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A METHOD FOR IMPLEMENTING THE MECHANICAL PROPERTIES OF MALEIC ANHYDRIDE DERIVATE GRAFTED NATURAL RUBBER-CLAY NANOCOMPOSITE VULCANIZATE PREPARED FROM ACID FREE CO-COAGULATION TECHNIQUE

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ABSTRACT: Two types of nanocomposite vulcanizates, Nanocomposite A and Nanocomposite B, were successfully prepared from maleic anhydride derivative-grafted natural rubber latex (NRL). Bis(triethoxysilylpropyl) tetrasulfide (TESPT) grafted organoclay (OMMT-S) was incorporated at loadings of 2 and 5 phr. The coagulation of the rubber-clay mixture in an acid-free environment was expedited by employing two gelling agents: sodium dodecyl sulfate (NADS) and cetyl trimethyl ammonium bromide (CTAB). In comparison to the vulcanized control sample of un-modified un-filled NR prepared by the conventional method (Control-A), the addition of 5 phr OMMT-S to vulcanized grafted NR (B-5) resulted in a notable improvement in mechanical properties. Specifically, B-5 demonstrated an increase in tensile strength by 167%, a rise in modulus at 300% by 56%, and elongation at break enhancement by 36%.

Keywords: clay nanocomposite, natural rubber, NR grafting, rubber-filler interactions

1. INTRODUCTION

The co-coagulation method in absence of a co-coagulating agent like acid would be an alternative method to prepare NR-clay nanocomposites with retention of exfoliated clay structures during the destabilization of both clay and rubber which was also practiced in previous studies (Jayaraj et al., 2017; Jayaraj et al., 2018). In this method, destabilization would occur during oven drying, and therefore only water will be removed by evaporation without removing non-rubber substances. The speed up of co-coagulation is also vital to uniform dispersion of clay in rubber but it is difficult to obtain by traditional evaporation method. Use of organoclay by modification of Montmorillonite clay (MMT) with a long-chain cationic surfactant would facilitate further retention of exfoliated clay structures in the rubber phase and better tensile strength and elongation at break were obtained. Those properties were further improved in another study by grafting Bis(triethoxysilylpropyl) tetrasulfide (TESPT) coupling agent on to organoclay (Perera et al., 2020). However, neither of previous studies exhibited improved modulus at 300% elongation and tear strength, even though other mechanical properties were exhibited as a satisfactory level. Retaining exfoliated clay structures and strong interactions between rubber and clay is necessary to obtain better overall mechanical properties. Maleic Anhydride (MAH) Derivative-Grafted NR is suggested in current study to promote strong interaction with modified nanoclay to enhance mechanical properties.

2. METHODOLOGY

The dry rubber content (DRC) of centrifuged NRL was adjusted to 30% (w/w) with deionized water. Urea 0.1% (w/w), Sodium dodecyl sulfate 1% (w/w) and 0.025% (w/w) each of the solvents (acetone, ethanol, and isopropanol) were then mixed with the diluted NRL at 30 ˚C for 60 min. It was then centrifuged to obtain de-proteinized NRL having a DRC of 60% (w/w) according to the method described in the literature (Wongthong et al., 2013). Maleic Anhydride (MAH) was heated to its melting temperature, and it was mixed with 25 % (w/w) excess ammonia to obtain maleamic acid (MA) under isopropanol medium. It was dried at 50 ˚C for two hours in the oven to eliminate excess ammonia and isopropanol. It was then diluted with distilled water to prepare 12.5 % (w/w) maleamic acid solution. The de-proteinized NRL was stabilized by the addition of 10.0 % (w/w) NADS dispersion and transferred into a 500 ml reactor equipped with a reflux condenser, a mechanical stirrer, and a thermometer. Isopropanol and the MA solution were then added according

to the formulation given in Table 1. The mixture was stirred for 30 min under a nitrogen atmosphere to remove dissolved oxygen. Afterward, the mixture was heated up to 50 ˚C and homogenized dispersion of 10.0 % (w/w) TEPA and Cumene hydroperoxide (ROOR) were added. The mixture was then kept at the same temperature for 2 h to complete the grafting reaction of succinimide (SI) into NRL and is called SI-grafted NRL.

Table 1: Formulation of SI grafted NRL

Ingredient	Loading, in dry weight
60% (w/w) de-proteinized NRL	85 phr
12.5% (w/w) MA solution	15 phr
10% (w/w) NADS dispersion	1.3 phr
Isopropanol	7.6 pph
25% (w/w) TEPA dispersion	0.5 pph
25% (w/w) Cumene hydroperoxide	0.1 pph

Note: phr – parts per hundred parts of rubber; pph = parts per hundred parts of the organic component, which included both rubber content of the centrifuged latex and MA solution.

20 % (w/w) grafted deprotenized prepared NRL according to the Table 1 was blended with 80% (w/w) of centrifuged latex (60% DRC) to obtain the final NRL.

Different NRL-clay mixes and their controls were prepared using the mechanical stirrer operated at a speed of 60 rpm for 24 h, and 1 phr loading of NADS was added to each NR-clay mix and control, and mixing was continued under the same conditions for 15 min. After that, 2 phr loading of CTAB was mixed with each mix for gelling, and the nanocomposites and the controls were prepared by drying the gels in an air circulated oven at 50 ˚C for 48 h, according to the acid free co-coagulation method described in some studies (Jayaraj et al., 2017; Jayaraj et al., 2018; Perera et al., 2020).

