

## Research Article

# Effects of Polarity on the Filler-Rubber Interaction and Properties of Silica Filled Grafted Natural Rubber Composites

Wanvimon Arayapranee<sup>1</sup> and Garry L. Rempel<sup>2</sup>

<sup>1</sup> Department of Chemical and Material Engineering, Rangsit University, Pathum Thani 12000, Thailand

<sup>2</sup> Department of Chemical Engineering, University of Waterloo, ON, Canada N2L 3G1

Correspondence should be addressed to Wanvimon Arayapranee; wanvimon@rsu.ac.th

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The grafting of an olefinic monomer like acrylonitrile (AN), methyl methacrylate (MMA), and styrene (ST) onto natural rubber (NR) was carried out to enhance the polarity of the new chemical groups on the NR backbone and, in turn, to improve the filler-rubber interaction. The grafted natural rubber (GNR) produced was compounded and then vulcanization was carried out in the presence of silica as a reinforcing filler. The physical properties and aging resistance provided by the presence of the polar functional groups of the GNR composites were investigated and compared with other rubbers such as SBR, NBR, and NR. The GNRs provided significant improvements in resistance of the composites to thermal, oil, and ozone while maintaining the mechanical properties of the rubber. Therefore, these properties can be controlled as a function of the polarity of functional groups on the NR backbone. Morphological studies confirmed a shift from ductility failure to brittle with the presence of the polar group on the rubber chains.

## 1. Introduction

Natural rubber (NR) obtained from *Hevea brasiliensis* is a natural biosynthesis polymer possessing excellent characteristics such as high tensile strength due to its ability to crystallize upon stretching. However, NR is highly susceptible to attack by atmospheric oxygen and ozone, and hence, its heat and ozone resistance are very poor, mainly due to the presence of the double bonds in the main chain [1]. In addition, it does not perform well when exposed to oils and hydrocarbon solvents, as a result of its nonpolar character [2]. In general, the improved products from natural rubber (NR) have potentially wide applications as a result of reinforcing by fillers such as carbon black or silica [3, 4], as well as physical blends with other polymer particles [5, 6] or chemical modification [7], thus enabling these materials to compete with synthetic rubbers.

In order to increase polarity and widen the application of natural rubber, natural rubber was modified by graft copolymerization with a polar functional monomer to produce grafted natural rubber (GNR) having good thermal, oil, and ozone resistance and high tensile strength. Several

studies have been carried out on the grafting of NR with various olefinic monomers like acrylonitrile (AN), methyl methacrylate (MMA), and styrene (ST) which are capable of being polymerized to produce hard plastic materials [8–14]. The combination of high strength and oil resistance properties of GNR with a polar functional monomer is being evaluated in such applications as oil-resistant oil handling hoses, seals, and grommets. Lu et al. [10] incorporated MMA grafted NR latex to improve the modulus and hardness of the film and developed it for the improvement of antiaging properties. George et al. [11] studied radiation grafting of MMA onto NR for improving the mechanical properties of the dry films. Man et al. [12] studied the curing behavior and mechanical properties of ST/MMA grafted deproteinized NR latex. They found that the increase in the monomer concentration resulted in a stiffer rubber with increased modulus and reduced elongation at break. Kawahara et al. [13] reported that NR particles of about 0.5  $\mu\text{m}$  in diameter were dispersed in a polystyrene matrix of about 15 nm thickness having outstanding mechanical strength.

The objective of this research was to investigate the performance of modified NR by graft copolymerization of

NR as the core with three types of olefinic monomers, that is, AN, MMA, and ST as the polymer shell, in order to improve certain antiaging properties, while maintaining the mechanical properties of the rubber. In addition, the increase of polarity within the rubber chains is believed to play a significant role in providing better reinforcement by polar fillers such as silica without the need for coupling agents. The obtained GNRs were compounded and processed into test specimens. Subsequently, the processability and mechanical properties, that is, tensile properties, and thermal, oil, and ozone resistance of the prepared GNRs were examined and then compared with those of NBR, SBR, and NR. A morphological study of tensile fracture surfaces of rubber vulcanizates was also carried out.

