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High performance elastomer blend based on maleated natural rubber and hydroxyl-terminated polydimethylsiloxane

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Abstract

In an attempt to improve the mechanical and thermal properties of natural rubber (NR) in order to expand its range of application, this work aims to prepare a high performance elastomer blend (MNR- PDMS) of it with hydroxyl terminated polydimethylsiloxane (PDMS-OH). The elastomer blend (MNR-PDMS) was prepared by first modifying the surface of NR with maleic anhydride and then blending it with PDMS-OH using a laboratory roll mill. A sulfur-based curing system was used to cure the blend. Different loadings of PDMS-OH (2, 3, 4 phr) were used to determine the optimum one. Fourier transform infrared spectroscopy (FTIR) was used to characterize the structure of MNR-PDMS elastomer blends. The cure characteristics, mechanical and thermal properties of the MNR-PDMS elastomer blends were studied in detail. Moreover, the surface morphologies of the prepared MNR-PDMS elastomer blends were studied using scanning electron microscopy (SEM). The results showed a remarkably improvement in the mechanical and thermal properties of the prepared MNR-PDMS elastomer blends compared to the unmodified vulcanized natural rubber, and 2 phr was the optimal loading to obtain elastomer with superior mechanical properties.

Keywords: Natural rubber, Polydimethylsiloxane, Blend, Mechanical properties, Thermal properties

1. Introduction

With increasing global environmental awareness, the use and develop renewable materials have attracted the interest of researchers around the world [1-3]. Hence, in the recent years there has been a growing concern in developing the properties of green polymers such as natural rubber (NR) to reduce the environmental issues and broaden their application [1, 4-6]. NR is an eco-friendly polymer that was obtained from Hevea Brasiliensis tree. It possesses unique characteristics that distinguish it from its synthetic counterparts such as having a high resilience, high flexibility, high strength and fatigue resistance [7, 8]. As a result, it has been used in many industrial products, e.g. car tires, gloves, rubber springs, vibration mounts etc [8, 9]. NR products are often exposure to sunlight and elevated temperature which cause the properties of NR to deteriorate [6, 10]. Therefore, it was necessary to work on improving the mechanical and thermal properties of

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NR to withstand environmental conditions and perform its services [11]. Various attempts have been used to enhance these properties of NR; including adding fillers, mixing it with other polymeric materials, and surface modification [10-12]. From these attempts, Nguyen et al. made surface graft copolymerization of methyl methacrylate onto the Vietnam deproteinized natural rubber (DPNR) and investigated the effect of this grafting onto the NR properties [11]. They found that the grafted DPNR exhibited better thermal and mechanical properties than the unmodified DPNR. Parvathi K and Ramesan MT used zinc ferrite nanoparticles to enhance the properties of NR [13]. They found that the addition of zinc ferrite improve the thermal stability and mechanical properties of NR. In this regard, this paper also aimed to improve the thermal and mechanical properties of NR compound by blending it with polydimethylsiloxane monohydroxy terminated (PDMS). PDMS is a semi-inorganic polymer and is considered one of the most important biomaterials widely used for manufacture of biomedical devices [14]. In addition, it is extensively used in many industrial fields and systems such as micro/nanofluidics, soft lithography, organ-on-a-chip platforms, sealants, adhesives, fabric finishing agents, electronic components, separation membranes, coatings, optical and thermal devices [15, 16]. The wide use of PDMS has been attributed to its extraordinary properties which include good biocompatibility, excellent biostability, good thermal and oxidative stability, high flexibility and good dielectric properties [15, 17]. Because of its unique properties, it has also been used to improve the properties of other compounds [15, 18]; for instance it was incorporated into polyurethane elastomers that are used in medical implants to increase their bio-stability [19]. In line with this, here PDMS is also incorporated into NR in an attempt to improve the properties of NR. To the best of our knowledge, no report of such blending has been reported yet. Different concentrations of PDMS-OH (2, 3, 4 phr) were used to determine the optimum one. PDMS-OH was used here in low concentrations, as a previous report showed that using low concentrations of PDMS-OH was preferable for producing blends with good mechanical properties, as high concentrations of it led to the production of phase separation. This separation has a negative effect on the mechanical properties of the produced elastomers as it causes a decrease in intermolecular forces between the hard and soft segments [19-21]. To prepare a blend of NR with PDMS-OH, NR was first modified with maleic anhydride (MAH), and then blended with PDMS-OH using a laboratory roll mill. A sulfur vulcanization system was used to cure the produced blend (MNR-PDMS) at 142^{o}C. The cure characteristics, thermal and mechanical properties of the resulting blend vulcanizate were studied. SEM was also used to study the morphology of the resulting blend.

