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Reactive Compatibilization of Natural Rubber (NR)/Carboxylated Nitrile Rubber (XNBR) Blends By Maleic Anhydride-Grafted-Polyisoprene (MAPI) And Epoxy Resin Dual Compatibilizers

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ABSTRACT: *Cure characteristics and mechanical properties of reactive compatibilized natural rubber (NR)/carboxylated nitrile rubber (XNBR) blends were studied using maleic anhydride-grafted-polyisoprene (MAPI) and epoxy resin (EPX) dual compatibilizers. The results show that the scorch time and cure time decrease with increasing composition of XNBR in the blend. The presence of MAPI/EPX dual compatibilizers exhibited improvement in processability by decreasing and increasing the cure time and scorch time of the NR/XNBR blends, respectively. Whereas increasing compositions of XNBR brought decreases in tensile strength, tear strength and elongation at break, these properties were found to increase in the presence of MAPI/EPX dual compatibilizers. The results also show that increasing compositions of XNBR and the presence of MAPI/EPX dual compatibilizers resulted in increases in solvent resistance of NR/XNBR blends.*

Keywords: *blends, carboxylated nitrile rubber, natural rubber, reactive compatibilization*

I. Introduction

Natural rubber (NR) is an important elastomer which exhibits excellent mechanical properties, and has been widely used in several areas of engineering and industry. However, due to its non-polar nature and reactive double bonds in the structure, the resistance of NR in oil and aging on exposure to oxygen, ozone and heat is poor.

In order to achieve properties that cannot be obtained by individual polymers, polymer blends are often used to combine the physical characteristics of both polymers. Thus, elastomer blends are frequently used in a wide range of engineering and industrial applications to obtain the best compromise in compound physical properties, processability and cost [1]. However,except for a few polymer pairs that are known to be thermodynamically miscible, most polymer pairs are immiscible.

Immiscible polymer systems display lower mechanical properties than those of their components, due to their unstable morphology and poor adhesion between phases. The desired properties of immiscible polymer systems are not achieved without a third component, i.e., a compatibilizer, which reduces the interfacial tension and enhances the interfacial adhesion between component phases so that applied force can be effectively transmitted between component phases [2, 3].

Over the years, traditional compatibilization strategies have been employed to alleviate the problem of poor interfacial adhesion between polymer phases, which involve the addition of a pre-made block or graft copolymers composed of the blocks or grafts, which are identical with or miscible with the component polymers [4, 5]. A more recent approach which has proved to be generally more effective and less expensive, and more frequently used for industrial applications is the reactive processing or the reactive blending, in which the block or graft copolymer can be generated in-situ at the interface between phases by the coupling reaction of functionalized components [6, 7, 8, 9].

Basically, the performance of elastomer blends is largely governed by various factors which includes the nature of elastomers [10, 11, 12], blend compositions [13], phase morphology of elastomer blends [14], nature of compatibilizer [15, 16] and interfacial cross-linking in elastomer blends [17]. For example, in a study by Kwaruethai et al. [16], zinc salts of sulphonated natural rubber (Zn-SNR)(a rubbery ionomer) containing 17.5meq/100 of SNR was prepared and used as a new compatibilizer for the preparation of NR and chlorosulphonated polyethylene rubber (CSM) blends. Epoxidized natural rubber (ENR-20) was also used as compatibilizer for such blends. They found that the shear viscosity of the blends with ionomers was higher than that of the neat blends, suggesting strong interaction between rubber phases. They also reported a greater level of enhancement in 100% modulus, tensile and tear strength for the blends containing 17.57 Zn-SNR compared to those of ENR-20. Similarly, Sirinha et al. [11] reported improved oil and thermal aging resistance when NR was blended with chlorinated polyethylene rubber.

Blends of NR with carboxylated styrene-butadiene rubber (XSBR) [10] and ethylene-propylene-diene rubber (EPDM) [12] were reported to have better aging and ozone resistance. Sirinha et al. [14] have demonstrated that improved phase morphology in blends of NR and nitrile rubber (NBR) resulted in an increased oil resistant property of the blends. Blends of CSM and NR have been studied by Tanrattanakul and Petchkaew. [18]. They reported that blends of NR and CSM were immiscible, except for NR-rich blends (70-80 wt% of NR), and that oil and ozone resistant properties of the blends increased with increase in CSM loading. They also found that further improvement in mechanical properties and compatibility of the blends could be obtained when a suitable compatibilizer, such as epoxidized natural rubber (ENR), was added to the blends.

Carboxylated nitrile rubber (XNBR) is an important elastomer which has found increasing use in many engineering and industrial applications due to its outstanding oil and solvent resistant properties [13, 17]. In the present study, the reactive compatibilization of NR/XNBR blends by maleic anhydride-grafted-polyisoprene (MAPI) and epoxy resin dual compatibilizers is reported. The presence of a multifunctional epoxy resin in the XNBR-NR-MAPI blend has the potential to produce XNBR-co-epoxy-co-MAPI copolymer at the interface, which is able to function as an effective compatibilizer.

