Characterization of Elastomer Nanocomposite Blends Based on NR/EPDM/Organoclay

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Elastomer nanocomposites based on NR/EPDM/organoclay were prepared by two-roll mill to investigate the effect of different percentages of nanoclay (0, 1, 3, 5 & 7 Wt%) and different matrix compositions (100/0, 75/25, 50/50, 25/75 & 0/100) on the microstructure, mechanical properties and best applicability of the mathematical models. Results of X-ray diffraction showed that enlargement of the silicate layers, penetration of polymer chains into layers and formation of an intercalated and exfoliated structure which was confirmed by TEM analysis. Mechanical properties as well as heat build up of the samples improved by addition of nanoclay. Addition the compounds with EPDM leads to an increase in compression strength, modulus and compressin set and decrease in tensile and tear strength. The prepared samples receive more aging resistance by addition of more clay and EPDM.

Keywords: Organomodified Nanoclay, Microstructure, Mechanical Properties, Aging Resistance

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1. INTRODUCTION

The blending of two rubbers is a useful method to improve certain properties, which are not inherent in a single rubber. The properties of any blend are functions of the adhesion between the components. While most of the blends are thermodynamically incompatible, many have been found to have technological importance [1]. Natural rubber (NR) can exhibit crystallization when stretched. Stress-induced crystallization can be used to increase modulus and resistance to deformation, preventing the propagation of defects. However, ethylene propylene diene monomer (EPDM) rubber has saturated hydrocarbon backbones, which impart usually good weathering oxidation and chemical resistance [2, 3]. The blending of EPDM with NR and other diene rubbers has given rise to compounds with good ozone and chemical resistance and reduced compression set [4]. More recently, polymers containing dispersion of nanometer size (1 – 100 nm) particles have been studied [4-9]. Among the different nanoparticles, clay has attracted significant attention because it provides two distinct opportunities of processing polymer nanocomposites through intercalation and exfoliation. In an intercalated nanocomposite, the polymer penetrates between the galleries of the clay layers, whereas in exfoliation, the clay layers are completely delaminated and dispersed individually in the polymer matrix. A number of studies have proven that polymer nanocomposites exhibit increase in strength, modulus, flame retardancy and heat distortion temperature that are not possessed by the individual phases or conventional composites containing micrometer size particles or fibers. The aim of this study is to evaluate the properties of NR/EPDM nanocompounds prepared with an organo-modified montmorillonite.

2. EXPERIMENTAL

2.1 Material

NR, EPDM, nanoclay and cure ingredients were supplied by Malaysia, Korea, Southern clay company (U.S.A) and Bayer Co, respectively. Samples were prepared by two-roll mill at temperature of 25°C and the rotor speed of 70 rpm for 10 min. Curing agents (Zinc Oxide, Sulfur, Stearic Acid, MBTS and TBBS) were mixed with compound on two-roll mill (Polymix-200L) , too.

2.2 Samples Preparation

Nanocomposite samples, were prepared by a 2 Kg Polymix 200 L two-roll mill for 15 min at room temperature, according to the compositions summarized in Table 2

3. CHARACTERIZATION

X-ray diffraction patterns of the samples were recorded on a Philips model X'Pert (50 kV, 40 mA) by using Cu-Kα radiation (λ = 1.540598 Å) with a scanning rate 2°/min at room temperature. The basal spacing of silicates was estimated from the position of the plane peak in the WAXD intensity profile using the Bragg's law, $d = \lambda / (2\sin\theta_{max})$. The nanostructure of the clay was observed by a transmission electron microscopy (TEM) (JEM-2100F, JEOL) of cryogenically microtomed (with a diamond knife at -100°C) fracture surface of the samples with a voltage accelerator of 200 kV. Tensile strength and compression strength of samples were carried out according to ASTM D 412 and ISO 7743 respectively, by a Hiwa machine (Iran). For Accelerated Thermal Aging Test, the rubber samples were subjected to accelerated thermal aging in an air circulated oven at 90 °C for periods of 96hr according to ASTM D573-88. Compression Set results for a material are expressed as percentage. The specimens are compressed by 50% at 100 °C for 24 hr. The heat build up of each sample was measured on a Goodrich flexometer at 35 Hz again under standard ISO conditions. The heat index was measured as the ratio between the Goodrich HBU and the hardness IRHD.