2. Materials and experimental methods

2.1. Materials

Natural rubber SIR 20 (NR) was kindly supplied from Transport and Engineering Company, Alexandria. Maleic anhydride (MA), benzoyl peroxide (BP) and polydimethyl siloxane monohydroxy terminated (PDMS -OH; Mn ~ 4670) were obtained from Aldrich company, Germany. Rubber ingredients such as zinc oxide (ZnO; activator), stearic acid (St.Ac.; activator), N-cyclohexyl-2-benzothiazole sulfonamide (CBS; accelerator), and sulfur (S; curing agent) are commercially available and were obtained from El Nasr pharmaceutical chemicals Co.

2.2. Experimental

2.2.1. Synthesis of maleated natural rubber (MNR)

MNR was prepared by mixing 4 g of MA with 100 g of NR in a Brabender Plasticorder mixer with a rotor speed of 60 rpm at 150°C for 10 min [22]. The resulting rubber (MNR) was purified by dissolving it in toluene at 25^{o}C for 24 h and then refluxing at 100oC for 3 h. After that, the solution was precipitated in acetone and the precipitate was collected and dried in an oven at 40°C for 24 h.

2.2.2. Preparation of MNR-PDMS elastomer blends

The MNR-PDMS elastomer blends were prepared by mixing the prepared MNR with different concentrations of PDMS-OH using a laboratory two-roll mill at 25^{o}C. Table 1 shows the used ingredients for preparation of MNR-PDMS elastomers. After mixing the ingredients, the MNR-PDMS elastomer blends were left at 25^{o}C for 24 h before curing (molding) process.

2.2.3. Curing process

The prepared elastomers were cured in a compression molding machine (Mackey Bowley, C1136199) at 142 ± 1^{0}C with pressure approximately 4 MPa. The curing time of the elastomers was measured on MDR one Moving Die Rheometer (TA instruments, USA).

Table 1. Formulation used for preparation of MNR-PDMS elastomer blends

	Formulation code number				
Ingredients (phr)[a]	**N**	**P0**	**P1**	**P2**	**P3**
NR	100	----	----	----	----
MNR	----	100	100	100	100
PDMS-OH	-----	-----	2	3	4
ZnO	5	5	5	5	5
St. Ac	2	2	2	2	2
CBS	1.5	1.5	1.5	1.5	1.5
S	1.5	1.5	1.5	1.5	1.5

[a] Part per hundred parts of rubber

3. Characterization techniques

FTIR spectrophotometer (FTIR-8400 Shimadzu, Japan) equipped with KBr discs was used to determine the Fourier-transform infrared (FTIR) spectra of the raw NR, MNR and prepared elastomers in the range of 400 to 4000 cm^{-1}. TGA-50 Shimadzu thermogravimetric analyzer with a heating rate of 10^{o}C/min was used to detect the thermal stability of NR and prepared elastomers. Scanning electron microscopy (SEM; model Quanta FEG-250) was used to determine the morphology of the prepared elastomers. The MDR one Moving Die Rheometer (TA instruments, USA) was used to measure the cure characteristics of the prepared elastomers (N, P, P1, P2 and P3) such as maximum torque (M_H), minimum torque (M_L), torque difference (ΔM), optimum cure time (tc_{90}), scorch time (ts_2) and cure rate index (CRI) according to ASTM D2084. The M_H and ΔM (M_H- M_L) give an idea about the modulus and crosslink density of the elastomer system; respectively [23]. Whereas, CRI gives an idea about the curing process rate and is determined from the following equation [24]:

$$\mathbf{CRI = 100/ (tc_{90} - ts_2)}$$

An electronic Zwick tensile testing machine (Germany) was used to measure the mechanical properties; such as tensile strength (MPa) and elongation at break (%); of the prepared elastomers according to ASTM D412 [25, 26]. Furthermore, the hardness (Shore A) of the elastomers was determined using a durometer Shore A (Bareiss, Oberdischingen, Germany) according to ASTM D2240 [25, 26].

4. Result and discussion

A high performance elastomer blend (MNR-PDMS) based on maleated natural rubber (MNR) and hydroxyl terminated polydimethylsiloxane (PDMS-

OH) was prepared by using a laboratory roll mill and was vulcanized by sulfur curing system. Different concentrations of PDMS-OH were used to determine its optimum concentration for obtaining elastomer blend with superior mechanical properties. The cure characteristics, mechanical and thermal properties of the prepared blends were investigated.

4.1. Characterization of MNR

4.1.1. FTIR

FTIR spectra of raw NR and MNR are shown in Figure 1. By comparing FTIR spectra of NR and MNR, it was observed that there were only new absorption bands appeared in MNR spectrum at 1784 and 1858 cm^{-1} , which were assigned to the symmetric and asymmetric stretching vibrations of anhydride groups in the succinic anhydride rings that were formed after grafting MA groups onto NR chains. Moreover, it was observed in MNR spectrum that there was new band appeared at 1712 cm^{-1} which was due to the stretching vibration of -C=O groups of carboxylate groups that might be formed from the opening anhydride ring of succinic anhydride by reaction with the moisture [22, 27].

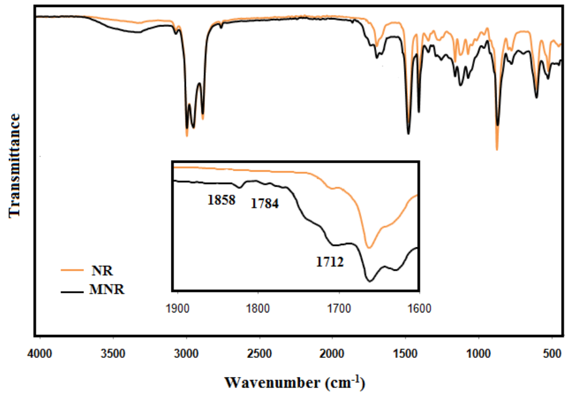


Figure 1. FTIR spectra of NR and MNR.

4.2. Characterization of MNR-PDMS elastomer blends

4.2.1. FTIR

Figure 2 presents the FTIR spectra of the prepared elastomer blends. It was observed that the all spectra were quite similar. However, in the spectra of MNR-PDMS (P1, P2 and P3) elastomer blends, there was a new band appeared at 1745 cm^{-1} which could be assigned to the stretching vibration of C=O of ester groups that could be resulted from reaction of PDMS-OH with anhydride groups of succinic ring in MNR [28]. The formation of this band indicated the occurrence of the reaction between MNR and PDMS-OH via the ring opening of MA. Additionally, a new band at 3327 cm^{-1} was noticed in the P2 and P3 spectra, which might be explained by the presence of hydroxyl groups as a result of the presence of a greater amount of PDMS-OH in the elastomer blends. The possible mechanism of reaction MNR with PDMS- OH is suggested in Scheme 1.