To the author's knowledge, there has been no attempt to use maleic anhydride-grafted-polyisoprene/epoxy resin as compatibilizer for NR/XNBR blends. However, Naskar et al. [13] had reported a novel method for preparation of carboxylated nitrile rubber (XNBR)-natural rubber (NR) blends using Bis(diisopropyl)thiophosphoryl polysulphides as a compatibilizer. They found that oil resistance and mechanical properties of the NR/XNBR blends strongly depended on blend ratios and the degree of interfacial cross-linking between NR and XNBR components.

II. Experimental

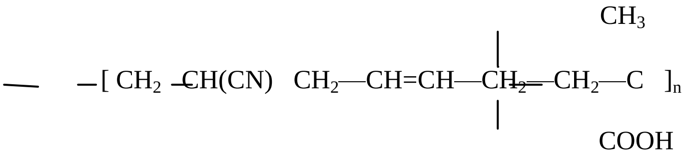
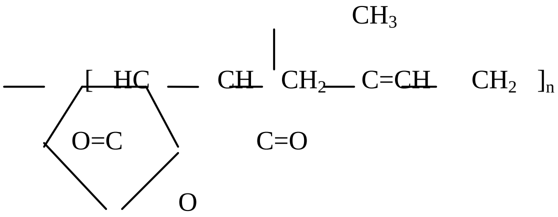
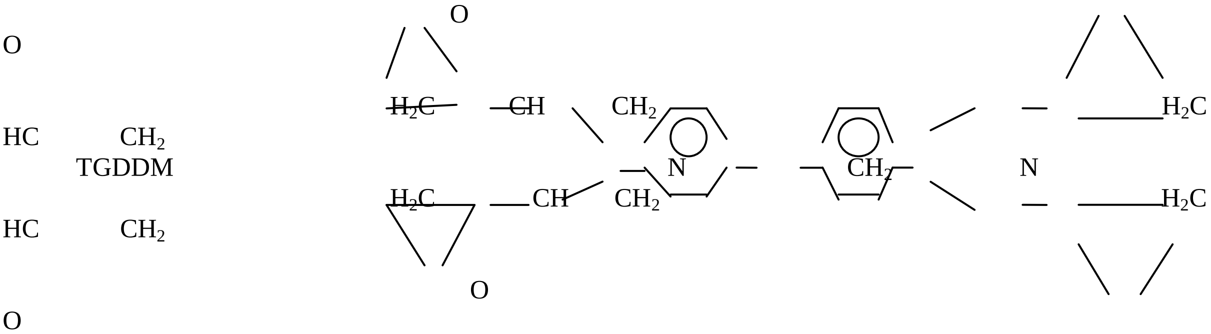
2.1. Materials

Natural rubber (Standard African Rubber, SAR 3) having the properties given in Table 1 was obtained from the Rubber Research Institute of Nigeria (RRIN), Iyanomo, Benin City. The maleic anhydride-grafted-polyisoprene containing 8wt% maleic anhydride (ARCO Chemical Co.); epoxy resin (tetra-glycidylether of diphenyldiaminomethane) (TGDDM), with the trade mark of NPEH-434 (Nan Yea Plastics Co. of Taiwan) and carboxylated nitrile rubber (acrylonitrle-butadiene-methacrylic acid terpolymer) (Dow Chemical Co.) were purchased from Rovet Chemicals Ltd, Benin City, Nigeria. The rubber compounding ingredients such as carbon black (N 330), sulphur, accelerator (MBT), Zinc Oxide, stearic acid, wax and anti-oxidant (TMQ) were of commercial grade and kindly supplied by Dunlop Plc, Lagos, Nigeria. Table 2 represents the repeating units of the polymers employed in this study.

Table 1: Properties of Standard African Rubber (SAR 3) [19]

Parameters	
Volatile matter	0.40
Dirt content retained on 45µm sieve (%)	0.02
Nitrogen (%)	0.23
Ash content (%)	0.32
Initial Plasticity (P^0)	36
Plasticity Retention Index (PRI)	67
Plasticity after aging for 30 min @ 140^0C (P^{30})	24
Mooney Viscosity, ML (1+4), 100^0C	70

Table 2: Repeating **units of each component**

Component	Repeating unit
NR	$—\,—[CH_2\ \ C(CH_3)=CH\ \ CH_2\ ]_n$
XNBR	 $—\,—[CH_2-CH(CN)\ \ CH_2—CH=CH—CH_2—CH_2—\underset{COOH}{\overset{CH_3}{C}}\ ]_n$
MAPI	
TGDDM	

2.2. Preparation of NR/XNBR Blends

The recipe used in the formulation of NR/XNBR is given in Table 3. TGDDM WAS DRIED AT 60^{0}C for 2 hours before using. Mixing was carried out in an internal mixer, Haake Rheomix, Model CTW 1OO. NR and XNBR were first pre-mixed, prior to the addition of other ingredients. Mixing was done at a temperature of 60^{0}C and at a rotor speed of 60 rpm. The total mixing cycle was ~ 10 min. Finally, the blend was sheeted out on a laboratory two-roll mill size (160 x 320 mm) in accordance with ASTM-D 3184-80. The nip gap and mill roll speed ratio were kept the same for all the blend samples. The sheeted rubber compound was conditioned at room temperature, 27^{0}C for 24 hours in a closed container and was further processed by curing. The cured samples were coded accordingly for property testing.

