is to examine how the quality and quantity of conventional commercially available carbon blacks (N330, N550, N660, N772), pCB and novel fillers (graphene, graphene oxide, carbon nanotubes, carbon nanotube oxide) affect mechanical and dynamic properties, and how they can improve the resistance of rubbers to crack propagation in quasi-static loading. In my work I analyze the relationships between mechanical and dynamic mechanical properties, and the structure of rubbers (macro- and microstructural characteristics, average molecular mass between apparent cross-linking points: M_c). In the case of graphene oxide (GO) and carbon nanotube oxide (MWCNT-O) I also examine how their incorporation in an aqueous medium and cation surface treatment (cetyl trimethyl ammonium bromide CTAB) influence the examined properties and the dispersion of fillers.

2. LITERATURE REVIEW, GOALS

Many papers investigate the mechanical properties and fracture mechanical characteristics of rubbers containing carbon blacks of various activity. Many researchers research the processes during the failure of rubbers and the deformation mechanisms. Most papers, however, report the results and do not explain the underlying processes. Therefore, it is important to examine the fracture mechanical properties of rubbers and connect them to materials structure characteristics.

Characteristics determined in quasi-static loads are very important when rubber mixtures are compared and designed. Rubber parts mostly have to endure dynamic or cyclic loads, performing the fatigue tests and analyzing fatigue life span is a very long and tiresome process. Therefore simpler and faster failure tests which provide data for the estimation of the long-term behavior of rubbers are valuable.

Nanofillers in rubbers is a popular field of research but a great problem is poor dispersion due to their large specific area. Theoretically, associating graphene oxide and carbon nanotube oxide with natural rubber in latex can produce better dispersion but it often does not happen. The exfoliation of nanofillers can be increased effectively with certain surface treatment methods, and this way the properties of the elastomer nanocomposites can be improved. The homogeneous dispersion of nanofillers in an uncured rubber matrix is an unsolved problem; researching it is necessary and justified.

A value-added recycling method of used tires can be by pyrolysis. The resulting solid fraction (pCB) can be used as rubber industry carbon black, and can complement or even substitute commercially available carbon blacks in rubber manufacturing. Many researchers investigate this new type of filler, but they have yet to provide reliable results concerning the rubber industry utilization of pCB. One reason for this is that pCB is usually of varying quality and composition, due to its manufacturing technology and the many types of tires used. Another reason is that pCB has not been comprehensively compared to commercially available carbon blacks; researchers publish smaller results which do not make it possible to classify pCB into rubber industry fillers. A comprehensive comparison of pCB with

conventional, commercially available carbon blacks would fill a void and facilitate the use of pCB as a rubber industry carbon black.

I examine how pCB and the new type of nanofillers can improve the resistance of rubbers to crack propagation under quasi-static loading. In my dissertation I compare carbon-based fillers of various shapes (0D, 1D, 2D) with regard to the failure of rubbers. In addition to conventional mechanical and dynamic mechanical (DMTA) tests, I perform fracture mechanical tests, too. For evaluation I use the J integral CTOD (crack tip opening displacement) method together. I characterize the forming of the crack with the J_{critical} value, which I calculated with a 0.1 mm CTOD*. The measure of resistance against crack propagation is the tearing modulus (T_J), which I determine from the J integral values associated to the CTOD values (0.1, 0.2, 0.4, 0.6, 0.8).

I present how the quality and quantity of various fillers (carbon blacks, graphene, graphene oxide, carbon nanotubes, carbon nanotube oxide) affect mechanical properties (hardness, tensile strength, modulus, tear strength), dynamic mechanical properties (storage modulus, loss factor, Payne effect) and fracture mechanical properties (J_{trouser} , J_{critical} , T_J).

Based on this, the goals of my dissertation are:

- Examining the carbon black obtained from the pyrolysis of used tires (pCB), and comparing it to conventional commercially available carbon blacks (N330, N550, N660, N772). Examining the effect of using pCB on the mechanical, dynamic mechanical and fracture mechanical properties of natural rubber (NR)-based and styrene-butadiene rubber (SBR)-based rubbers.
- Comparing the characteristics that can be determined in the various crack-opening modes (mode I, tear strength and mode III, trouser tear strength, J_{trouser}) in NR and SBR-based rubbers.
- Determining the average molecular mass (M_c) values between apparent cross-linking points of NR and SBR-based rubbers. Finding relationships between the examined mechanical, dynamic mechanical and fracture mechanical properties, and M_c .
- Determining the macro and microstructural characteristics of NR and SBR-based rubbers (dispersion coefficient, average particle diameter) with an optical microscope (OM) and an atomic force microscope (AFM). Finding relationships between the examined mechanical, dynamic mechanical and fracture mechanical properties, and the structure of the rubbers (macro and microstructural characteristics).
- Examining how the association of the aqueous dispersion of graphene oxide (GO) and carbon nanotube oxide (MWCNT-O) to natural rubber latex influences examined mechanical, dynamic mechanical and fracture mechanical properties and the dispersion of the fillers. Examining how cation surface treatment (cetyl trimethyl ammonium bromide CTAB) affects the dispersion of graphene oxide.

