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EFFECT OF A NEW TYPE OF COUPLING AGENT ON THE MECHANICAL PROPERTIES OF VARIOUS MULTI-WALLED CARBON NANOTUBE/RUBBER COMPOSITES

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In our experimental work application of carbon nanotubes in rubbers have been investigated. The effects of the type of the rubber matrix, the concentration of the carbon nanotubes and the effects of a coupling agent on the mechanical properties of the composites have been studied. The strength of the rubber matrix had great influence on the strengthening behaviour of the carbon nanotubes. By application of surface treated carbon nanotubes the strength of the composites made from a rubber matrix having the tensile strength under 10 MPa could be improved by 35%. However, the composites from the rubber with higher tensile strength contained treated carbon nanotubes afforded balanced performance against fatigue stresses probably due to the effect of the coupling agent and the homogenous distribution of the carbon nanotubes.

Introduction

Rubbers reinforced with carbon black (CB) are used for numerous industrial applications, such as vibration-resistant structures, electromagnetic interface (EMI) shielding materials, antistatic devices, etc. [1–4]. CB improves the mechanical properties (modulus and strength) of the rubber due to the interactions among the fillers and the fillers and the other components of the rubber. The CB particles were proven to form aggregates because of the strong bonding effects to each other. A part of the rubber is encapsulated in those aggregates because of the branched structures of the latter one and is shielded from macroscopic deformations [1]. Small domain size is required for effective reinforcement. On the one hand only branched structures small enough (< 50 nm) can be trapped and thereby achieved a strongly bonded system, and on the other hand only the adequately small domains have high surface activity [1, 2].

In the last two decades researches focused on to substitute CB with another fillers (eg. caolin, sepiolite, SiO_2, zinc-disorbate, titania) also having reinforcing effects [4–6] and also on to reduce the particle size of the CB to improve their dispersion in the rubber matrix [2]. In the former step modification of the surface of the fillers had to be also solved because they are incompatible with the most organic matrices, therefore, coupling agents were being used [5, 7]. The fillers for substitution of CB like SiO_2 have been spread in the recent years especially due to the higher demand for non-black applications [7–11].

Several solutions have been developed in the CB/rubber research area: as two step grinding technology, application of dispersants or coupling agents, pre-treatment of the carbon surface or chemical modification of the elastomer chains, moreover distribution of the CB in a latex solution instead of solid mixing [2]. Not much significant improvements were achieved by the first three solutions. In case of the latter one the modification of the CB surface represented the largest difficulty in order to disperse them homogeneously in the water solution of latex [4, 12].

Application of CB has been still significant because besides it can increase the strength of the vulcanized rubber; it also has a positive effect on the optical and electrical properties, and reduces production cost [3]. Application of carbon nanotubes (CNT) may represent a breakthrough in rubber matrices either but only small quantities have been introduced because of their relatively high price. Furthermore, by dispersion of the CNT arisen the same problems like the CB due to the high surface charge [13, 14].

A lot of papers were published about CNT/epoxy and CNT/thermoplastic composites but only a very few about CNT/elastomers [4, 8, 15–18]. The most exciting challenge in the area of CNT containing composites was to solve the proportional dispersion of the CNT because absence of a well-homogenized morphology the distinguished mechanical improvements of the reinforcement can not be achieved in elastomers either. E.g. Das and co-workers [19] used untreated and modified multi-walled carbon nanotubes (MWCNT) in a blend of styrene-butadiene rubber (SBR) and butadiene rubber (BR) with 50/50 ratio. Hydroxyl-groups were enacted to the surface of the modified MWCNT (Nanocyl®-3153), and bis(triethoxy-silylpropyl)tetrasulfone was applied as the coupling agent for bonding to the rubber. Composites were manufactured by a two-roller mill and a stabilized non-ionic surfactant/ethanol solution was used for MWCNT-treating. The coupling agent was applied in 2.5% related to the mass of the rubber. Strength of composites containing 5% MWCNT could be enhanced from 1MPa to 4.5 MPa. The new process with the ethanol solution was more effective then other traditional methods in the given concentration range. Similar properties were obtained by MWCNTs having hydroxyl-groups. Application of a silane type coupling agent did not significantly affect the mechanical properties.