Table 3: Compounding recipe for NR/XNBR blends

Ingredients (Phr)	Formulation		
NR$^{\alpha}$	80	50	20
XNBR$^{\beta}$	20	50	80
Stearic acid	2	2	2
Zinc Oxide	5	5	5
TMQ	1	1	1
MBT	1	1	1
Sulphur	2	2	2
Processing aid	2	2	2
MAPI^{a}	3.5	3.5	3.5
EPX$^{\#}$	1.5	1.5	1.5

[a] Maleic anhydride-graft-polyisoprene
[#] Epoxy resin
[α] Natural rubber
[β] Carboxylated nitrile rubber

2.3. Measurement of Cure Characteristics

The cure characteristics of the blends, such as scorch times (t_2), cure times (t_{90}) and torque values (ML) were measured at 150^{0}C using a Monsanto Moving Die Rheometer (MDR 2000 Model) as described in ASTM Standard Test Method D 1646-94.

2.4. Measurement of Mechanical Properties

The tensile properties and tear strength of the blends were measured on a Monsanto Tensometer (Model T10), according to BS 903. The cross-head speed for the tensile and tear tests was set at 500 mm/min. All tests were performed at room temperature, 27^{0}C.

2.5. Measurement of Solvent Resistance

Toluene, a solvent commonly used in the rubber industry was chosen in this study. The test for solvent resistance of the blend was conducted according to ASTM D 471. The tensile and tear test specimens were immersed in toluene at room temperature, 27^{0}C for 20, 60, and 160 hours. When the specific time was reached, the test specimens were removed from the toluene, wiped with tissue paper to remove excess toluene from the surface and tested for tensile properties and tear strength.

III. Results and Discussion

3.1. Cure Characteristics of NR/XNBR Blends

A compound or a copolymer containing reactive functional groups that are able to react with one or more of the blend components to form a new graft or block copolymer in the blend is referred to as a reactive compatibilizer. This in-situ formed copolymer containing segments of the blend constituents tends to remain at the interface between the two incompatible polymers and acts as a phase emulsifier of the blend. The viscosity of the blend will increase when reactions occur among functional groups due to increase in molecular weight of the blend. Torque measurement has proved successful as a method for obtaining qualitative information concerning the chemical reactivity and the extent of reaction in a reactively compatibilized blend [3, 20].

Fig. 1 shows the effect of compatibilizer and blend ratio on maximum torque (MT) value of the NR/XNBR blends. Hanafi and Hairunezam {15] reported that maximum torque generally correlates with durometer hardness and/or modulus.

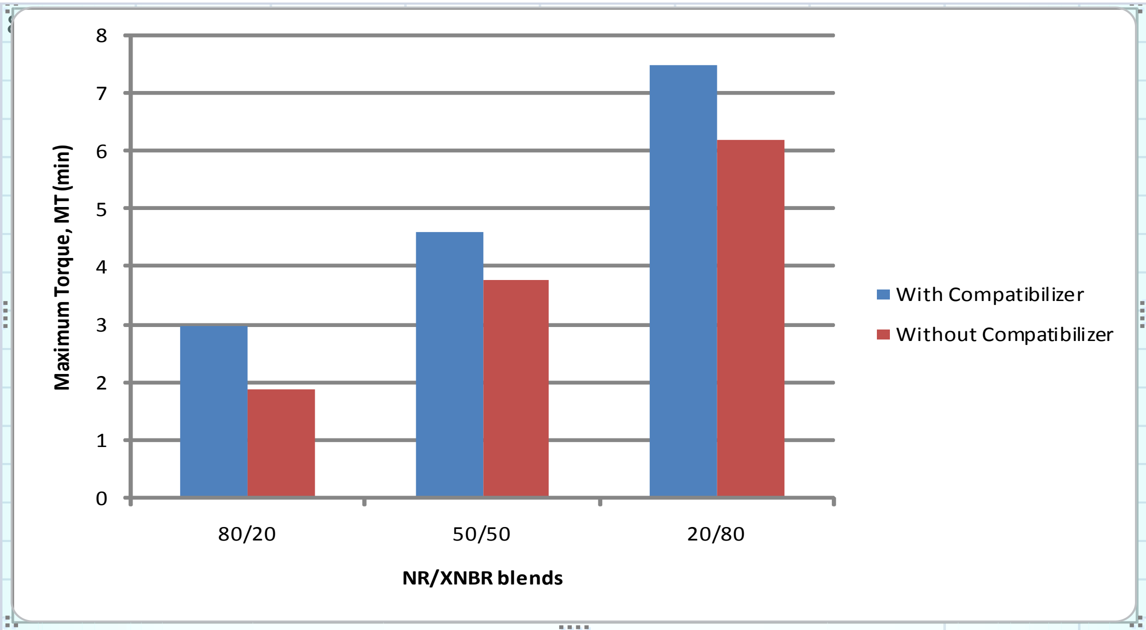


Figure 1. Effect of compatibilizer and blend ratio on maximum torque value of NR/XNBR blends.