## 2. Materials and Methods

**2.1. Materials.** NR latex was grafted with AN, MMA, and ST according to a procedure described in a previous article [14]. NR and free polymer were removed from the crude sample by soxhlet extraction [9, 14]. The graft copolymer was characterized by Fourier transform infrared (FTIR) spectroscopy and gravimetric methods. The GNR products were composed of 68.7, 79.3, and 87.8 wt% graft copolymer, 2.4, 1.6, and 0.9 wt% free polymer, and 28.9, 19.1, and 11.3 wt% free rubber for NR-g-PAN (GAN), NR-g-PMMA (GMA), and NR-g-PST (GST), respectively.

Figure 1 shows the transmission FTIR spectra of NBR, SBR, GAN, GMA, GST, and NR, respectively. The vibration of nitrile stretching at  $2236\text{ cm}^{-1}$  and the C–H stretching (out of plane) of the butadiene double bond at  $969\text{ cm}^{-1}$  from NBR (Figure 1(a)), the monosubstituted benzene ring at  $699\text{ cm}^{-1}$  and the C–H stretching (out of plane) of butadiene double bond at  $969\text{ cm}^{-1}$  from SBR (Figure 1(b)), and the C=C stretching for the unconjugated linear olefin at  $836\text{ cm}^{-1}$  of NR (Figure 1(f)) are shown. After solvent extraction, the graft copolymer was analyzed by FTIR. There are four characteristic peaks attributed to  $\text{R}_2\text{C}=\text{CHR}$  of isoprene, C≡N stretching vibration of AN (Figure 1(c)), C=O stretching vibration of MMA (Figure 1(d)), and the monosubstituted benzene ring vibration of ST (Figure 1(e)) at wavenumbers of 836, 2236, 1731, and  $699\text{ cm}^{-1}$ , respectively. This provides evidence that the graft copolymers were formed during the grafting of AN, MMA, or ST onto NR.

In this study, three different types of rubbers: NR grade STR-5L (Thai Hua Rubber PCL., Rayong, Thailand), SBR (styrene: 23.5%, BST Elastomers Company Limited, Rayong, Thailand), and NBR (acrylonitrile: 32–34%, Nantex Industry Co., Ltd., Kaohsiung, Taiwan) were employed. Sulfur (S8, Chemmin Co. Ltd., Thailand), paraffin oil (GSP Products Co., Ltd., Thailand), N-cyclohexyl-2-benzothiazole-2-sulphenamide and tetramethylthiuram disulphide (CBS and TMTD, Flexsys Co. Ltd., Germany), zinc oxide (activator, Gradmann, Thailand), stearic acid (activator, P. T. Cisadaneraya Chemical, Indonesia), Poly(ethylene glycol) (PEG, Brand Co., Ltd., Thailand), silica (HiSil 233s with specific surface area of  $165\text{ m}^2/\text{g}$ ) supplied by PPG-Siam Silica Co., Ltd., Thailand, and IRM901 and IRM903 oils (Japan Sun Oil Co.