3. MATERIALS USED, CREATING OF SAMPLES

In this part I present the materials, including the production of graphene oxide and carbon nanotube oxide. I list the examined sample groups, the method of producing mixtures and the association methods of the fillers used.

Producing the graphene oxide

I used the improved Hummers method to produce graphene oxide (GO). I used mineral graphite (Graphit Kropfmühl KFL 99,5 Small flake, 5 g/lot), and concentrated sulphuric acid (200 cm³), 85% phosphoric acid (25 cm³) and solid potassium permanganate (25 g) for the oxidation. The reaction lasted 3 hours. I used continuous magnetic stirring and kept the temperature below 40°C. After the reaction time ended, I thinned the mixture with distilled water and neutralized the remaining potassium permanganate with hydrogen peroxide. After sedimentation and decanting I washed the mixture with 1 mol/dm³ hydrochloric acid to remove the sulphate ions, then neutralized the suspension by washing it with distilled water. The procedure of washing was always suspending, sedimentation with a centrifuge, then decanting. The product was ca. 1 m/m% GO aqueous suspension, which I diluted to containing exactly 1 m/m% GO. I used lyophilization to produce solid GO, because when the suspension is dried, the plates exfoliated during oxidization stick together.

Producing the carbon nanotube oxide

I used a procedure similar to the one described for the production of GO, to produce carbon nanotube oxide (MWCNT-O). I oxidized industrial multi-walled carbon nanotubes (NANOCYL NC7000, 10 g/lot) in a concentrated nitric acid medium. I added 4x50 cm³ concentrated nitric acid to the MWCNT, then added 4x50 cm³ distilled water. The reaction lasted 3 hours with magnetic stirring. I diluted the mixture with distilled water and filtered it through filtering paper. I removed the broken nanotubes (which formed through the aggressive oxidation process) and the remaining catalyst (that remained after the manufacturing of MWCNT) from the MWCNT-O by Soxhlet extraction. I performed the extraction until the pH value was neutral. The product was ca. 4 m/m% MWCNT-O aqueous suspension. The MWCNT-O aqueous suspension is less stable than the GO. The 1 m/m% suspension is not stable even temporarily, (it settles immediately), therefore I only diluted the product to containing exactly 2 m/m% MWCNT-O immediately before use.

Mixture production

The fillers were added to the uncured rubber matrix in two ways: mixing on a roll mill (NR and SBR mixtures containing carbon black), and the reference NR mixtures containing graphene, graphene oxide, MWCNT and MWCNT-O), and association in latex.

Association in latex was done at room temperature. I used a 1 m/m% aqueous dispersion in the case of GO, and a 2 m/m% dispersion in the case of MWCNT-O. I stirred the mixture for 5 minutes then let it rest for 20 minutes in a vacuum drying chamber. Then I put the associated latex on a tray, coagulated it for 30 min at 80 °C, then dried it for 1 day at room temperature.

I added the necessary activator and curing systems to the mixtures on a roll mill. I used the roll mill to produce the mixtures containing carbon black, too. The roll mill is a Labtech Scientific LRM-SC-110 roll mill (first cylinder 26 1/min, 70 °C; back cylinder 20 1/min, 50 °C; 1.3 friction).

The curing additives were 5 phr (mass related to 100 mass unit of uncured rubber) zinc oxide, 2 phr stearic acid, 1.5 phr CBS and 2 phr sulphur in the case of the NR matrix, and 3 phr zinc oxide, 2 phr stearic acid, 1.5 phr MBTS and 2 phr sulphur in the case of the SBR matrix.

Mixtures, sample groups

One part of my dissertation is rubbers of NR CV60 and SBR 1502 matrix containing carbon black. When producing the rubber mixtures, I used N330, N550, N660 and N772 commercially available carbon blacks and pCB. N330 is a high-activity, small particle size carbon black with a narrow distribution of particle size. Pyrolytic carbon black also has small particles but the distribution of particle size is wide. I used the carbon blacks in varying amounts, (30, 45, 60 phr) alone and mixed with each other. In all three filling ratios I substituted N330 and N660 carbon black with pCB in 10% and 50%. In the case of N550 and N772 I only substituted 50% with pCB at a carbon black content of 60 phr. In the case of more detailed examinations I chose a high activity carbon black (N330) and a carbon black similar to pCB (N660). Considering the secondary structure, which can be characterized with the oil number, N550 is similar to N330, and N772 to N660, therefore they are suitable for verifying tests.