The improved compatibility of the NR/XNBR blends in the presence of MAPI/EPX compatibilizer is shown in Fig. 1 where maximum torque (MT) value for NR/XNBR blends with MAPI/EPX compatibilizer is higher than the similar blends without MAPI/EPX compatibilizer. Fig. 1 also shows that maximum torque (MT) increases with increase in XNBR composition in the blend. According to Zanzig et al. [1], one way to improve compatibility of immiscible blends is through the use of block copolymers with segments chemically identical to the individual homopolymers. The XNBR carboxyl terminal groups do not react with the anhydride of MAPI, while the reaction between XNBR cyano groups (-CN) and the anhydride is insignificant without the presence of a catalyst. A similar problem is expected when MAPI is used as a compatibilizer in NR/XNBR blends and only secondary physical interaction is expected. Sevaral authors [21, 22, 23, 24, 25] have reported that epoxy is able to react with polyester terminal carboxyl group to compatibilize effectively many polyester-related blends. Epoxy is also well known to react with anhydride readily. These reactions are attributed to the multi-functionality of epoxy. In the present, from moleculer structural perspective, MAPI should be compatible with NR, whereas EPX should be compatible with XNBR. Thus, the presence of a multi-functional epoxy (EPX) in the XNBR-NR-MAPI blend is expected to produce XNBR-Co-EPX-Co-MAPI copolymer at the interface, which is able to function as an effective compatibilizer. This explains the increase in maximum torque (MT) with increase in XNBR composition due to increase in the number of reactive terminal carboxyl groups arising from increase in XNBR composition.

Fig. 2 shows the effect of compatibilizer and blend ratio on scorch time, t_2 of NR/XNBR blends. Clearly, t_2 decreases with increase in XNBR composition in the blends. The result also shows that the t_2 for XNBR is shorter than that of NR. This is due to the activation of an adjacent double bond by the carboxyl group. However, at a similar blend ratio, NR/XNBR blends with MAPI/EPX compatibilizer exhibit longer scorch time, t_2 than the NR/XNBR blends without MAPI/EPX compatibilizer. This indicates that the incorporation of MAPI/EPX compatibilizer increases the processing safety of the blends. Fig. 3 shows the effect of compatibilizer and blend ratio on cure time, t_{90} of NR/XNBR blends. As for scorch time, $t_{2,}$ the t_{90} value also exhibited a decreasing trend with increase in XNBR composition in the blends. However, at a similar blend ratio, in contrast to the scorch time, t_2, the incorporation of MAPI/EPX compatibilizer reduced the cure time, t_{90} of the blends. This again indicates the beneficial effect of MAPI/EPX compatibilizer.

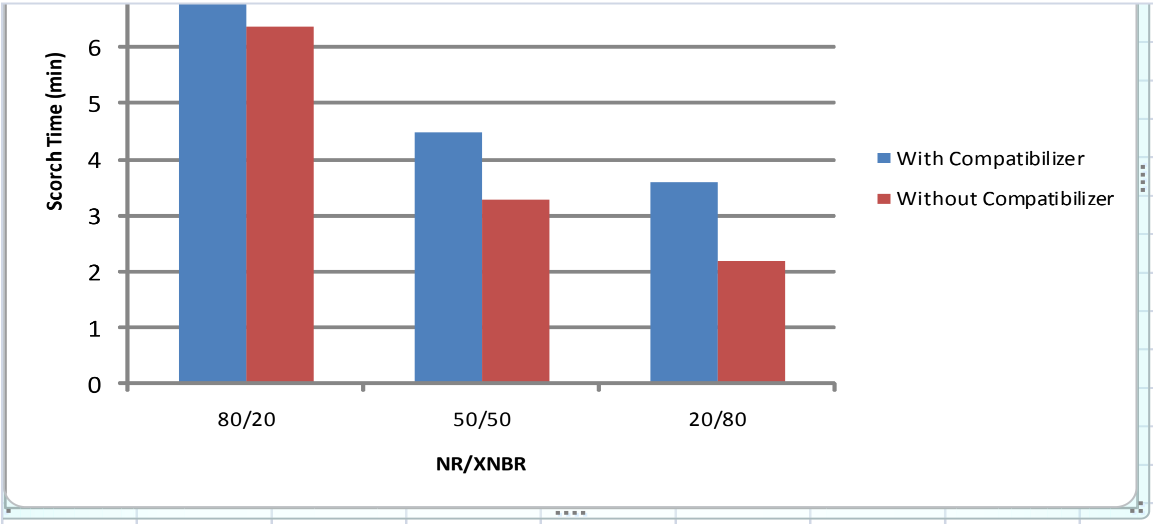


Figure 2. Effect of compatibilizer and blend ratio on scorch time of NR/XNBR blends.