Our research has been directed to the application of MWCNT in rubbers. The MWCNT has the same favourable effect in the point of view of the mechanical properties [20–22] as CB, and moreover by introduction of a proper coupling agent strong interaction can be established between the MWCNTs and the rubber. As MWCNTs have excellent mechanical properties they should have better strengthening effect than CB has. If mechanical properties of rubber composites can be improved to a large extent enough then the cost reduction can become less important.

For the surface treatment of MWCNT an olefin-maleic-anhydride copolymer based coupling agent has been applied [24]. Not only the possible effects of the coupling agent but also effects of the mechanical properties of the initial rubber matrix as raw material have also been investigated in MWCNT/rubber composites.

2. Experimental

2.1. Materials

Multi-walled carbon nanotubes (MWCNT) were produced at 700°C by chemical vapor deposition (CVD) process over Fe-Co bimetallic catalyst at the Institutional Department of Chemical Engineering (Institute of Chemical and Process Engineering, University of Pannonia). Purity of MWCNT was higher than 90 wt%, the diameter was between 10 nm and 20 nm, the average length was above 30 μm. Natural rubber (NR) and styrene-butadiene rubber (SBR) based (R-I and R-II) and nitrile-butadiene rubber (NBR) (ACN content: 45%, Mooney viscosity, 100°C: 60) based blends (R-III) were used as matrix material.

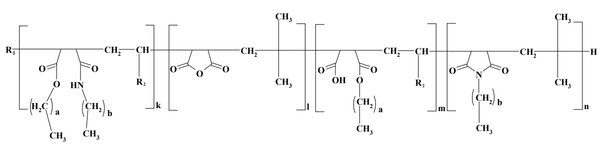

Figure 1: Structure of the ester-amide-imide derivative of the experimental olefin-maleic-anhydride copolymer (R1: alkyl group with length of the olefinic monomer (C16-C18); R2: alkyl group with R1-2 carbon number; a: 3-40, b: 3-32; k: 0,2-2; l: 1-7; m: 1-7 and n: 0,3-2)

The coupling agent was produced at the Institutional Department of MOL Hydrocarbon and Coal Processing (Institute of Chemical and Process Engineering, University of Pannonia) that was an ester-amide derivative of an experimental olefin-maleic-anhydride copolymer *(Figure 1)*.

2.2. Preparation of composites

Compounds were prepared by a milling process. A two-roller mill was applied also for mixing the carbon nanotubes into the basic mixture of rubber. Sheets of the mixtures were compression moulded at 180°C for 5 minutes vulcanization time. Dog-bone samples for mechanical testing were cut from the sheets. Compositions of the samples were given in *Table 1*.

Table 1: Composition of the different MWCNT/rubber composites

sample	rubber matrix type	MWCNT content, wt%	coupling agent, wt%
C-1	R-I	0	-
C-2	R-I	1.0	-
C-3	R-I	1.0	0.2
C-4	R-II	0	-
C-5	R-II	1.0	-
C-6	R-II	1.0	0.2
C-7	R-III	0	-
C-8	R-III	1.0	-
C-9	R-III	1.0	0.2
C-10	R-III	1.5	-
C-11	R-III	2.4	-
C-12	R-III	2.4	0.5

Effects of the coupling agent were also studied by application with an experimental treating method developed for surface treating of MWCNTs for PP [24]. Surface of MWCNT was covered by the coupling agent from the hydrocarbon solution of the additive with stirring the mixture for 1 hour at 60°C then the solvent was distilled out. Treated MWCNTs were then dried at 110°C for 2 hours and were mixed into the basic mixture of rubber by a two-roller mill.

R-I and R-II matrices were NR and SBR based blends with lower and medium mechanical strength, R-III matrix was an NBR based one with high mechanical strength. Thus effects of the type of the rubber were also studied on the properties of the composites. MWCNTs were applied in untreated and in treated form in order to investigate the influence of the coupling agent either.