The second part of my dissertation is rubbers of NR matrix filled with nanofillers. In this part I examine the usability of the GO MWCNT-O aqueous suspensions associated in NR latex. The aqueous media of the latex facilitates the uniform distribution of the fillers. Nanofillers were used in small amounts: 0.1, 0.25, 0.5 phr. In the case of samples associated in latex (samples marked with L) I made 2 phr GO and MWCNT-O masterbatches. I added these to the NR natural rubber and made samples with the same filler content as the latex matrix samples (samples marked with M). The references were NR matrix with dried GO and MWCNT-O, and unoxidized XGnP graphene (samples marked with G) and MWCNT added as fillers in the same filler content as in the case of the latex matrix samples. The fillers were added on a roll mill.

Another part of my dissertation is improving the distribution of GO in NR latex with the use of cation surfactant material (CTAB). The use of CTAB is justified by the fact that π -cation interaction can form between the graphene (sp² hybrid state) and the CTAB, which can significantly improve exfoliation and the dispersion of the filler.

The manufacturing of samples

I made 2 mm thick plates from rubbers containing carbon black and 1 mm thick plates and trouser tear specimens from rubbers containing graphene and carbon nanotubes by pressing. I used a Teach-Line Platen Press 200E laboratory press (Dr. Collin GmbH, Munich, Germany) at a nominal pressure of 5 MPa. I cured the samples for a time of $t_{0,9}$ at

160 °C in the case of the SBR and 150 °C in the case of the NR. I cut the specimens from the rubber sheets.

4. TEST METHODS

Examining the fillers

I did the thermogravimetric analysis (TGA) on a TGA Q500 (TA Instruments Co., New Castle, Delaware, USA) in air on samples of ca. 10 mg. Heating speed was 10 °C/min, the tested temperature range was between room temperature and +1000 °C.

In the case of iodine adsorption tests I added an iodine solution to carbon black sample. After shaking I determined the amount of unadsorbed iodine by adding Na-tiosulphate. I gave the mass of the adsorbed iodine related to the mass of the carbon black (g/kg). I made two measurements according to the standard.

I determined the BET (BRUNAUER-EMMETT-TELLER theory) specific area according to the ISO 4652:2012 standard with a NOVA 2000 (Quantachrome Instruments, Boynton Beach, Florida, USA) instrument. I cooled the cleaned 1-1,5 g samples (vacuum, 25 °C, 24 hours) with liquid nitrogen. The measurement temperature is was -195,8 °C, the boiling point of nitrogen. The surface requirement of nitrogen is known, therefore the specific surface can be determined if the amount adsorbed nitrogen is known.

I did the oil absorption tests according to the ISO 4656:2007 standard. I did not have an absorptometer, which the standard required so instead of measuring the torque, I looked for the endpoint with my eye. I conditioned the samples in a drying chamber (125 °C, 1 hour), then cooled it to room temperature in an exsiccator. I continuously added paraffin oil to the sample (~2,5 g) during magnetic stirring (120 1/min) at a rate of 4 cm³/min, as the standard required. The oil caused the carbon black to first form little balls, then a dense mass. When the balls started appearing, the speed of mixing changed so I chose this state as endpoint. The results are the averages of three measurements.

The Raman spectra were made with a Labram 300 (Horiba Jobin Yvon, Kyoto, Japan) instrument (CCD detector, grid: 1800 lines/mm). The measurements were mad at an optical magnification of 50 x, with a shutter speed of 20 s and a repetition of 3. The laser was 532 nm NdYAG laser. The range was between 3400 cm⁻¹ and 70 cm⁻¹.

The X-ray photoelectron spectroscopy (XPS) tests were made with an Al/Mg twin anode non-monochrome X-ray source and a Phoibos 100 MCD-5 hemispherical energy analyzer Specs (Berlin, Germany) instrument. The pressure of the test chamber was 5x10 mbar. The threshold energy in the detailed spectra for element analysis was 10 eV, while for the wide spectra it was 100 eV. The reference was freshly sprayed Au 4f 7/2 tip, and 84.0 eV binding energy. CasaXPS software was used for the evaluation.

The SEM images for the morphology tests of fillers and rubber mixtures were made with a Jeol JSM-6380LA (Jeol LTD., Tokyo, Japan) instrument. I achieved the required conductivity by sputtering a thin layer of gold on the samples.

Following vulcanization

I did the vulcanization measurements with a MonTech Monsanto R100S (MonTech Werkstoffprüfmaschinen GmbH, Buchen, Germany) rheometer (1,667 Hz, 1°, in the case of SBR at 160 °C, while in the case of NR at 150 °C; the time of the test was 45 min). The data obtained from the vulcanization curves are maximum and minimum torque (M_h and M_l), the times required for 10, 50, 90% relative curing ($t_{0,1}$, $t_{0,5}$, $t_{0,9}$) and burn-in times, the times corresponding to torques exceeding minimum torque by 1 and 2 dNm (t_{s1} , t_{s2}).