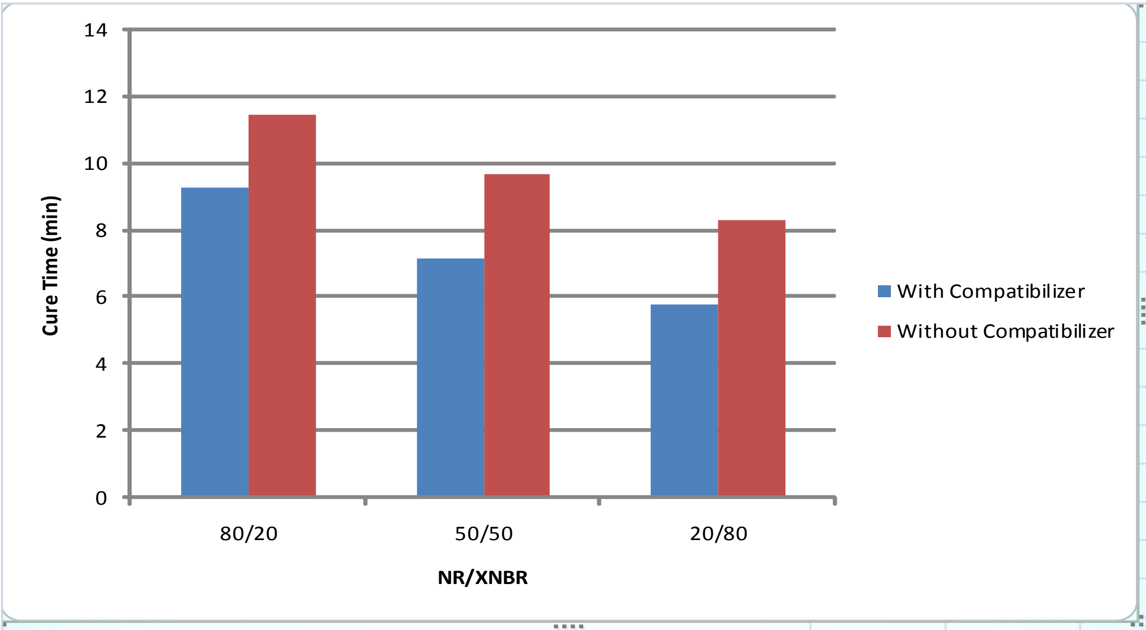


Figure 3. Effect of compatibilizer and blend ratio on cure time of NR/XNBR blends.

3.2. Mechanical Properties

The effect of compatibilizer and blend ratio on tensile strength, tear strength and elongation at break of NR/XNBR blends is shown in Figs. 4, 5 and 6, respectively. It can be seen that all properties decreased with increase in XNBR composition in the blends, but increased with MAPI/EPX compatibilizer in the blends. NR is a strain-crystallizing rubber due to its stereo-regular chain structure, whereas XNBR is a non-strain crystallizing rubber. The decrease in tensile strength and tear strength of NR/XNBR blends with increase in XNBR composition is attributed to the decrease in the strain-induced crystallization of NR arising from the decrease in NR composition in the blends. This observation is consistent with the report of Hanafi and Hairunezam [15]. In their study on the effect of a compatibilizer on curing characteristics, mechanical properties and oil resistance of SBR/ENR blends, the authors reported an increase in the tensile strength and tear strength of the blends with increasing ENR composition, which they attributed to strain-induced crystallization of ENR due to its stereo-regular cis 1, 4-configuration. Similarly, Folt and Smith [26] had earlier reported that the strength of strain-crystallizing rubbers is substantially superior to that of non-crystallizing rubbers, where the dissipative process is predominantly visco-elastic. The decrease in elongation at break with increase in XNBR composition (Fig. 6) is attributed to the greater chain mobility of NR than XNBR since the Glass transition temperature (T_g) of NR (-72^{0}C) is lower than that of XNBR (-26^{0}C) (AL-Gahtani [27]).

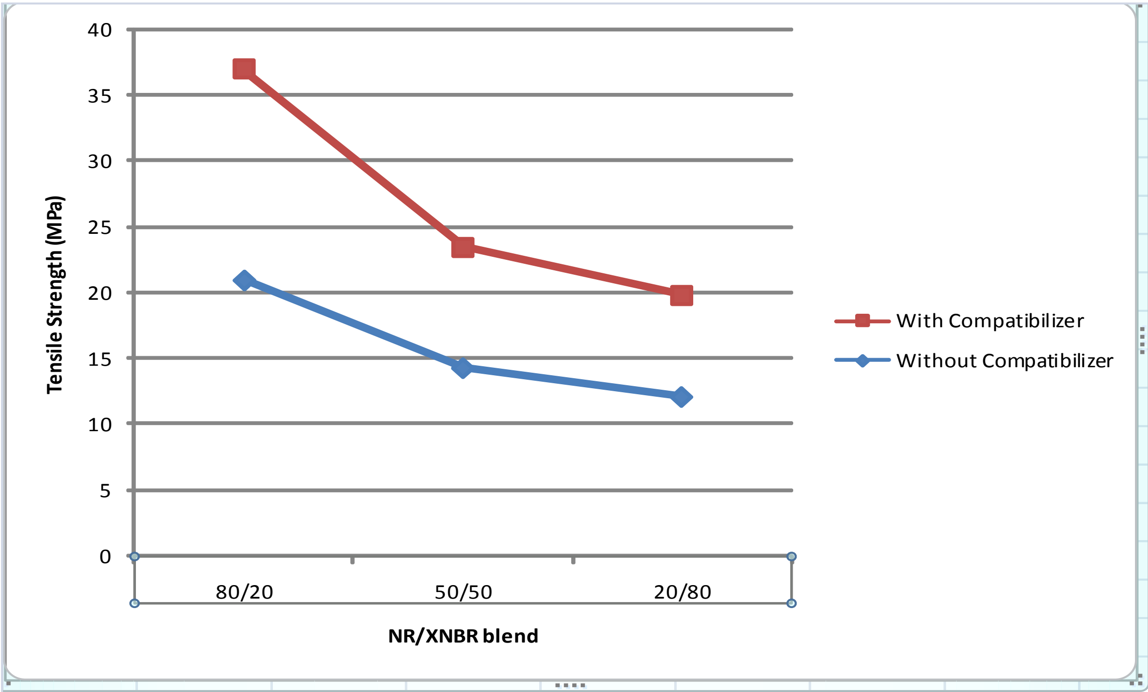


Figure 4. Effect of compatibilizer and blend ratio on tensile strength of NR/XNBR blends.