2.3. Measurement of tensile properties

To determine the tensile and fatigue tensile properties (mainly stress, modulus and extension) (MSZ EN ISO 527-1-4:1999) an INSTRON 3345 universal tensile testing machine was used. The temperature in the laboratory was 23°C and the relative humidity was 50% during the mechanical tests which were carried out at 90 mm/min crosshead-speed both in case of tensile and fatigue tensile tests.

Structural information about the developed coupling agent was obtained by infrared technique with a TENSOR 27 type FTIR[1], illumination: SiC Globar light, detector: RT-DLaTGS type) in the 400-4000 cm^{-1} wavenumber range.

Scanning Electron Microscopy (SEM) was used to study the structure of fractured faces of the specimens and to follow the possible interaction between the reinforcements and the matrices. The applied apparatus was a Phillips XL30 ESEM instrument.

3. Results and discussion

Discussion of the results was divided into three parts. On the first hand effects of the type of the rubber matrix were detailed then on the second hand effects of the MWCNT concentration and finally the effects of the coupling agent were demonstrated.

3.1. Effect of the change in the rubber matrix on the tensile properties

In the present work effects of multi-walled carbon nanotubes (MWCNT) in three rubber matrices (signed as R-I, R-II, R-III) with different tensile strengths were investigated. Different effects were measured for the rubber matrices *(Figure 2)*. Introduction of MWCNTs into the rubber either in treated or in untreated form resulted in both increase and in decrease of the tensile strengths.

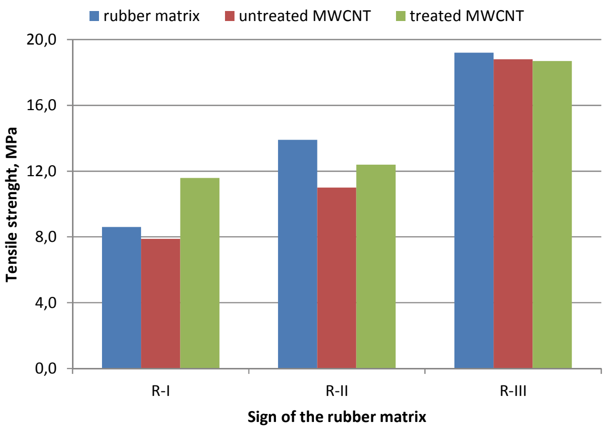

Figure 2: Effects of type of the rubber matrix on tensile properties (1wt% MWCNT-content)

Different effects were measured for the samples where treated MWCNTs were incorporated. Tensile strength enhanced from 8.6 MPa to 11.6 MPa meaning a 35% increase for the R-I matrix. Meanwhile in the case of R-II signed rubber the tensile strength reduced by 26% in the presence of untreated MWCNT. Application of the coupling agent improved the tensile strength by 12% but tensile strength of the original matrix could not be achieved. Tensile strengths of the MWCNT containing composites did not differ to that of the R-III matrix having the highest tensile strength (19.2 MPa).

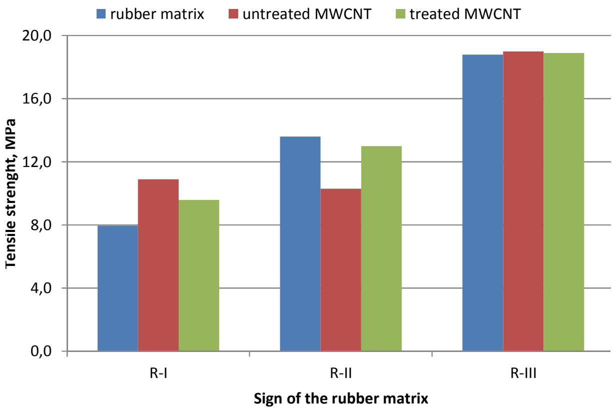

Figure 3: Effects of type of the rubber matrix on fatigue tensile properties (1 wt% MWCNT, fatigue conditions: 100 cycles and 10 N)