Quasi-static mechanical tests

I did the hardness tests on the pressed sheets according to the DIN 53505 standard with a Zwick H04.315.000 instrument (Zwick GmbH & Co. KG, Ulm, Germany) in Shore A mode with a load of 12.5 N. Each result is the average of 10 measurements.

I did the tensile tests according to the ISO-37 standard on type 1, 2 mm thick specimens. The tensile tester was a Zwick Z250 (Zwick GmbH & Co. KG, Ulm, Germany), with a load cell of 20 kN, a clamping length of 60 mm and a crosshead speed of 500 mm/min. The tests were conducted at room temperature and each result is the average of five measurements.

Tear tests were performed according to the ISO 34-1 standard in mode B (56 mm clamping length). I used the Zwick Z250 here, too and the conditions were the same as in the tensile test.

Trouser tear tests are difficult to reproduce since the direction and path of crack propagation can be different in every test. For this reason I made a press tool, where the legs are thicker and the middle of the specimen at the location of crack propagation is lightened, thus leading the crack and reducing the flexible energy stored in the legs. With the use of this special specimen, reproducibility improved and the results can be evaluated better. To determine $J_{trouser}$, I used specimens of 100 mm x 30 mm x 6 mm (length x width x thickness; thickness in the plane of crack propagation is 1 mm) in the case of mixtures containing carbon black, while in the case of mixtures with nanofillers (G, GO, MWCNT, MWCNT-O) size was 100 mm x 30 mm x 3 mm (length x width x thickness; thickness in the plane of crack propagation is 0.5 mm). Tests were conducted on a Zwick Z250 tensile tester (clamping length 40 mm) with a load cell of 20 kN, at a crosshead speed of 100 mm/min at room temperature. The results are the average of 5 measurements. I used the formula below to calculate $J_{trouser}$, where t is thickness in the plane of crack propagation, while F_{tear} is the average constant force measured during a stable tear.

$$J_{trouser} = \frac{2 \cdot F_{tear}}{t} \quad (1)$$

I performed the fracture mechanics tests on SEN-T (100 mm x 25 mm x 2 mm) specimens. The initial notch was 10 mm, test speed was 10 mm/min, and clamping length was 50 mm. I followed the opening of the crack tip with a digital microscope (Dino-Lite Premier AM4113ZT (R4)). In the case of filled specimens, I used talc, in the case of the reference samples I used carbon black to achieve proper contrast. I used the CTOD values (determined from the photos and measured with the DinoCapture 2.0 program) and the J

integral values calculated from the test results. I used the formula below, where η is a geometric factor; its value in the case of this SEN-T specimen is 0.9. To calculate the J_{critical} value, I used the 0.1 mm CTOD*.

$$J = \frac{\eta \cdot U}{t \cdot (w - a_0)} \quad (2)$$

If we follow the change of CTOD, we can assign a J value to each selected CTOD value. This method provides information about crack propagation, in the phase directly after the crack starts. We assume that the speed of crack propagation initially is constant, then it gets faster. If a straight line is fitted to the initial section of the curve, its slope can provide information about the speed of crack propagation. If our assumption is correct, the J value extrapolated to a CTOD value of 0 mm would yield the J value that could be detected when the crack starts. In other words, if the tendency is examined in a wider range of CTOD, then the initial slope of the function fitted to the points, that is the value of the derivative at CTOD = 0 mm would give T_J , that is, the tearing modulus. This relationship can be seen in the formula below. In this case I fitted a straight line only to the initial part, therefore the slope of these lines also give the value of T_J .

$$T_J = \left. \frac{dJ}{d(\text{CTOD}^*)} \right|_{\text{CTOD}^*=0} \quad (3)$$

Dynamic mechanical tests

DMA tests were performed on a DMA Q800 instrument (TA Instruments Co., New Castle, Delaware, USA), in tensile mode, at a frequency of 10 Hz, at a preload of 0.1 N and a deformation of 0.1% and at a heating rate of 3 °C/min. The investigated temperature range was -100 °C to +60 °C. I used the same DMA instrument in tensile mode to investigate the Payne effect, at room temperature at a frequency of 10 Hz. Preload was 0.01 N, and the investigated deformation range was 0.01 – 10%. I used specimens of 25 mm x 2,5 mm x 2 mm and a clamping length of 10 mm.