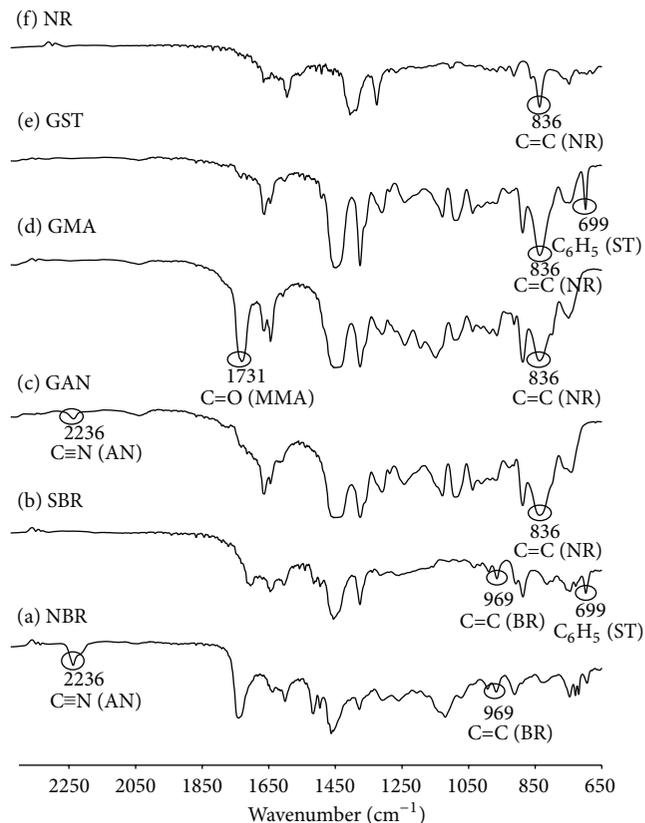


FIGURE 1: FTIR spectra for (a) NBR, (b) SBR, (c) GAN, (d) GMA, (e) GST, and (f) NR.

Ltd., Tokyo, Japan) were of commercial grade and used as received.

**2.2. Compounding and Processing.** The GNRs were compounded using a laboratory-sized two-roll mill (Kodaira Seisakusho Co., Ltd., Tokyo, Japan) with various chemicals, according to the formulations for mixing shown in Table 1. For comparison purposes, NR, SBR, and NBR were also compounded using the same recipe. First, each rubber was initially masticated for 3 min, followed by addition of the plasticizer (paraffin oil), activators (ZnO and stearic acid), filler, PEG, and accelerators (CBS and TMTD). Second, mixing was completed by the addition of sulfur at  $70^\circ\text{C}$  for 3 min. In advance of the processing, the optimum cure time,  $t_{90}$ , was determined on the basis of the results of curing characteristics using a rheometer (TECH-PRO, Cuyahoga Falls, Ohio, USA) according to ASTM D5289-07A [15] for 30 min at  $150^\circ\text{C}$ . The Mooney viscosity ( $\text{ML}_{1+4}$  at  $100^\circ\text{C}$ ) was determined by using a Mooney viscometer (TECH-PRO, Cuyahoga Falls, Ohio, USA) according to the method described in ISO 289-1 [16]. Each rubber compound was compression molded at  $150^\circ\text{C}$  with a force of 17.5 MPa using a hydraulic press according to their respective cure time. Vulcanizates were conditioned for 24 h before testing.

**2.3. Characterization.** Tensile properties were determined on an Instron universal testing machine (model 4466; Instron

TABLE 1: Formulations of the vulcanized rubbers.

Ingredient	phr <sup>a</sup>
Rubbers (NBR, SBR, GAN, GMA, GST, and NR)	100
Paraffin oil	4.0
Zinc oxide (ZnO)	5.0
Stearic acid	2.0
CBS	1.5
TMTD	0.5
Sulfur	2.0
Silica (HiSil 233s)	40
PEG	1.0

<sup>a</sup>phr: parts per hundred of rubber.

Corp., Canton, MA) using C-type Dumbbell-specimens, according to ASTM D412 [17]. Tensile specimens were aged at 100°C for 72 h in an air-circulating aging oven according to ASTM D573 [18] and were immersed in hydrocarbon oils at 100°C for 72 h. Oils used in this testing, IRM901 and IRM903, have different polarity, the latter of which has higher polarity. When the specified time was reached, the test specimens were removed from the oil and wiped with tissue paper to remove the excess oil from the surface. Finally, tensile properties of the specimens after aging were measured to estimate oil resistance according to ASTM D471-06 [19]. The aging resistance is expressed as a percentage of retention in tensile properties calculated by the following equation [20]:

$$\text{Retention (\%)} = \frac{\text{value after aging}}{\text{value before aging}} \times 100. \quad (1)$$

Ozone aging studies under static conditions were conducted according to ISO 1431/1-1980 [21] in a Hampden (Model 1008-AH, Northampton, England). Photographs were taken using an optical microscope Carl Zeiss Stemi 2000 C (Werk Göttingen, Germany) with a magnification of 50.

