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THE EFFECTS OF SEPIOLITE LOADINGS ON MECHANICAL, THERMAL, AND MORPHOLOGICAL CHARACTERISTICS OF NATURAL RUBBER/EPOXIDISED NATURAL RUBBER (NR/ENR-25) BLENDS

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ABSTRACT

Sepiolite has been used widely as nanofillers to improve the properties and compatibility of rubber blends, and due to its magnesium silicate hydrates contents, the sepiolite may also function as a thermal stabilizer. These works investigate the effects of sepiolite loadings on curing, mechanical, thermal, and morphological characteristics of natural rubber/epoxidized natural rubber (NR/ENR-25) blends. The blends were made using a two-roll mill technique using standard vulcanization reagents of sulfur and carbon black as the main filler, and their vulcanization characteristics were investigated using the rheometry technique. Furthermore, the thermal, mechanical, and morphological characteristics of the blends were evaluated using thermogravimetry, tensile tests, and electron microscopy, respectively. It was found that an increase in the sepiolite loadings decreased scorch times (t_{s2} and t_{90}), whereas optimum sepiolite loading with higher tensile strength was 3 phr, which lowered down when the sepiolite loading was increased up to 9 phr. The thermogram of blend specimen with 3 phr sepiolite loading also exhibited superior thermal stability, that is, has higher degradation temperature at 5% weight loss. Fracture surface SEM photographs of the blend specimens showed finely distributed sepiolite particles at optimum sepiolite loading 3 phr and exhibited agglomerations when the loadings were increased up to 9 phr.

Keywords: Sepiolite, Natural Rubber, Epoxidized Natural Rubber, Sepiolite Loading, Characterization.
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INTRODUCTION

Natural rubber has long been blended with synthetic and semisynthetic rubbers by previous researchers to improve its specifications as engineering elastomers. Ismail *et. al*[1] demonstrated natural rubber (NR) with epoxidized natural rubber (NR/ENR 25) blending improved its tensile, tear, and swelling properties. Chitosan powder has also been used as filler for NR/ENR 25 blends to improve the biodegradability behaviour of the rubber blends[2]. Poh, *et. al*[3] have blended both rubbers and loaded them with silica and carbon black fillers and studied their cure behaviours, in which those filled with carbon black cured faster due to better interaction and dispersion of carbon black with rubber matrices than those of silica filler. One of the nanofillers used for rubber blends to improve their mechanical properties is sepiolite. This was due to the porous and fibrous solid structure of sepiolite. The physical characteristics of sepiolite include a thickness of 5-10 nm, width of 10-30 nm, and length of 0.2-2 µm. These specifications have increased its aspect ratios also its surface area tremendously by about 300 m^2/g[4].

Improved thermal and flammability properties of sepiolite-filled ethylene-propylene-diene-monomer rubber (EPDM) blends have also been reported that the sepiolite functioned as a thermal insulator and the unburnt sepiolite created a protected barrier on the surface of the burning composites.[5] Winya *et. al*[6] also investigated the effectiveness of silica and sepiolite clay as fillers in NR/EPDM, focusing on both reinforcing efficiency and thermal stability.

Zhan *et. al*[7] reported that silica particles aggregated on the surface of burning Sepiolite/linear low-density polyethylene (SEP-LLDPE), reducing heat and gas release rates. Montmorillonite and sepiolite have been used as fillers in biomedical nanocomposites to increase the efficiency of drug distribution.[8] These works

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investigate the effects of sepiolite loadings on mechanical, thermal, and morphological properties of NR/ENR-25 blends, to improve specifications of the rubber blends for engineering elastomers.

EXPERIMENTAL

Material and Methods

The materials utilized were epoxidized natural rubber (ENR-25), natural rubber (NR), Guthrie (M) Sdn Bhd, and sepiolite (Hebei DFL Minmet Refractories Corp., China). Whereas: *N*-cyclohexyl-2-Benzothiazyl Sulfenamide (CBS), zinc oxide, carbon black N330, stearic acid, sulfur, *N*-isopropyl-*N*'-phenyl-*p*-phenylenediamine (IPPD) were all ex. Anchor Chemical Co (M) Ltd.

General Procedure

To remove the remaining water content in the sepiolite, the water content reduction was carried out in an oven (24 hours at 80°C) before mixing. NR/ENR 25 mix ratio of 50/50 and the synthesis of compounds are given in Table-1. The mixing procedure was done with a two-roll mill (model XK-160).