To characterize the filler-uncured rubber connection, I used the maximum of the loss factor, $\tan \delta$. To determine the R_{lf} parameter (it characterizes the efficiency of amplification), I used the formula below, where $\tan \delta_{\text{max,ref}}$ is unfilled reference, and $\tan \delta_{\text{max}}$ is the maximum loss factor of the rubber containing a filler. A higher R_{lf} value indicates stronger adhesion.

$$R_{lf} = \frac{\tan \delta_{\text{max,ref}} - \tan \delta_{\text{max}}}{\tan \delta_{\text{max,ref}}} \quad (4)$$

Determining the average molecular mass between apparent cross-linking points

I used the formula below to calculate average molecular mass between apparent cross-linking points, where ρ is density, R is the universal gas constant (8.314 J/molK), T is temperature, 296 K, while E'_{rubbery} is the storage modulus measured at the given temperature.

$$M_c = \frac{3 \cdot \rho \cdot R \cdot T}{E'_{\text{rubbery}}} \quad (5)$$

The value of M_c through the value of E'_{rubbery} and density contains not only the real chemical cross-linking structure but also the physical cross-linking structure, which may contain the percolation network made up of particle aggregates and agglomerates. The density of rubbers was measured in methanol with a pycnometer.

Morphology tests

For optical microscopy (OM) and atomic force microscopy (AFM) tests I embedded the samples in polyester resin. After the resin cured, I polished the embedded samples with a Struers LaboPol-5 polishing machine in 5 steps (p320, p1000, p2000, p4000 SiC papers, polishing disk 1 μm diamond paste). I took the OM and AFM images of the polished cross sections.

I did the macrodispersion tests with an Olympus BX51M optical microscope (Olympus GmbH, Hamburg, Germany), at a magnification of 100x. I analyzed the images with a C-5060 CAMEDIA digital camera and the AnalySIS software. Before evaluation I set the proper contrast on the images and with this the macrodispersion coefficient can be well approximated from the ratio of dark and light sections. The macrodispersion coefficient (OM dispersion coefficient) was determined with fractions larger than 1 μm . The dispersion coefficient is the area occupied by the detected particles in percentage, subtracted from 100%. The obtained dispersion coefficient is the part of the examined area that does not contain particles and so it describes homogeneity. The software also calculated the average particle cross section. I assumed the particles are spherical and calculated their average diameter using this. I took photos of the samples in 5 different locations and determined the values based on these.

I used the Nanosurf FlexAFM (Nanosurf AG, Liestal, Switzerland) device to take 25 μm x 25 μm images in tapping mode (tapping, TAP190 AL-G cantilever). In this mode more accurate information can be obtained of the different phases and their distribution. Of the AFM images I examine the phase images, where white is the hard phase (carbon black) and black is the soft phase (rubber). The ranges are well separated. I analyzed the images with the Gwyddion software. The dispersion coefficient (AFM dispersion coefficient) and the average particle size were determined with the method presented above, with the optical microscope. I evaluated the images by examining fractions larger than 0.2 μm . In each sample I analyzed 3 images.

I did the DSC tests to determine the mass ratio (χ_{im}) of the immobile polymer layer. This method is simpler than the conventional Soxhlet extraction method, therefore it is gaining popularity. I did the tests with a DSC Q2000 instrument (TA Instruments Co., New Castle, Delaware, USA). Heating speed was 5 $^{\circ}\text{C}/\text{min}$, the range was -90 $^{\circ}\text{C}$ to +60 $^{\circ}\text{C}$, the program was single modulated heating program, samples were ~5 mg. I used the reversible heat capacity curves in the vicinity of the glass transition. I determined the ΔC_p value at T_g , which I normalized with the formula below, where w_f is the mass fraction of the filler.

$$\Delta C_{pn} = \frac{\Delta C_p}{1 - w_f} \quad (6)$$

I calculated the mass ratio of the immobile polymer layer (χ_{im}) from ΔC_{pn} with the formula below, where ΔC_{p0} is the detected ΔC_p of the unfilled reference mixture detected at T_g .

$$\chi_{im} = \frac{\Delta C_{p0} - \Delta C_{pn}}{\Delta C_{p0}} \quad (7)$$

5. SUMMARY

I made NR and SBR rubber mixtures containing commercially available carbon blacks (N330, N550, N660 and N772), and carbon black obtained from the pyrolysis of used tires (pCB). I added nanofillers (graphene, graphene oxide, carbon nanotubes and carbon nanotube oxide) to NR and NR rubber latex. I examined how the quality and quantity of fillers and the method of association affects mechanical, dynamic mechanical and fracture mechanical properties in quasi-static loading.

I found that pCB contains both carbon black and mineral fillers. It is because the different used tires contain different rubbers, carbon black, mineral fillers (SiO_2 , metal oxides) and additives (ZnO, MgO, CaO). Therefore, pCB can be considered a dual filler, which is indicated by its nearly 20% ash content (SiO_2). The specific area, particle size and oil number of pCB is closest to those of N330, but it also contains larger particles and non-spherical stuck-together particles. As a result, its distribution of particle size is wider and has a different secondary structure than conventional commercially available carbon blacks.