Scanning electron microscopic studies of the compounds' tensile fracture surfaces were carried out on gold-coated samples using a JEOL Microscope (model JSM 5600 LV; Tokyo, Japan) at a magnification of 3,000.

### 3. Results and Discussion

The effect of different types of rubber on the variation of Mooney viscosity versus time for silica filled rubber compounds are shown in Figure 2. The results reveal that the Mooney viscosity of the synthetic or modified rubbers was higher than that of NR which possessed the lowest viscosity, followed by GAN, NBR, GMA, GST, and SBR. This is due to higher chemical interaction between molecules of rubber and filler via polar functional groups. NR, nonpolar rubber, has a poor filler dispersion because NR is considered as a nonpolar rubber, respectively, compared with NBR whereas the silanol groups on a silica surface provide a highly polar filler. Therefore, the silanol groups could form hydrogen bonds resulting in a strong filler-filler interaction leading to poor filler dispersion. Compared to polar rubber filled with silica, NBR with its strong polar group produced

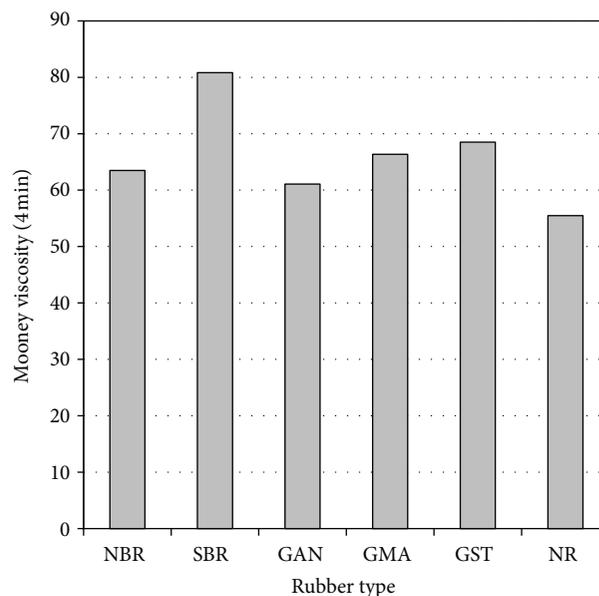


FIGURE 2: Mooney viscosity of various rubber matrices filled with 40 phr silica.

a stronger filler-rubber interaction between the nitrile groups and silanol groups, which normally give rise to an increase in the viscosity [22, 23]. The higher value of viscosity for silica filled NBR materials indicated that there was a high restriction in the mobility of the macromolecules, probably caused by the greater interaction between both filler and the rubber matrix. Nonpolar SBR had the highest viscosity along the rubber chains which obstructed the movement of the rubber chains due to the presence of the styrene pendant groups, and therefore, the Mooney viscosity was higher compared to that of NBR and NR. In this case, the grafting was carried out to obtain polar functional groups on the NR. Relative to GNRs (GAN, GMA, or GST), higher Mooney values were observed compared to NR. The Mooney viscosity of silica filled GNRs exhibited similar trends; the higher value was due to the filler-rubber interaction strengthening with the presence of functional groups in GNR containing a number of relatively short segments of rather high polarity grafted onto NR to relatively long chains of low polarity and the silanol group on the silica surface. Based on the GNRs, the polarity can be ranked in the following order: GAN > GMA > GST. As expected, the Mooney viscosity of silica filled GAN (high polar rubber) was therefore lower than those of GMA and GST. However, the lowest Mooney viscosity for the silica filled NR indicated that it could be processed more easily than the other silica filled rubbers.