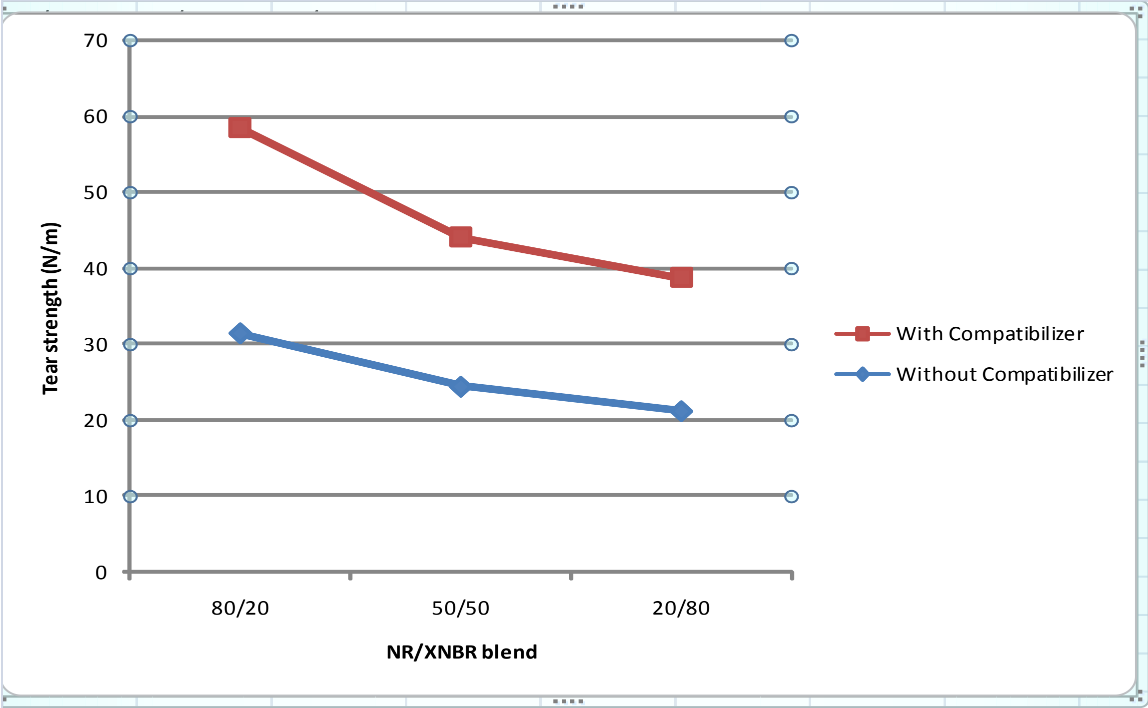


Figure 5. Effect of compatibilizer and blend ratio on tear strength of NR/XNBR blends.