Table 2. Formulations of NR-clay mixes and their controls

	Control-A	A-2	A-5	Control-B	B-2	B-5
Ingredient	**Loading (dry basis), phr**					
NRL	100	100	100	-	-	-
SI-grafted NRL	-	-	-	100	100	100
OMMT-S	-	2	5	-	2	5

Tensile properties such as tensile strength, elongation at break and modulus at 300% elongation (mod 300%) were measured using Hounsfield H10KT tensile tester as per ISO 37 and ISO 34-1, respectively.

3. RESULTS AND DISCUSSION

Fig. 1 shows stress-strain curves for the four nanocomposite vulcanizates and its controls. It is intriguing to observe that Control-A exhibits breakage at a lower tensile stress. The presence of assembled structures resulting from the addition of CTAB, NADS, and ZnO may create weak sites that are unable to withstand higher tensile stresses, leading to fractures even at minimal stress levels. This phenomenon is effectively regulated by the incorporation of clay layers and the modification of NR. In essence, the introduction of clay layers and modification prevents the formation of larger assembled structures, thus contributing to the improved strength of the material at higher stress. The

strain-induced crystallization of B-2 and B-5 nanocomposite vulcanizates is greater than that of A-2 and A-5 nanocomposite vulcanizates and may be due to improved rubber filler interactions. The effect is higher for B-5 nanocomposite vulcanizate than B-2 nanocomposite vulcanizate due to reinforcement effect by higher number of clay exfoliation. In general, when strain-induced crystallization is increased, elongation at break is reduced. Most interestingly, B-2 and B-5 nanocomposite vulcanizates claimed an increase of strain-induced crystallization without reduction of elongation at break and is mainly associated with the stronger rubber-clay interactions developed between MAH derivatives grafted NR and OMMT-S. The tensile strength, mod 300%, and elongation-at-break of Control-B vulcanizate are greater than those of Control-A vulcanizate by 150%, 24%, and 16% respectively (Fig. 2). With the addition of 2 phr loading of OMMT-S, B-2 nanocomposite vulcanizate exhibits better mechanical properties; B-5 nanocomposite vulcanizate shows remarkably increased tensile strength (41 MPa), mod 300% (6 MPa), and elongation at break (630%). The slippery action of plasticizers arranged as assemble structures would make it possible for the highly strained molecular chains to relieve the tension caused by stretching; hence, they will not break permanently, resulting in a higher strain at break and strength (Wu et al., 2004).

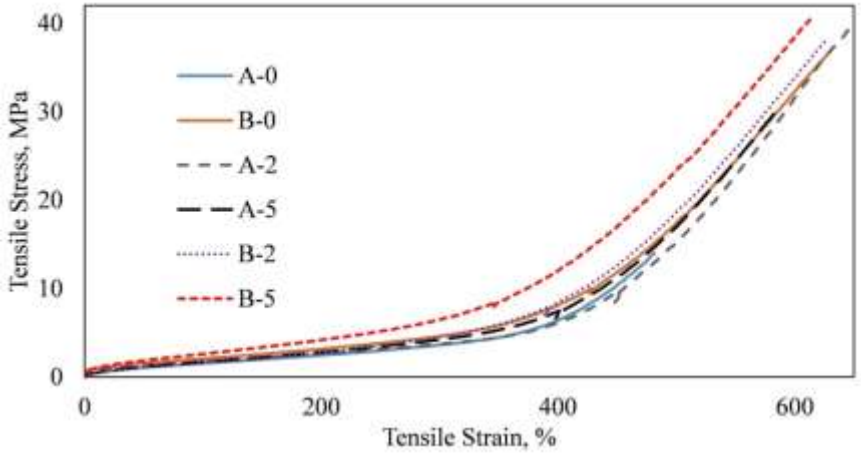

Fig. 1. Stress strain curves of the NR nanoclay composite vulcanizates

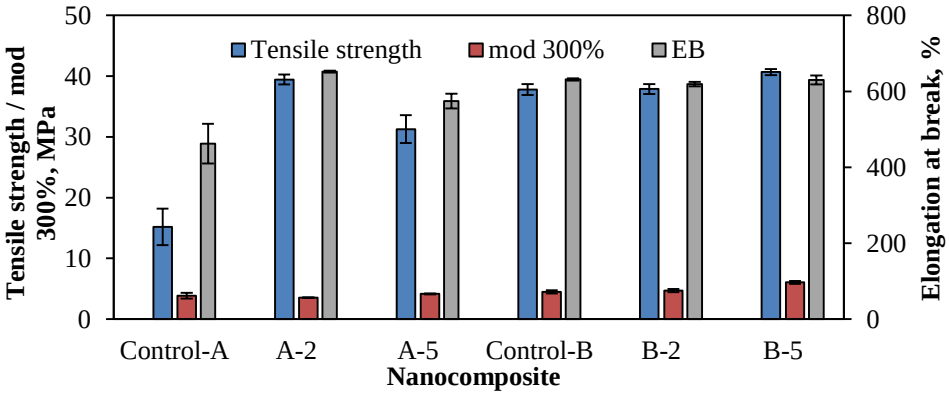

Fig. 2. Tensile properties of the NR nanoclaycomposite /control vulcanizates

4. CONCLUSION

This enhancement in strength is attributed to the improved interactions between maleic anhydride derivative grafted NR and clay, particularly evident at 5 phr of OMMT-S. The remarkable mechanical properties were achieved due to formation of physical crosslinks in acid free co-coagulated environment. The plasticizing effect of surfactant addition is counteracted by the presence of NR-clay interactions.

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