Figure 3 shows the effect of various rubbers on the cure characteristics of silica filled rubber compounds. It can be observed that GST had the longest cure time, followed by SBR, GMA, NBR, GAN, and NR. NR having more double bonds was more reactive in forming crosslinks during vulcanization than the synthetic rubbers or GNRs; thus, a shorter cure time was observed in the former. It was found that the silica filled SBR exhibited the highest cure time, but the NBR compound showed a shorter cure time. This implied

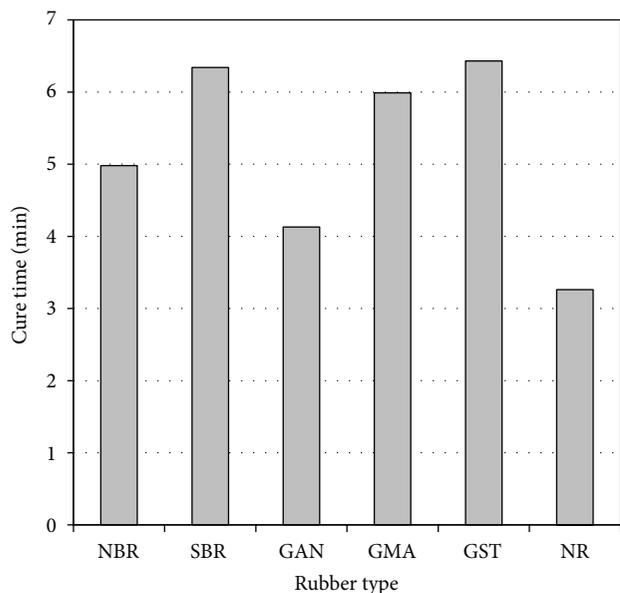


FIGURE 3: Optimum cure time ( $ML_{1+4}$  at  $100^{\circ}C$ ) of various rubber matrices filled with 40 phr silica.

that for strong polar groups, such as in NBR, a hydrogen bond could be formed between the cyanogen groups to provide an improvement during processing, compared with a less polar rubber such as SBR, due to the accelerating effect on the vulcanization of the NBR compound. On the contrary, the longest cure time was exhibited for the SBR rubber, which may be attributed to the presence of bulky pendant groups, resulting in retardation of the vulcanization process [24, 25]. GNR had the same reactivity as NR but a longer cure time was observed in the former. Man et al. [12] reported that the longer cure time for ST/MMA grafted deproteinized NR latex was due to the lower concentration of double bonds and allylic hydrogen in the modified deproteinized NR molecular chain. Furthermore, a longer cure time of silica filled GNR composites decreased with increasing polarity of grafted side chains. A similar result is observed for the synthetic rubbers, NBR and SBR, in that the polarity of the grafted side chains was increased; the polar functional groups could form hydrogen bonds towards each other resulting in acceleration of the vulcanization process. Consequently the curing rate of the compound increased with increasing polarity of the grafted side chains.

Figure 4 shows the silica filled NR composite exhibited the highest tensile strength, followed by GAN, GMA, GST, NBR, and then the SBR composites. The highest tensile strength was exhibited by the NR composite, which was due to strain-induced crystallization [26]. Since, during vulcanization, NR had more reactive sites to form crosslinks which were more reactive to improve tensile strength than those in synthetic rubbers, NR, therefore, possessed the highest tensile strength, compared to the synthetic or grafted rubbers. The tensile strength of the NR composite was higher than that of synthetic rubbers having irregular chain structures, that is, amorphous; they do not crystallize when stretched [27]. The lowest tensile strength was exhibited by SBR, which may be

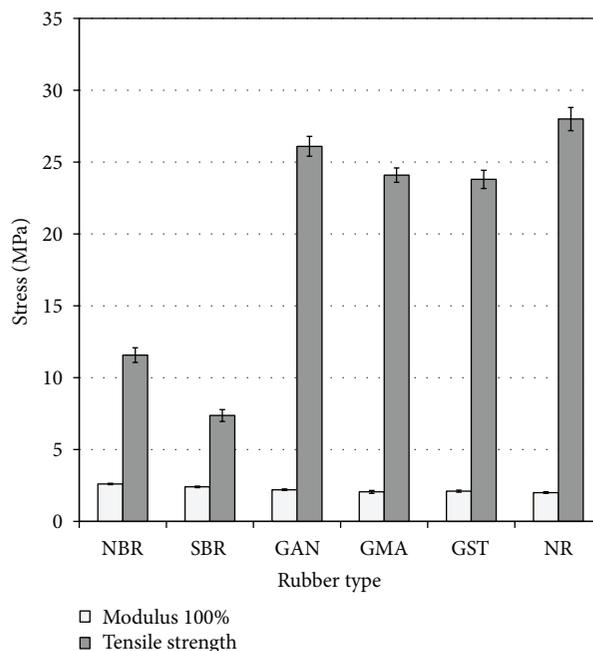


FIGURE 4: Tensile properties of various rubber matrices filled with 40 phr silica.