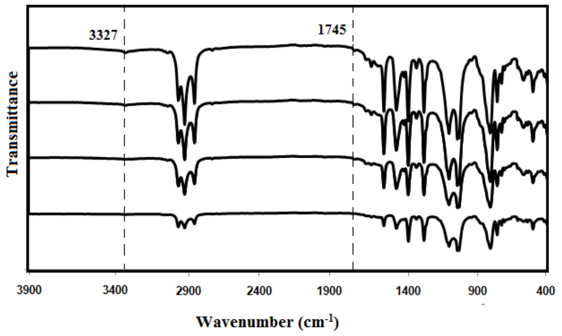
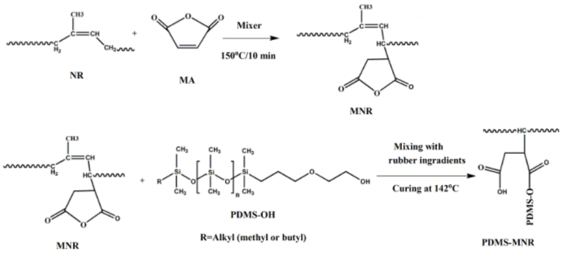


Figure 2. FTIR spectra of (a) P0, (b) P1, (c) P2 and (d) P3 elastomer blends.



Scheme 1. The possible reaction mechanism of MNR with PDMS- OH to obtain MNR-PDMS elastomer blend.

4.2.2. Cure characteristics

Table 2. The cure characteristics of the prepared N, P0 and P1, P2 & P3 elastomers.

Formulation code number **Curing parameters**	**N**	**P0**	**P1**	**P2**	**P3**
M_H	**11.12**	**10.6**	**10.34**	**9**	**7.8**
$\Delta M(M_H-M_L)$	**10.48**	**9.9**	**9.73**	**8.43**	**7.31**
ts_2	**8.1**	**9.8**	**9.2**	**10.3**	**10.9**
tc_{90}	**15**	**19.3**	**20.4**	**24.3**	**16.6**
CRI	**14.5**	**10.5**	**8**	**7**	**17**

Table 2 shows the cure characteristics of the prepared elastomers. It was clearly observed that the M_H-M_L values of the P0, P1, P2, and P3 elastomers were lower than that of N elastomer (control). This indicated that these elastomers had a low degree of cross-linking density. This decrease in the cross-linking density was attributed to the presence of succinic anhydride groups in P0 elastomer and succinic ester/ acid groups in P1, P2, and P3 elastomers. These groups have an acidic nature and will cause an accelerator adsorption [22]. As a result, a decrease in the number of polysulfide bonds occurred leading to lower the crosslinking densities within the resulting elastomers [29, 30]. Moreover, it was observed that as PDMS loading increased, the M_H and M_H-M_L decreased. This decrease can be attributed to the presence of an excessive amount of PDMS within the elastomers networks.

Table 2 also shows the tc_{90} and CRI of the prepared elastomers. From this table, it was observed that the vulcanized P0, P1, P2, and P3 elastomers displayed the longest tc_{90} compared to N elastomer. This would due to the presence of succinic anhydride groups in P0 elatomer and succinic ester/ acid groups in P1, P2, and P3 elastomers structures that had an adsorption effect on the accelerator; resulting in a lower cure rate i.e. cure time (tc_{90}) increased. However, it was noticed that with increasing the concentration of PDMS- OH beyond 3 phr, the tc_{90} decreased and CRI increased. This different behavior can be attributed to the presence of excessive amount of PDMS-OH in the P3 elastomer. Their excessive presence led to increased OH groups resulting in an increased in the curing rate or the production of PDMS-OH agglomerates, which might prevent the homogeneous distribution of activators and other constituents of the curing system within the elastomer matrix.

4.2.3. Physico-mechanical properties

The tensile strength and elongation at break (%) of the prepared elastomer blends are shown in Figures 3& 4. It was revealed that the elastomers with PDMS-OH exhibited a remarkable enhancement in the tensile strength up to 2 phr of PDMS-OH (P1 elastomer) and then decreased. However, elongation at break showed a gradual increase with increasing PDMS-OH loading. The improvement in the tensile strength of P1 elastomer blend might be attributed to PDMS-OH had a certain reinforcing effect on the elastomer. In addition, the decrease in the tensile strength beyond 2 phr PDMS-OH loading might be attributed to the greater addition of the flexible PDMS-OH molecules [31]. The increase in elongation at break of elastomer blends with increasing concentration of PDMS-OH (P2 & P3) might be ascribed to the softening effect of PDMS-OH.