Resistance of the samples against fatigue tensile stresses of 100 cycles and 10 N as loading force were also studied *(Figure 3)*. Comparing the results of the fatigue tensile tests to those of the static tensile tests two important outcomes could be stated. First of all MWCNTs in the rubber blends could either improve or deteriorate the mechanical properties depending on the type of the rubber matrices. On the second hand composites made from basic mixture of R-II showed different behaviour than the others. Fatigue tensile strength was found to have been deteriorated by 6.5% if the MWCNT was incorporated in untreated form. The opposite behaviour was experienced by MWCNTs treated by the coupling agent since a 5% increase was measured. Standard deviation (SD) was calculated to be 0.8 MPa for unteated and 1.0 MPa for surface treated MWCNT containing samples.

Elongation at break was also represented for both types of tensile tests *(Figures 4, 5)*.

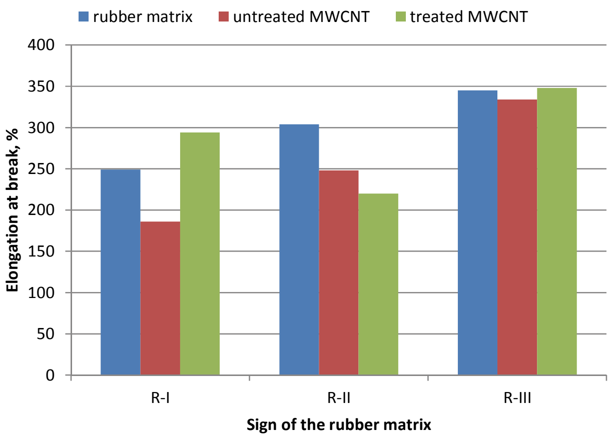

Figure 4: Effects of type of the rubber matrix on elongation at break (1 wt% MWCNT content)

Considerations for the elongation at break were established similar to the tensile strength. Type of the rubber was determinative in the evolution of the elongation at break *(Fig. 4)* either. Reinforcing rubber R-I with MWCNTs the value of 250% of elongation at break significantly decreased due to the pristine MWCNTs. Changing the reinforcement to surface treated MWCNTs an 18% improvement could be measured as the property increased to 290%. MWCNTs even in coupling agent treated form deteriorated the elongation at break of R-II rubber.

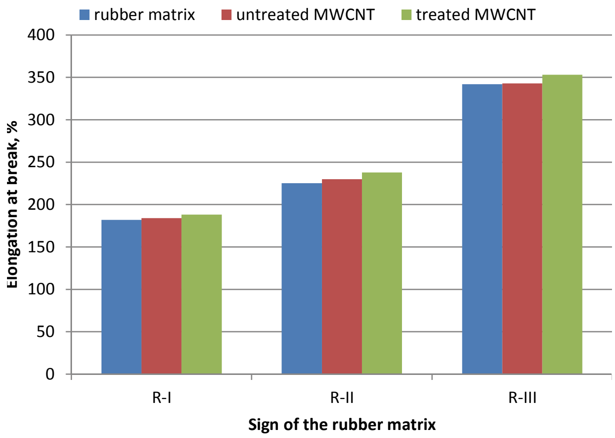

Figure 5: Effects of type of the rubber matrix on elongation at break for fatigue tensile tests (fatigue conditions: 100 cycles and 10 N, 1 wt% MWCNT)

Elongation at break did not change if the matrix with the highest elongation was reinforced with MWCNTS either in untreated or in surface treated form.

Regarding to the results for elongation at break after the fatigue tensile tests a more balanced picture could be drawn. Approximately a 20% decrease was measured for R-I and R-II matrices in the elongation at breaks for fatigue tensile testing compared to static tensile testing. But MWCNT containing composites had the same values for elongation at break both for R-I and for R-II based samples even for fatigue tensile tests. There were not any significant effects of the coupling agent on the elongation at break of all the rubber matrices.