Of all the tested carbon blacks, pCB resulted in the lowest hardness, modulus and tensile strength at the same carbon black content. This shows that the activity of pCB is lower than the other tested carbon blacks with regard to these properties. In the tear test and trouser tear test pCB produced the highest values of all the tested carbon blacks both in NR and SBR. In the SBR matrix pCB produced the highest J_{critical} value, too. pCB inhibits crack propagation, and in this respect it can be considered active. This outstanding property can be traced to the dual nature of pCB and the wide distribution of particle size. In a NR matrix pCB behaves similarly to N660 and N772. In a SBR matrix pCB behaves similarly to N660 and N772 considering the tearing modulus.

In both a NR and SBR matrix pCB had the smallest effect on the DMTA curves and had the smallest Payne effect (the reduction of storage modulus as deformation increases). These indicate that the activity of pCB is the lowest of all the tested carbon blacks. The particle size properties of pCB (specific area, oil number), however suggest higher activity. Therefore, it can be stated that the Payne effect cannot be correctly estimated with particle size properties. The oil number does not give sufficient information about the network of carbon black agglomerates in the rubber matrix, at least not in such complex, dual-natured fillers as pCB.

I found a relationship between tear strength and trouser tear strength. A straight line of slope 1 can be fitted on the results, the properties are directly proportional. This suggests

that in tear strength (mode I crack opening) and J_{trouser} (mode III crack opening) tests the mechanism of failure is identical. In the latter, mode I crack opening is likely in the failure zone. Carbon black-filled NR matrix mixtures have higher tear strength, the fitted line is shifted. Due to the shortening of ligament length, the crystallization of NR due to stretching occurs at lower relative deformation. The lower deformation speed used in the case of J_{trouser} tests enable polymer molecules to slip on carbon black particles and aggregates. The shortening of ligament length, therefore crystallization, does not occur here, the line is shifted.

I found that as filler content and the activity of carbon black increases, the average molecular mass (M_c) between cross-linking points decreases. In a SBR matrix hardness and tensile strength decreases close to linearly as $M_c^{1/2}$ increases. This is true to the hardness of NR rubbers, too, but not to their tensile strength because of the stretching-induced crystallization during the test. Tear strength decreases as M_c increases. Stretching-induced crystallization occurs in this test, too, but NR matrix samples still show a relationship. J_{critical} and tearing modulus (T_J) values decrease as a function of $M_c^{1/2}$ in the case of both the NR and SBR matrix. Cross linking density therefore inhibits crack initiation and propagation. A hyperbolic relationship can be observed between the Payne effect and M_c . NR and SBR samples containing carbon black and NR samples containing nanofillers are on the same curve. This relationship is independent of the type, amount, activity, and form factor of the filler used, the applied method of association and the type of uncured rubber in the case of the mixtures I tested. Based on this, it can be stated that the Payne effect of a mixture, let us characterize it with the initial E' or E'_{Payne} value, can be estimated well if the M_c value and the relationship is known.

As carbon black content and activity increases, the homogeneity of the NR and SBR rubbers increases. Therefore, pCB results in the lowest dispersion coefficient and largest average particle size, whether examined with an optical microscope or atomic force microscope. I found a relationship between the macro and micro-sized distribution of carbon blacks in both a SBR and a NR matrix. This means that the homogeneity of the samples can be characterized well with both an optical microscope and an atomic force microscope. I showed that as the homogeneity of the NR and SBR samples increases, M_c decreases linearly, therefore apparent cross-linking density increases. In a SBR matrix as the dispersion coefficient increases, hardness, tensile strength, J_{critical} and T_J increase linearly. In a NR matrix it is the same with the exception of tensile strength, because stretching induces crystallization and so a direct relationship cannot be found. Tear strength increases as homogeneity and average particle size increase in both NR and SBR rubbers. A straight line can be fitted on the results, which is shifted to the positive direction in the case of NR samples as a result of the crystallization during the test. The Payne effect increases as the homogeneity of the samples increase. A finer dispersion of carbon blacks facilitates the forming of a network of a carbon black agglomerate in the rubber matrix.

In the case of graphene oxide (GO), the exfoliated layers are larger and more intact than the layers of XGnP (the commercially available graphene used in the test). Oxidizing the multiwall carbon nanotubes (MWCNT) resulted in an increase of the diameter of the nanotubes (from ~40 nm to ~70 nm). GO exhibited a higher degree of oxidization than

MWCNT-O (oxidation only affected a few outer layers), therefore the aqueous dispersion of GO is more stable than MWCNT-O.