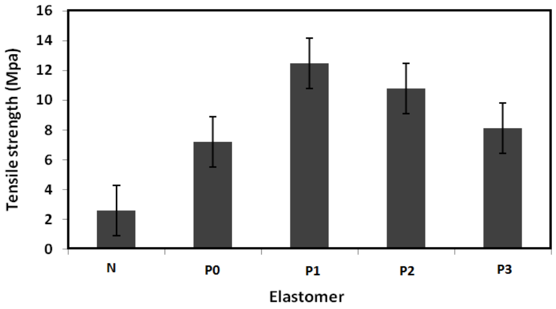


Figure 3. Tensile strength of vulcanized N, P0 and P1, P2 & P3 elastomer blends.

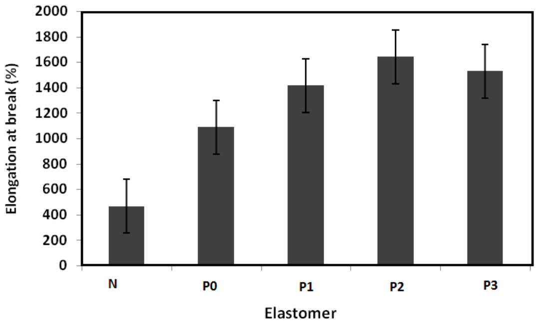


Figure 4. Elongation at break (%) of vulcanized N, P0 and P1, P2 & P3 elastomer blends.

Modulus at 100% elongation and hardness (Shore A) of the prepared elastomer blends are shown in Figures 5& 6. It was observed that the elastomer blends with PDMS-OH showed a decrease in the modulus and hardness values with increasing the concentration of PDMS-OH. This decrease was ascribed to the presence of PDMS-OH which imparted flexibility to the resulting elastomers [31].

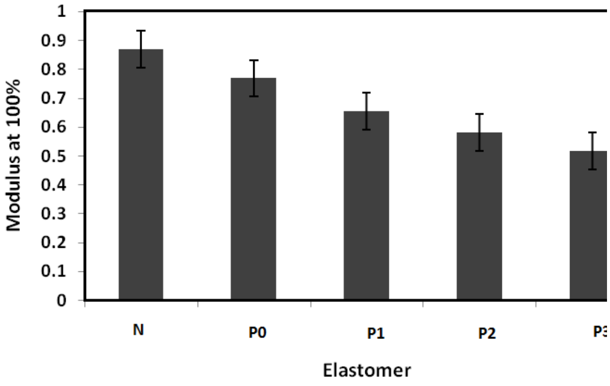


Figure 5. Modulus at 100% elongation of vulcanized N, P0 and P1, P2 & P3 elastomer blends.

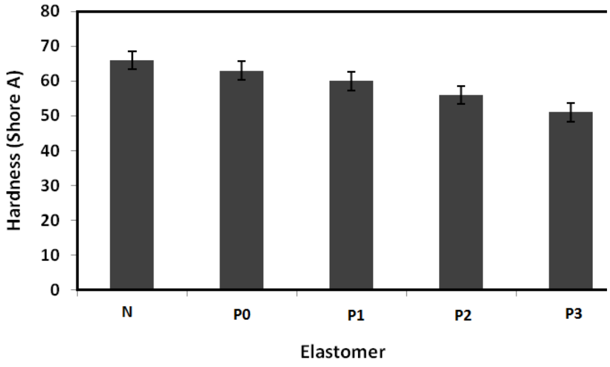


Figure 6. Hardness (Shore A) of vulcanized N, P0 and P1, P2 & P3 elastomer blends.