3.2. Effect of carbon nanotube concentration

In that chapter changes in tensile strength, tensile modulus and elongation at break of R-III based composites was discussed in function of the concentration of the MWCNT.

Lower tensile strength was measured for R-III matrix after fatigue tensile tests *(Figure 6)*. Regarding to the static tensile strength approximately 1.5 wt% MWCNT was required for a slight increase.

The fatigue tensile results were represented for the same fatigue load (10 N) with two different cycles: 100 and 1500 cycles *(Fig. 6)*. Resistance of the rubber (R-III) deteriorated with the duration of the fatigue test. The same trends were observed for carbon nanotube containing samples either. 2.4 wt% MWCNT was needed to exceed the tensile strength of R-III after long time fatigue stresses. With lower concentration of MWCNTs in the rubber there was no difference among the property at the same fatigue conditions.

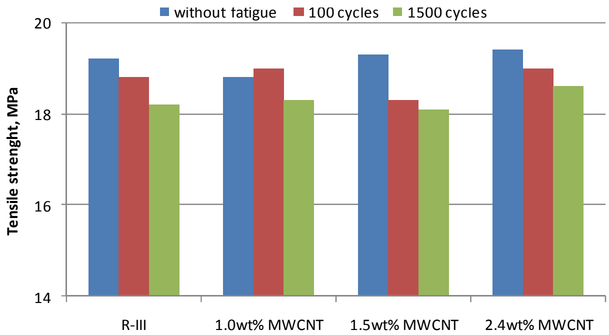

Figure 6: Effects of carbon nanotube concentration on the fatigue tensile strength (fatigue load: 10 N for both 100 cycles and 1500 cycles)

Figure 7 represented the effects of filler concentration on the tensile modulus. On the first hand, values of modulus by the static tensile test increased with the MWCNT content. The modulus of the samples containing 1 wt% MWCNT have been enhanced by 13% related to the reference. The same extent of improvement was measured for the other two MWCNT/rubber composites.

Fig. 7 showed the results for fatigue tensile test either. Depending on the duration of the fatigue tests positive changes were getting lower with increasing MWCNT contents. In that case moduli for the fatigue conditions were compared to the results of the simple tensile test. All the reinforced samples performed higher tensile modulus than that of the rubber matrix, so toughness of the composites enhanced by incorporation of MWCNTs. The modulus of the sample with 2.4 wt% MWCNT depended the less on the duration of fatigue stresses. That phenomenon could be related to orientation of the MWCNTs into the direction of the periodic stresses based on previous experiments with carbon fibres.

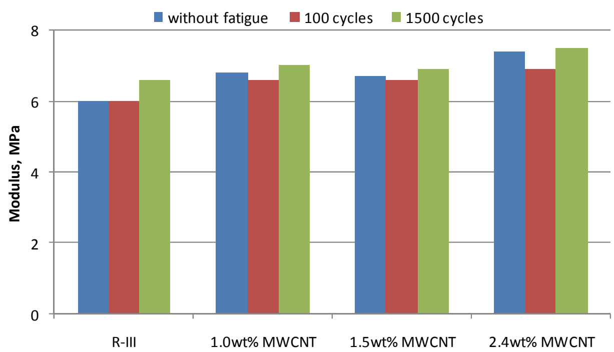

Figure 7: Effects of carbon nanotube concentration on fatigue tensile modulus (fatigue load 10N)

Figure 8 reperesented changes in the elongation at break in the function of the MWCNT content. Elasticity of the samples had been expected to decrease with the MWCNT content. Thus, a reduction in elongation at break was observed above 1 wt% MWCNTs in the rubber. Not a significant change was calculated for 1 wt% MWCNT/rubber samples. Samples containing 2.4 wt% MWCNT had a value of 300% for elongation at break meanwhile the same property was 345% for the basic rubber.