Graphene oxide (GO) and carbon nanotube oxide (MWCNT-O) speed up vulcanization. As the amount of GO and MWCNT-O is increased, hardness, tensile strength, tear strength and trouser tear strength increase both in a NR and a NR latex. The highest values were obtained with samples associated in latex. In the case of carbon nanotubes, $J_{critical}$ and the tearing modulus (T_J) increased as filler content increased, regardless of the method of association. In the case of graphene, only association in latex resulted in measurable increase in T_J and $J_{critical}$. Carbon nanotubes are easier to disperse due to their needle-like shape, and have a more pronounced reinforcing effect than graphene, which is composed of larger planes. Therefore, it can be stated that association in latex produces a more homogeneous distribution of fillers in the rubber matrix, which increases hardness, tensile strength, tear strength, $J_{trouser}$, $J_{critical}$ and tearing modulus (T_J).

Associating graphene oxide and carbon nanotube oxide in latex increased storage modulus and resulted in small Payne effect and high initial E' . The association of these fillers on a roll mill resulted in a low initial E' and big Payne effect. Aqueous association facilitates more homogeneous dispersion but without this, the nanoparticle aggregates in the matrix fall apart as a result of dynamic loading, causing a pronounced Payne effect. Association in latex, therefore, has a clearly beneficial effect on the DMTA properties of rubbers containing graphene and carbon nanotubes. From the point of view of the Payne effect, the use of a masterbatch, previously associated in an aqueous media, can be beneficial when adding nanoparticles.

To increase the dispersion of graphene oxide, I surface treated it with cetyl trimethyl ammonium bromide (CTAB). As a result of surface treatment, the average molecular mass between apparent cross-linking points (M_c) increased, that is, apparent cross-linking density decreased. The π -cation interaction between the CTAB and GO plates effectively decreased the Payne effect and the interaction between the filler particles, and increased the loss factor measured during the T_g transition.

6. THESES

Based on the test results, the following theses can be formulated:

Thesis 1

The reinforcing effect of carbon black produced by the pyrolysis of used tires (pCB) for rubber industry applications corresponds to the reinforcing effect of N660 and N772 commercially available carbon blacks; therefore, it can partially or completely replace them. I proved this by testing natural rubber (NR)-based and styrene-butadiene rubber (SBR)-based rubbers that contained different types of carbon black. pCB combined with carbon blacks of higher activity (e.g. N330) improves tear strength, and reduces crack propagation and failure, especially in the case of SBR rubbers (even compared to samples containing only commercially available carbon black) [2-5, 10, 11].

Thesis 2

Tear strength, trouser tear strength (J_{trouser}), J_{critical} and tearing modulus (T_J) all increase as carbon black content and the activity of carbon black increase in the case of natural rubber (NR)-based and styrene-butadiene rubber (SBR)-based rubbers containing carbon black. Of the investigated carbon blacks, the activity of carbon black produced by the pyrolysis of used tires (pCB) is the lowest but pCB reduces crack propagation and the Payne effect, that is, the reduction of storage modulus as the amplitude of deformation increases, due to the dual characteristic of the filler and the wide distribution of particle size [2-5, 10, 11].

Thesis 3

There is unambiguous correlation between the strength characteristics determined in mode I (tear strength) and mode III (trouser tear strength) in the case of natural rubber (NR)-based and styrene-butadiene rubber (SBR)-based rubbers. A straight line of slope 1 can be fitted on the results. According to this, in tear strength (mode I opening of cracks) and J_{trouser} (mode III opening of cracks) tests the mechanism of failure is the same. In the case of the latter, mode I crack opening is likely in the failure zone. In the case of NR and SBR rubbers containing carbon black, the lines that can be fitted are not identical. It can be assumed that the cause of this is the crystallization of NR as a result of stretching in the tear strength test [2, 4, 5, 11].

Thesis 4

As filler content and carbon black activity increase, the average molecular mass (M_c) between the apparent cross-linking points is reduced. As $M_c^{1/2}$ is increased, hardness and tensile strength are reduced close to linearly in a styrene-butadiene rubber (SBR) matrix, while in a natural rubber (NR) matrix only hardness is reduced linearly in this case. As M_c is increased, tear strength is reduced, but the relationship changes with different types of rubber. J_{critical} and the tearing modulus (T_J) decrease as $M_c^{1/2}$ increases. The relationship is the same in the case of NR and SBR rubbers containing carbon black. An increase in the density of cross-linking reduces crack formation and crack propagation. A hyperbolic relationship can be observed between the Payne effect and M_c . NR and SBR samples containing carbon black and NR samples containing nanosized fillers are on the same curve. The relationship is independent of the type, amount, form factor and activity of filler, the applied method of association and the type of uncured rubber in the case of the

investigated mixes. Based on these, it can be stated that the Payne effect of a mix (E'_{Payne} , that is, the difference of measured storage moduli at a deformation of 0.01% and 10%), can be estimated well if M_c and the relevant formula is known [1, 2, 5, 9].