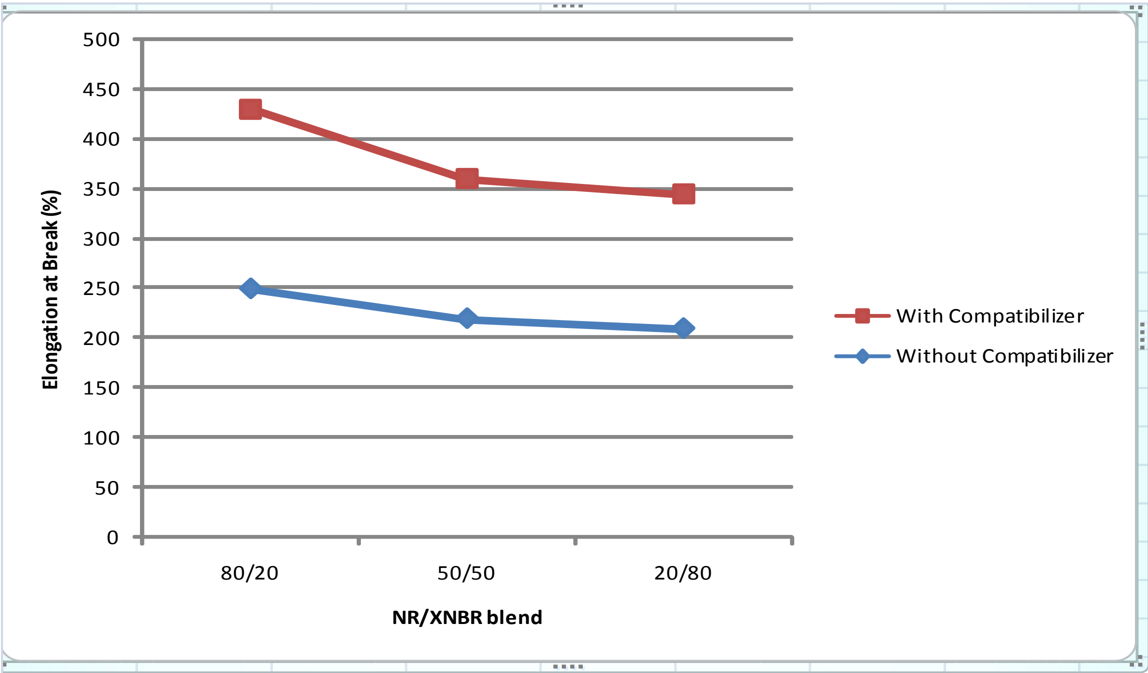


Figure 6. Effect of compatibilizer and blend ratio on elongation at break of NR/XNBR blends.

3.3. Solvent Resistance

Figs. 7-9 show the relationship between tensile strength, tear strength and elongation at break with immersion time at room temperature (27^{0}C) for NR/XNBR blends in the presence and absence of compatibilizer.

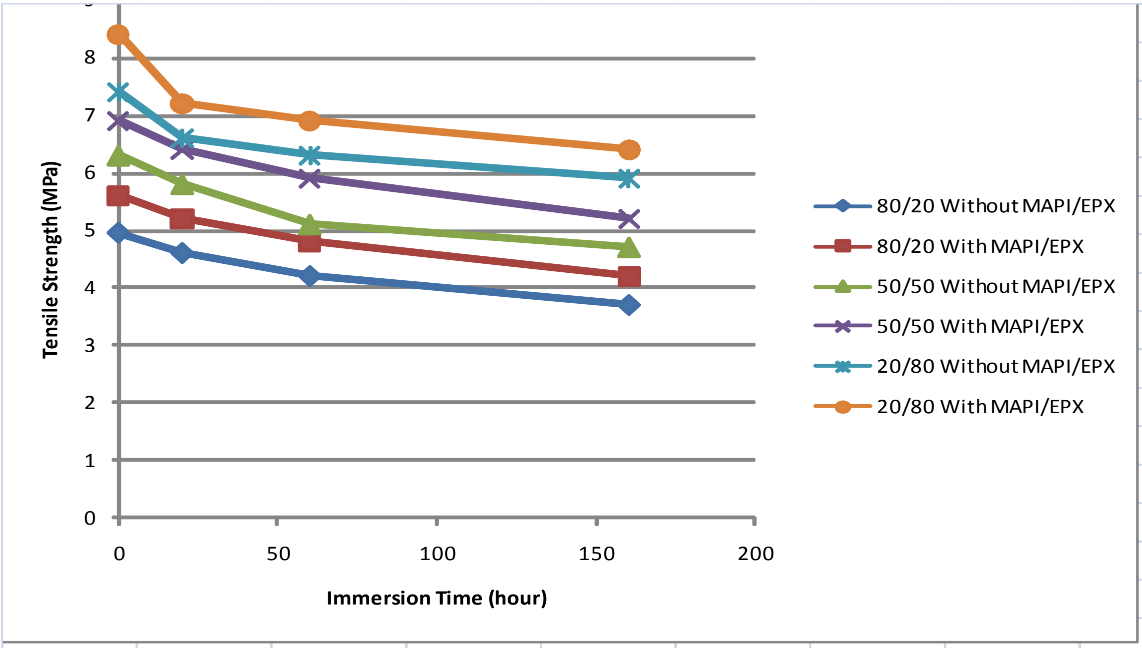


Figure 7. Variation of tensile strength and immersion time of NR/XNBR blends with and without MAPI/EPX compatibilizer.