Table-1: NR/ENR 25 Blends with Varying Sepiolite Loads

Content	Content (phr)
NR 25	50
NR L	50
Stearic acid	2
Zinc oxide	5
Sulfur	1.5
CBS	1.5
IPPD	2
Carbon Black (N330)	30
Sepiolite	0,1,3,5,7,9

Characterization

The cure properties, including scorch time (t_{s2}), optimal cure time (t_{90}), minimum torque (ML), and maximum torque (MH) were examined at 150ºC using a Monsanto Moving Die Rheometer (MDR 2000) using approximately 4 g of the individual compounds according to ASTM 2084. The sample was compressed into 2 mm rectangular sheets at 150ºC using a hot press machine based on cure time (t_{90}) values. Dumbbell-shaped specimens were punched using an ASTM Die-C cutter. Tensile strength (TS), elongation at break (EB), and modulus at 100% (M_{100}) and 300% (M_{300}) elongations were determined using an Instron 3366 universal testing equipment, in compliance with ASTM D412-92 standards.[9,10] The crosshead speed of 500 mm/min using a load cell weighing 10 kN occurred. A Perkin Elmer Pyris 6 thermogravimetric analyzer was used for thermal analysis. Ten mg of samples have been heated from 30 to 600 ºC at a ramp rate of 20 ºC/min, under a nitrogen flow of 50 mL/min. The investigation involved monitoring weight loss as a function of temperature. Tensile fracture surfaces of NR/ENR 25 filled with sepiolite were studied using scanning electron microscopy (FESEM) type Zeiss Supra 35-VP, Germany. The sample was covered (a thin layer of gold-palladium) to eliminate electrostatic charges created during examinations.[11, 12]

RESULTS AND DISCUSSION

Preparations and Characteristics of Curing NR/ENR Filled with Sepiolite

Results of the cure characteristics investigation of NR/ENR-25 samples are shown in Table-2. It was revealed that the loading of sepiolite decreased both cure times (t_{s2} and t_{90} with increased minimum and maximum torques ML and MH. These were related to the presence of sepiolite decreasing the molecular distance of the rubber chains, which then sped up vulcanization processes (decreased the values of cure times). It was also possible that the presence of sepiolite promoted further chain scissions, and hence crosslinking reactions, of the rubber molecules during blending in two roll mills and the curing process in the rheometer. Whereas, metal contents in sepiolite nanofiller may function as an accelerator for the vulcanization reactions. Evidence of the crosslinking (vulcanization) reactions was also revealed by increased minimum and maximum torques during curing processes in the rheometer.

Mechanical Properties of NR/ENR-25 Blends at Various Sepiolite Loading

The results of mechanical tests of the blends are shown in Table-3.

Tabel-2: Results of Cure Characteristics Measurements of NR/ENR-25 Blends using Rheometer

Sepiolite (phr)	t_{s2} (min)	t_{90} (min)	ML (dNm)	MH (dNm)	Δ (dNm)
0	2.68	5.40	0.25	10.08	9.83
1	2.44	5.06	0.37	11.49	11.12
3	2.34	4.61	0.46	11.4	10.94
5	2.28	4.56	0.5	11.81	11.31
7	2.18	4.47	0.51	13.28	12.77
9	2.15	4.22	0.54	13.81	13.27

Tabel-3: Tensile Results of NR/ENR 25 Blends, Loading of Sepiolite (phr)

Sepiolite Loading (phr)	TS (MPa)	EB (%)	M_{100} (MPa)	M_{300} (MPa)
0	19.29	572	1.89	6.55
1	22.65	641	1.95	6.95
3	24.88	744	2.03	7.32
5	23.35	676	2.16	7.6
7	21.28	606	2.52	8.72
9	20.56	595	2.67	9.13

From the above results, it was clear that the optimum tensile strength of the blends was found when the sepiolite loading was 3 phr, (tensile strength increase 19.29-24.88 MPa, increases elongation 572-744%). This was due to the presence of sepiolite-filled spaces between the elastomer molecules, which then increased compatibility and adhesion between the rubber matrix phases. Therefore, when the sepiolite loading was increased further, up to 9 phr, excess of the sepiolite was saturated and formed agglomerations, which then decreased adhesion and tensile strength as well as elongation of the rubber blends, to 20.56 MPa and 595%, respectively. On the other hand, both Modulus 100 and Modulus 300 of the rubber blends steadily increased, since a decrease in elongation was higher than the decrease of tensile strength, (1.89-2.67 MPa and 6.55-9.13 MPa, respectively at sepiolite loading 9 phr).