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4. RESULTS AND DISCUSSION

Fig. 1-a shows the XRD patterns of NR75/EPDM25/clay nanocomposite samples. The inter-layer spacing of the original Cloisite 15A is ($2\theta = 2.9$; $d_{001} = 31.5$Å). Shift of the organoclay diffraction peak to lower 2θ values indicated that elastomer chains inter-calated between consequent silicate layers. This clearly indicates that inter lamellar spacing of the clay are enlarged after melt compounding. As expected intensity increases with an increase in nanoclay.
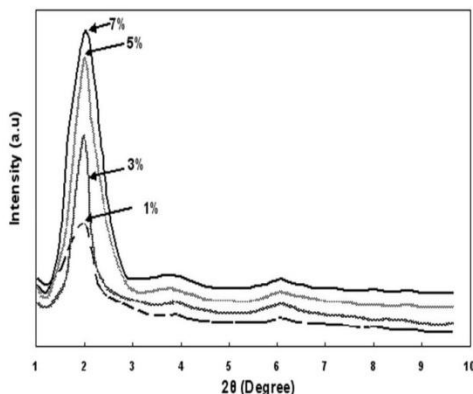

Fig. 1 – XRD Results of the NR75/EPDM25 with 1, 3, 5 & 7 Wt% of Nanoclay

Table 1 – Samples Composition

Sample Code	NR	EPDM	Nanoclay
$N_{75}E_{25}C_0$	75	25	0
$N_{75}E_{25}C_1$	75	25	1
$N_{75}E_{25}C_3$	75	25	3
$N_{75}E_{25}C_5$	75	25	5
$N_{75}E_{25}C_7$	75	25	7
$N_{100}E_0C_3$	100	0	3
$N_{50}E_{50}C_3$	50	50	3
$N_{25}E_{75}C_3$	25	75	3
$N_0E_{100}C_3$	0	100	3

Fig. 2 shows the TEM images of cryogenically fractured surfaces of 75NR/25EPDM/3Clay samples in which dark lines represent the Cloisite layers dispersed within the matrix. Light regions represent the phase with lower density (EPDM) and darker regions are representatives of the denser phase (NR). The TEM image of the nanocomposite sample show that the te obtained structure is the partially exfoliated as well as intercalated, as confirmed by XRD results.

Compression set evaluates the ability of the rubber to deform to its original thickness after prolonged compressive stresses at a fixed temperature and deflection. When a rubber material is compressed periodically, its ability to return to its original thickness will be losed. The results of the compression set for the NR/EPDM (75/25) samples containing 1, 3, 5 & 7 Wt% nanoclay and different compositions of NR/EPDM containing 3Wt% nanoclay are shown in table 2. Inserting the

organoclay in the rubber matrix greatly reduces the deformation sustained by the elastomer (see table 2). Therefore addition of nanoclay in the current study with resultant reduced compression set indicates such effects reported by previous researchers. Furthermore table 2 shows the results of compression set of different compositions of NR/EPDM containing 3Wt% nanoclay. As seen the compression set decreases as the EPDM content increases in the blend.
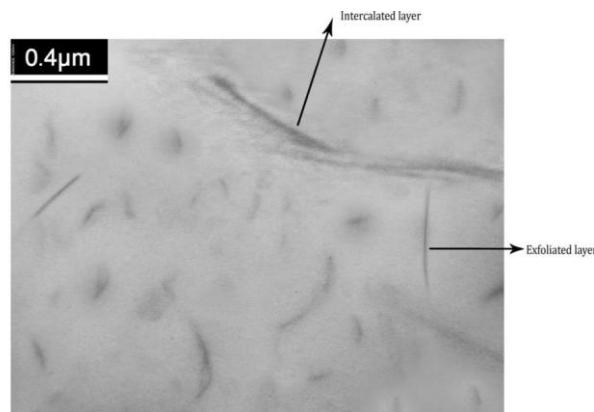