Thesis 5

With increasing carbon black content and activity, the homogeneity of NR-based and SBR-based rubbers increases. A relationship between the distribution of macro-sized and microsized carbon black in the case of NR and SBR rubbers. The homogeneity of the samples The homogeneity of the samples can be characterized well with an optical microscope or an atomic force microscope. With an increase in the homogeneity of the samples (dispersion coefficient) (whether it originates from a change in the type or in the amount of carbon black), the average molecular mass (M_c) between the apparent cross-linking points decreases linearly, while hardness, J_{critical} and tearing modulus (T_j) grows linearly in the case of NR and SBR rubbers. Tear strength increases with an increase in the homogeneity of the samples and an increase in the average diameter of the particles in the case of NR and SBR rubbers. The Payne effect increases as the homogeneity of the samples increases. A finer dispersion of the carbon blacks facilitates the forming of a carbon black agglomerate network in the uncured rubber matrix [5].

Thesis 6

If graphene oxide (GO) and carbon nanotube oxide (MWCNT-O) are dispersed in latex, it results in a more homogeneous dispersion of filler in the uncured rubber matrix, which increases hardness, tensile strength, tear strength, trouser tear strength (J_{trouser}), J_{critical} and tearing modulus (T_j). Cetyl trimethyl ammonium bromide (CTAB) surface treatment resulted in a more homogeneous dispersion of GO. As a result of CTAB, average molecular mass (M_c) between apparent cross-linking points increases, apparent cross linking density decreases. CTAB effectively reduced the Payne effect, the interaction between the filler particles, and increased the measurable loss factor during glass transition [6, 7, 12].

7. LIST OF PUBLICATIONS

Articles

1. E. Padenko, P. Berki, B. Wetzel, J. Karger-Kocsis; Mechanical and abrasion wear properties of HNBR of identical hardness filled with carbon black and silica. *Journal of Reinforced Plastics and Composites* 35(1), 81-91 (2016) **IF=1,086**
2. P. Berki, J. Karger-Kocsis; Comparative Properties of Styrene-Butadiene Rubbers (SBR) Containing Pyrolytic Carbon Black, Conventional Carbon Black and organoclay. *Journal of Macromolecular Science, Part B: Physics* 55(7), 749-763 (2016) **IF=0,828**
3. Berki P., Karger-Kocsis J.; Pirolitikus úton előállított korom alkalmazása gumikban, *Polimerek* 2(2), 35-38 (2016)
4. Berki P., Szakál M., Karger-Kocsis J.; Repedésterjedés vizsgálata SBR gumikban törésmechanikai alapon, *Polimerek* 2(5), 142-146 (2016)

5. P. Berki, R. Göbl, J. Karger-Kocsis; Structure and properties of styrene-butadiene rubber (SBR) with pyrolytic and industrial carbon black. *Polymer Testing* 61, 404-415 (2017) **IF=2,350**
6. Péter Berki, Krisztina László, Ngo Trinh Tung, József Karger-Kocsis; Natural rubber/graphene oxide nanocomposites via melt and latex compounding: Comparison at very low graphene oxide content. *Journal of Reinforced Plastics and Composites* 36 (11), 808-817 (2017) **IF=1,086**
7. Péter Berki, Do Quang Khang, Do Quang Minh, Luong Nhu Hai, Ngo Trinh Tung, József Karger-Kocsis; Interphase tailoring via π -cation interaction in graphene and graphene oxide containing NR nanocomposites prepared by latex compounding. *Polymer Testing*, **submitted IF=2,350**
8. Péter Berki, Do Quang Khang, Do Quang Minh, Luong Nhu Hai, Ngo Trinh Tung, József Karger-Kocsis; Natural rubber/boehmite nanocomposites via latex compounding, mechanical and fracture mechanical properties, *Institute of Physics Conference Series: Materials Science and Engineering*, **submitted**

Conference articles

9. P. Berki, E. Padenko, B. Wetzel, J. Karger-Kocsis, Identical hardness carbon black and silica filled Hydrogenated Nitrile Butadiene Rubber mechanical and abrasion wear properties. *International Rubber Conference, Nürnberg*, conference paper, 8p. (2015)
10. Berki Péter, Karger-Kocsis József, Pirolízis korom hatása NR gumik mechanikai tulajdonságaira, XXIV. Nemzetközi Gépészeti Találkozó - OGÉT, Déva, conference paper, 51-54 (2016)
11. P. Berki, J. Karger-Kocsis, Tensile and fracture mechanical properties of styrene-butadiene rubbers (SBR) filled with industrial and pyrolytic carbon blacks, and organoclay. *Material Science Forum* 885, 292-297 (2017)
12. Berki Péter, Karger-Kocsis József, Grafén-oxid hatása természetes kaucsuk mátrixú gumik mechanikai tulajdonságaira és a repedésterjedésre, XXV. Nemzetközi Gépészeti Találkozó - OGÉT, Kolozsvár, conference paper, 83-86 (2017)