Thermal Characteristics of Sepiolite-filled NR/ENR-25 Blends

Results of the thermogravimetric analysis are shown in Table-4 and Fig.-1.

Table-4: Thermogravimetric Analysis (TGA) Data of NR/ENR-25 Blends Containing Various Loading of Sepiolite

NR/ENR 25 - Loading Sepiolite (phr)	Temp at 5% weight loss, ^{O}C	% Weight loss retention at					
		110^{O}C	200^{O}C	300^{O}C	400^{O}C	500^{O}C	600^{O}C
0	333.88	100	99.42	97.5	80.1	25.34	24.62
3	353.19	100	99.37	97.3	77.1	27.36	25.68
7	345.34	100	99.33	96.7	76.9	28.3	27.42
9	339.51	99.88	98.96	96.5	74.8	32.3	31.9

From the above data, the temperature for 5% weight lost (T5%) of the heated blend samples was the highest when the sepiolite loading was 3 phr, (T5% increase: 333.88°-353.19°C), which represented the highest adhesion between the rubber matrices with the sepiolite nanofillers. In other words, at 3 phr sepiolite loading, the rubber blend started to decompose slower due to its higher thermal stability. However, using a similar reason to that of mechanical properties investigations, when the loading of sepiolite was increased up to 9 phr, the excess of sepiolites were saturated, formed agglomerations, and decreased adhesions in the rubber blends, which in turn decreased the 5% weight lost temperature to 339.51°C. On the other hand, at the end of the decomposition processes when the temperatures reached 600°C, it was shown that the weight of residues (weight retentions) of the rubber blends was increased, which corresponded to the sepiolite loadings (24.62 - 31.9%, at 600°C), due to that the sepiolites did not undergo decompositions.

Morphology Investigations of Surface Fracture of Sepiolite-filled NR/ENR-25 Blends

Morphology investigations of surface fracture of the rubber blend specimens were carried out using SEM. The SEM photographs of the rubber blends are shown in Fig.-2a and 2d. It was shown that the control surface (Fig.-2a) exhibited rough phase boundaries due to lower adhesion and compatibility in the

NR/ENR-25 blend. When the sepiolite was introduced in the rubber blends at 3 phr, the SEM photograph (Fig.-2b) exhibited smooth surface fracture due to improved adhesion and compatibility in the rubber blend.

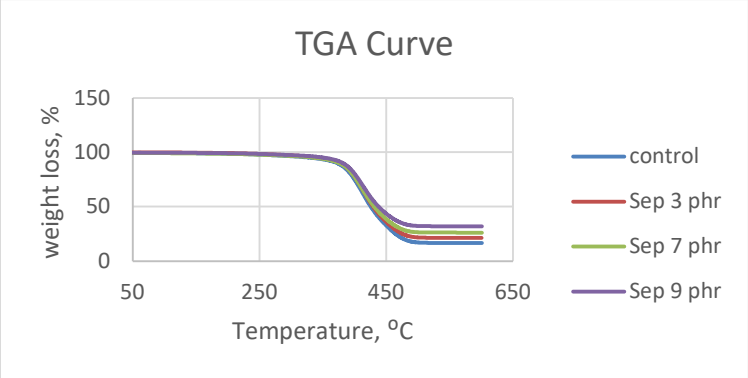

Fig.-1: TGA Thermograms of NR/ENR-25 Blends Containing Various Loading of Sepiolite

Further increase of the sepiolite loadings at 7 phr and 9 phr, the corresponding SEM photographs (Fig.-2c and 2d) showed agglomeration of the sepiolite fillers. These morphology investigation results clarified and supported results of cured characteristics, tensile and thermal properties of the elastomer blends at optimum sepiolite loading at 3 phr.