Fig. 2 – TEM image of the NR75/EPDM25/Nanoclay3

Table 2 – Compression set of the Nanocomposite

Sample Code	Compression Set(%)	Sample Code	Compression Set(%)
$N_{75}E_{25}C_0$	27/5	$N_{100}E_0C_3$	20/1
$N_{75}E_{25}C_1$	24/3	$N_{50}E_{50}C_3$	16/67
$N_{75}E_{25}C_3$	19/54	$N_{25}E_{75}C_3$	12/34
$N_{75}E_{25}C_5$	13/4	$N_0E_{100}C_3$	7/35
$N_{75}E_{25}C_7$	9/87		

In order to use a complete investigation into nano-composite samples we have used the classic test of the Goodrich flexometer and the temperature increase was then divided by the hardness of the sample to have a heat index (see table 3). It can be observed that the heat build up decreases by adding the nanoclay. Thus, the nanoclay offers also the beneficial effect of being able to reduce the hysteresis of a rubber compound.

Table 4 lists the mechanical properties of NR/EPDM and their composites before and after heat aging in air. As seen in Table 3 4, tensile and tensile modulus as well as tear strength of samples are improved by clay loading. The improvements of mechanical strength in case of polymer-clay nanocomposites were given by some researchers [4, 7-9].

On the other hand, the mechanical properties of NR rich vulcanizates decreased dramatically after the aging time. However, EPDM rich vulcanizates possessed thermally stable mechanical strength. The

Table 3 – Heat Build up and Heat Index of the Nanocomposite Samples

SAMPLE CODE	Tensile Strength	Tear Strength	Modulus 100%
Dimensions	MPa	MPa	MPa
Before aging			
S_0	1.403	18.1	0.90
S_1	5.3	19.64	1.07
S_2	8.247	21.1	1.09
S_3	10.12	22.8	1.14
S_4	10.795	24.75	1.26
S_5	18.5	28.59	1.09
S_6	4.4	19.3	1.10
S_7	3.89	18.8	1.17
S_8	1.59	16.2	1.20
After aging			
S_0	0.98	12.67	0.63
S_1	3.975	14.74	0.80
S_2	6.43	18.568	0.85
S_3	8.19	18.24	0.91
S_4	9.17	21.03	1.07
S_5	12.395	18.68	0.7
S_6	3.82	16.598	0.95
S_7	3.42	16.92	1.05
S_8	1.43	14.74	1.1

NR rich blends were affected more by the aging time

than the EPDM rich blends, as expected. Mechanical properties of NR rich vulcanizates highly decreased with thermal aging. However, EPDM rich vulcanizate showed more thermal stability because of the low diene content of EPDM. Furthermore, addition of nanoclay particles leads to thermal stability of samples. Clay platelets, hindering the thermally caused defects into the polymer bulk would increase the aging resistance of nanocomposites.

5. CONCLUSION

This work was devoted to the NR/EPDM nanocomposites prepared by two-roll mill. Based on the obtained results Experimental results of X-ray diffraction showed expansion of the distance between the silicate layers and transmission electron microscopy (TEM) proved that the silicate layers existed in the form of an intercalated and partially exfoliated layer structure.

In comparison with pure NR/EPDM, mechanical properties of the resulting nanocomposites receive markedly increases by clay loading. The more EPDM content, the more tensile modulus, compression strength, compression set and thermal stability would become.

Table 4 – Mechanical Properties of samples

Sample Code	Heat Build up (°C)	Heat Index (HBU/DURO)
$N_{75} E_{25} C_0$	79	1.26
$N_{75} E_{25} C_1$	75	1/12
$N_{75} E_{25} C_3$	69	1/03
$N_{75} E_{25} C_5$	63	0/56
$N_{75} E_{25} C_7$	56	0/49

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