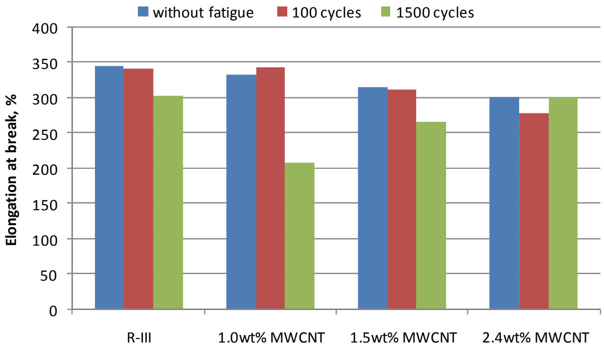

Figure 8: Effects of carbon nanotube concentration on fatigue elongation at break (fatigue load 10 N)

3.3. Effect of surface treatment

In that part of the paper effects of surface treatment were discussed on tensile and fatigue tensile properties. In Figures either results of the unreinforced rubber matrix with composition R-III or results of the composites containing 2.44 wt% MWCNT reinforcement were demonstrated. During the fatigue tensile tests a fatigue force of 10 N was applied with different duration times (100 and 1500 cycles).

Figure 9 represented the effects of untreated and coupling agent treated MWCNTs on tensile strength and fatigue tensile strength of the unfilled rubber. Changes for simple tensile test could be not significant both for untreated and treated MWCNT/rubber samples containing the same concentration of MWCNT. Change was calculated to be below 5%.

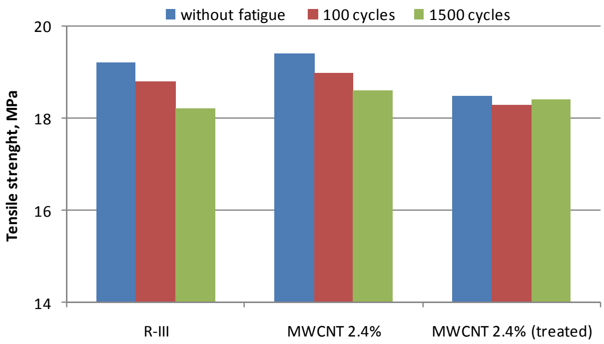

Figure 9: Effects of surface treatment on fatigue tensile properties (fatigue load: 10 N)

The same trend was observed for the fatigue tensile tests. As *Fig. 9* clearly showed, values of fatigue tensile strength slightly decreased for the rubber matrix and the pristine MWCNT/rubber composites with the increasing number of fatigue cycles. However, the composite containing surface treated MWCNTs afforded more balanced performance even for a long period of fatigue stress (1500 cycles) in the given range of concentration and the coupling agent has a higher stabilizing effect in the composite.

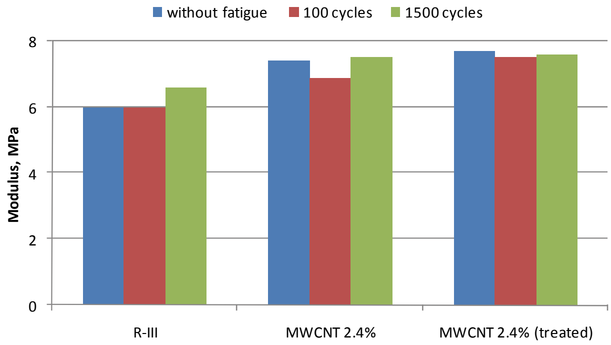

Figure 10: Effects of surface treatment on fatigue tensile properties of the composites (fatigue load: 10 N)

In *Figure 10* the effects of the surface treated MWCNTs were demonstrated on the tensile moduli in function of number of fatigue cycles. Due to application of MWCNTs in the rubber matrix the values of modulus enhanced compared to the rubber since the aforementioned reinforcing material can increase toughness of plastics, elastomers and rubbers.

Resistance against fatigue stresses were also showed in *Fig. 10*. The values of modulus have been increased both for untreated and treated MWCNT containing samples compared to the initial rubber matrix independently from duration of the fatigue stress. Almost the same moduli were determined for both MWCNT/rubber composites at the same level of fatigue conditions. Surface treatment was concluded not to have significant effects on tensile modulus but more balanced behaviour was experienced for treated MWCNT/rubber samples.