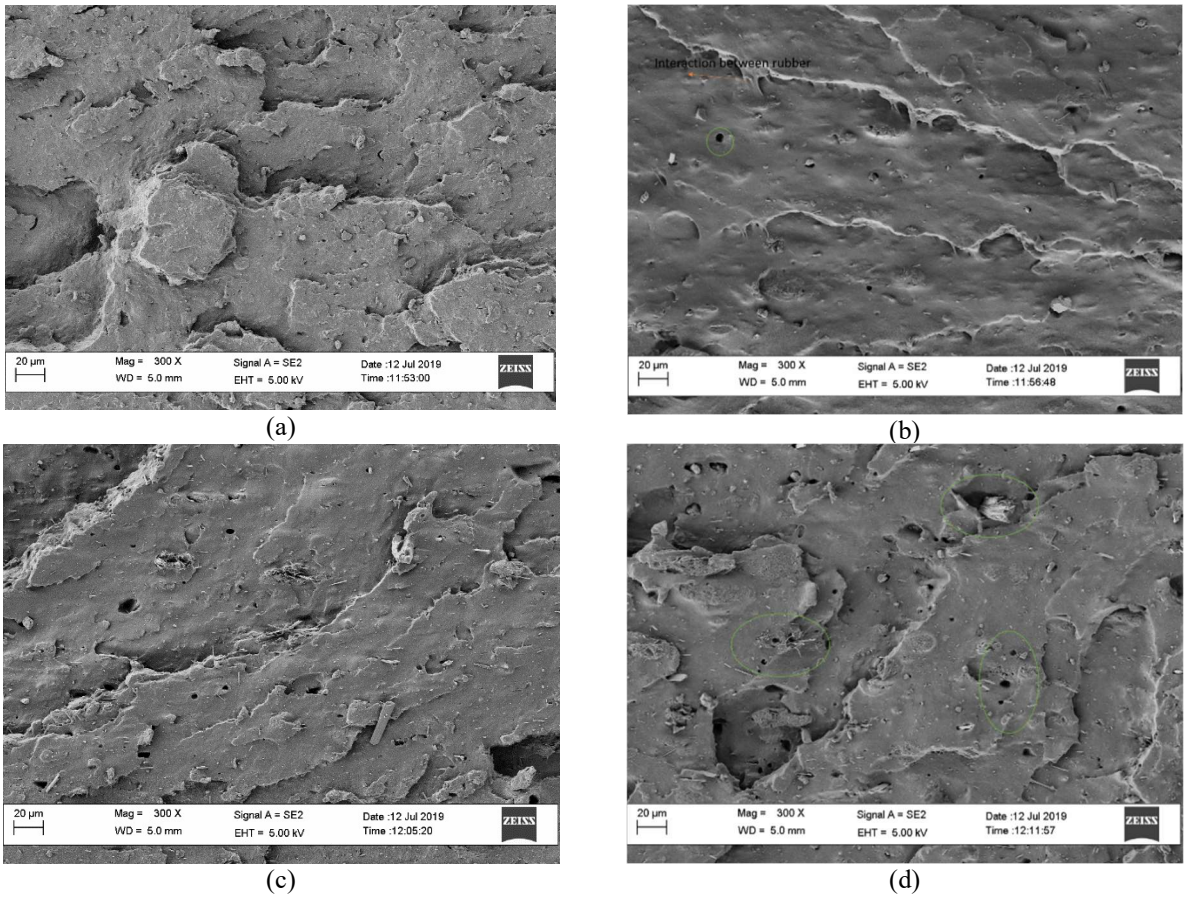

Fig.-2: SEM Photographs (magnification 300 times) of Surface Fracture of NR/ENR-25 Blend Specimens at Various Sepiolite Loading: Control Without Sepiolite (a), and Sepiolite Contents: 3 phr (b), 7 phr (c), 9 phr (d)

CONCLUSION

The presence of sepiolite decreased both cure times (ts2 and t90) and increased both maximum and minimum torques ML and MH. Optimum tensile strength of the blends was found when the sepiolite

loading was 3 phr, (tensile strength increase 19.29-24.88 MPa, increases elongation 572-744%). Temperature for 5% weight lost (T5%) of the heated blend samples was highest when the sepiolite loading was 3 phr, (T5% increase: 333.88º-353.19ºC). When the sepiolite was introduced in the rubber blends at 3 phr, the SEM photograph exhibited smooth surface fracture due to improved adhesion and compatibility in the rubber blend.

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CONFLICT OF INTERESTS

The authors state that there is no conflict of interest.

AUTHOR CONTRIBUTIONS

All the authors contributed significantly to this manuscript, participated in reviewing/editing and approved the final draft for publication. The research profile of the authors can be verified from their ORCID ids, given below:

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