4.2.4. Morphology

The morphology of the prepared elastomers was investigated by SEM, Figure 7. From this figure, it was observed that the surface morphologies of the prepared elastomers were smooth except for P2 elastomer which showed phase separation. This phase separation could be related to the presence of an excess amount of PDMS-OH within the elastomer [31]. This observation explained the deterioration of tensile properties beyond using 2 phr of PDMS-OH.

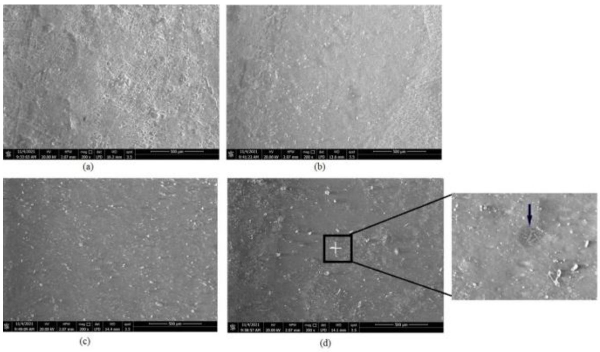


Figure 7. SEM micrographs of vulcanized (a) N, (b) P0, (c) P1 and (d) P2 elastomers.

4.2.5. Thermal properties

P1 elastomer was chosen from the prepared elastomers to study its thermal stability as it showed the highest mechanical properties in the prepared elastomers, and for comparing the thermal stability of N (blank NR) elastomer was measured, as presented in Figure 8. From this figure, it was observed that P1 and N elastomers had a single degradation step, corresponding to the oxidative decomposition of NR backbone. Moreover, it was found from the weight loss curves of P1 and N that the char residue of P1 (32%) was higher than that of N (24%) at 550 °C. This indicated that adding PDMS- OH into NR had a good influence on increasing the thermal stability of NR. Moreover, it was noticed from Figure 8 that the onset decomposition temperature of P1 elastomer (345°C) was higher than that of N elastomer (335°C). All these findings implied that the adding PDMS-

OH into NR increased its stability compared to N elastomer as it provided Si–O bond strength into NR matrix [32].

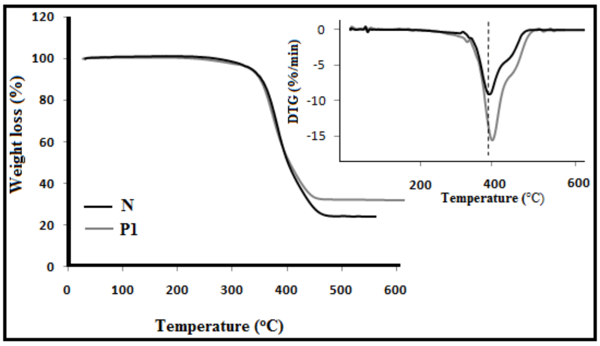


Figure 8. TGA and DTG of P1 and N elastomers

5. Conclusion

In this study, a high performance elastomer blend based on maleated NR (MNR) and PDMS-OH was successfully prepared. FTIR results confirmed the occurrence of a chemical reaction between the anhydride ring of maleated natural rubber and the hydroxyl group of PDMS-OH. Different loadings of PDMS-OH (2, 3 & 4 phr) were used to determine the optimum one for obtaining elastomer with superior properties. The curing, mechanical, thermal and morphology properties of the prepared elastomer blends (P1, P2 & P3) were studied and compared with the properties of unmodified NR (N elastomer, control). The results showed that adding 2 phr of PDMS-OH into modified NR (MNR) led to a significant improvement in the mechanical and thermal properties of the resulting elastomer and beyond this loading, deterioration in the mechanical properties was observed. SEM examination was consistent with the mechanical result as it showed phase separation in the elastomer surface when high concentration of PDMS-OH was used.

6. Conflict of Interest:

The author declares that there is no conflict of interest.

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