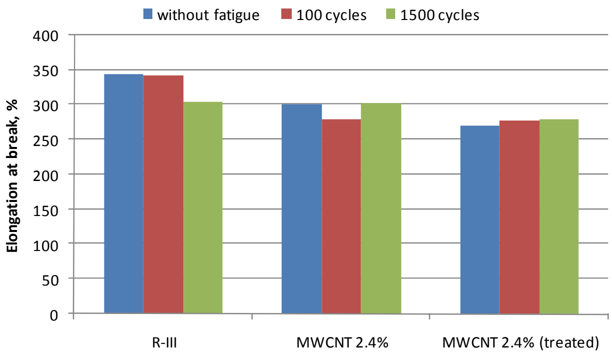

Figure 11: Effects of surface treatment on fatigue tensile properties of the composites (fatigue load: 10 N)

Figure 11 demonstrated the effects of both forms of MWCNTs on the elongation at break for distinct fatigue duration. Values of elongation at break for MWCNT/rubber composites were measured to be below the value of the rubber matrix. The trends were the same both for simple and for fatigue tensile tests.

Results were observed to be more balanced for coupling agent treated MWCNT reinforced rubber in that point of view too. Although elongation at break for the original rubber matrix was the highest among all the samples regarding the tensile test but after a longer fatigue tensile test significant (13%) deterioration was obtained and the value of the treated MWCNT/rubber was less sensitive against fatigue stresses.

3.4. SEM

Homogeneity of the samples based on R-I rubber was studied on the SEM graphs of the broken surface of the composites *(Figure 12–14)*.

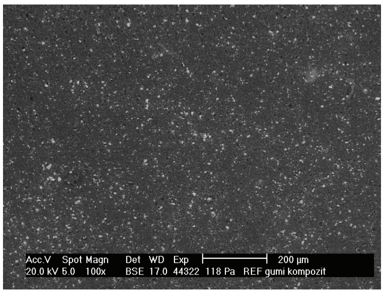

Figure 12: SEM graph of the broken surface of the original rubber matrix

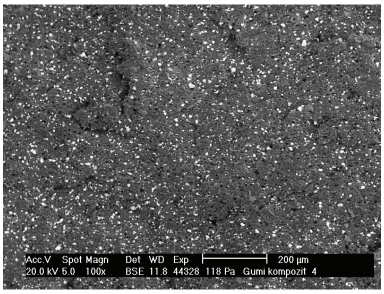

Figure 13: SEM graph of the broken surface of the pristine CNT containing rubber composite

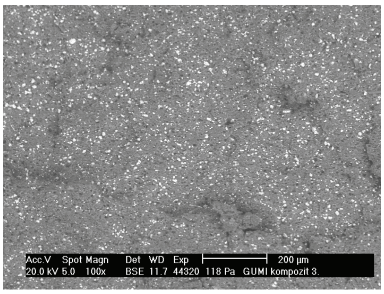

Figure 14: SEM graph of the broken surface of the coupling agent treated CNT containing rubber composite

Components of the rubber formula were clearly remarked (white spots) on SEM graph of all the samples. Difference was observed between the carbon nanotube containing samples. Composites with untreated CNTs showed a less smooth surface after tensile test than samples with surface treated reinforcements. Narrower and more homogeneous particle size distribution was experienced on the surface of coupling agent treated carbon nanotube/rubber samples indicating higher degree of compatibility of the components which could probably result the improvement of the mechanical properties.

Conclusion

Our research has been directed to the application of MWCNT in rubbers in which effects of an olefin-maleic-anhydride based coupling agent was also studied. The results were summarized as follows:

- Application of carbon nanotubes in a rubber matrix could both enhance and deteriorate the mechanical properties of the composites depending on the types and strength of the original rubber mixture.
- Difference in the behaviour in MWCNT containing composites could be experienced during the fatigue tensile test, which could be important especially for rubber products.
- At least 2.4 wt% MWCNT was required to achieve better performance during long time fatigue than the rubber matrix with the highest tensile strength (R-III).

Acknowledgement

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