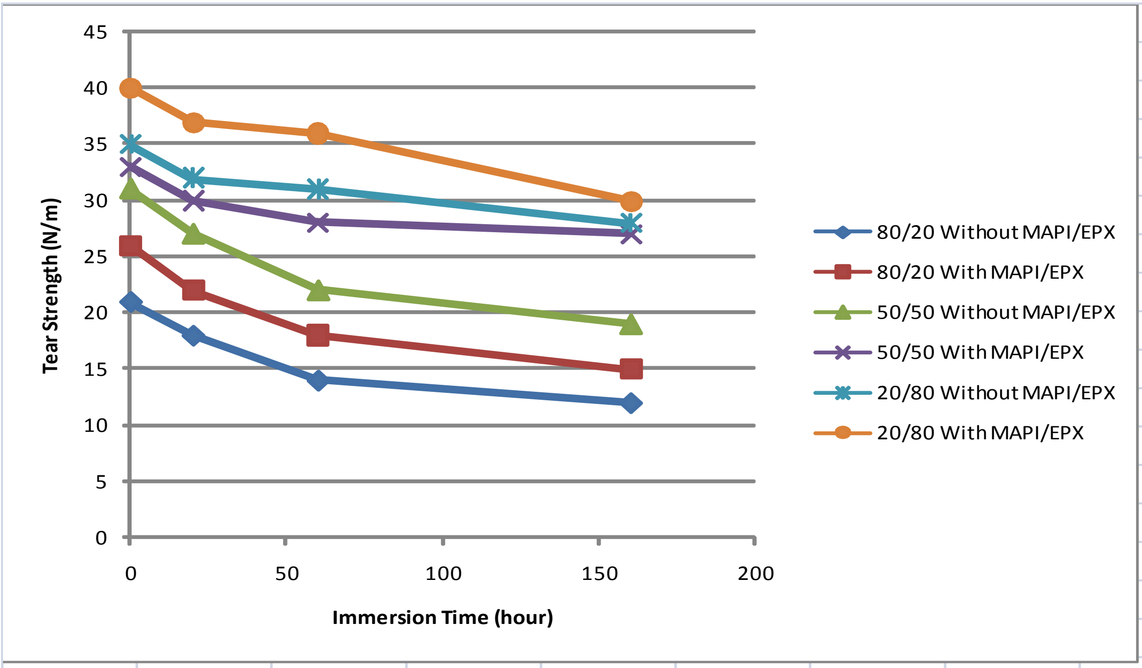


Figure 8. Variation of tear strength and immersion time of NR/XNBR blends.

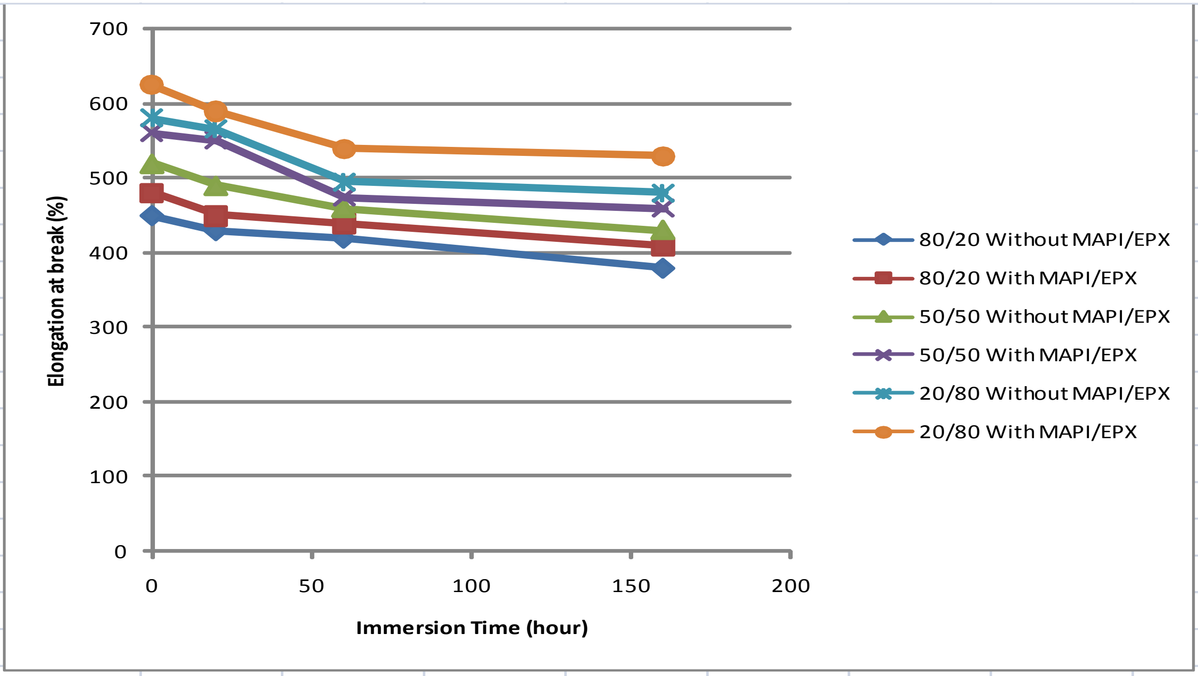


Figure 9. Variation of elongation at break and immersion time of NR/XNBR blends.

Clearly, all properties decrease with increasing immersion time. This is expected since more toluene diffuses into the blend with increasing immersion time. As a consequence, failure occurred at lower stress and strain during testing. However, at a similar immersion time, blends with higher composition of XNBR and blends with compatibilizer show higher values in these properties. XNBR is polar and therefore an oil/solvent resistant rubber due to the presence of carboxyl group in the chain structure, and the oil/solvent resistance is expected to increase with increase in polarity. Thus, polarity of NR/XNBR blend increases with increase in XNBR composition with corresponding increase in oil/solvent resistance as shown by the higher values in the properties investigated. Similarly, MAPI/EPX is a suitable compatibilizer for NR/XNBR blends as shown by the better properties of the blends with MAPI/EPX compatibilizer.

IV. CONCLUSIONS

The following conclusions can be drawn from this study:

1. Processability of NR/XNBR blends is improved by the presence of MAPI/EPX dual compatibilizers and by increasing the composition of XNBR.
2. MAPI/EPX dual compatibilizers exhibitbeneficial effect by decreasing the cure time and increasing the scorch time of the NR/XNBR blends.
3. Increasing compositions of XNBR brought decreases in tensile strength, tear strength and elongation at break. However, these properties increased in the presence of MAPI/EPX dual compatibilizers.

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