attributed to the presence of phenyl groups which prevented crystallization on stretching [28]. On the other hand, it can be seen that the silica distribution is affected significantly by the difference in polarity between NBR and SBR. This may be attributed to a higher filler-rubber interaction between the cyano groups in NBR and the hydroxyls on the silica surface which provided an improvement in the filler-rubber interaction and led to a better distribution of the filler in the rubber matrix; thus, a higher tensile strength should be observed in NBR when compared with that of SBR. Similar results have also been reported by Darwish et al. [29] who worked on the effect of polyacrylonitrile as a compatibilizer in SBR/NBR blends on their properties and compatibility. In addition, the higher tensile strength of NR was found to be slightly greater than that of the GNRs. The reduction in tensile strength of the GNRs was probably due to the grafting of vinyl monomeric molecules onto the backbone of the NR chains which provided more space between the polymers and reduced the entanglement of polymeric chains on applying stress, leading to a lower tensile strength. The order of the polarity of the vinyl monomers was AN, MMA, and ST. Therefore, it can be expected that, in the case of the stronger molecular polar grafting side chains of GAN, a stronger interaction was achieved, so that the silica filled composites possessed better tensile strength, relative to the grafting of a low polar (GMA) or nonpolar (GST) side chains. Sobhy et al. [30], in their study on the effect of  $CaCO_3$  addition to NR or NBR on the cure characteristics and physicochemical properties, reported that the dispersion of the filler on the rubber matrix or filler agglomeration depended mainly on both the filler content and type. The presence of polarity within the rubber chains is believed to play a significant role

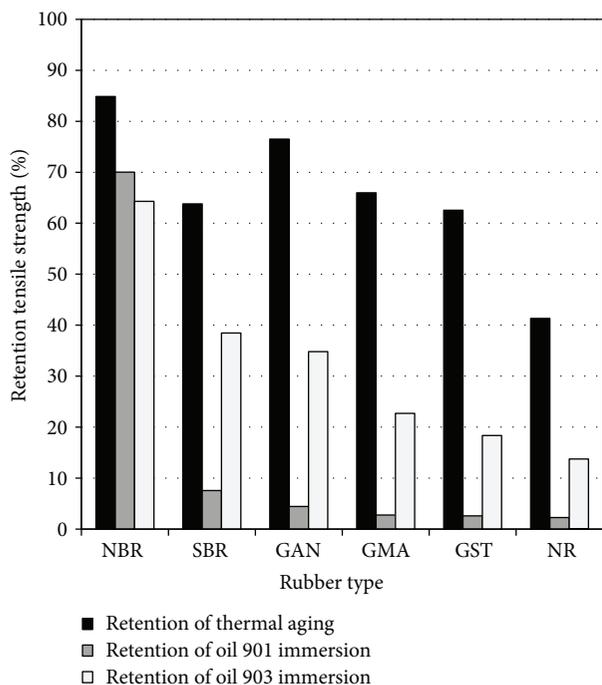


FIGURE 5: Percent retention of tensile strength of various rubber matrices filled with 40 phr silica after aging at 100°C for 72 h.

in providing a good interaction with silica, thus enhancing reinforcement [31].

The synthetic composites exhibited, in comparison, a higher Young modulus than the GNRs and NR composites as shown in Figure 4. This may be attributed to the restriction of molecular chain movements resulting from filler-rubber interaction and leading to an increase in the stiffness of the composites. As discussed before, a better filler-rubber interaction of silica in the NBR matrix, consequently, showed a higher value of the modulus compared to the SBR composite. The modulus of NR showed a lower value than GNRs. Again, this was probably due to the movement of molecular chains on stretching which was restricted by the grafted chains. Additionally, GNR containing high polarity functional groups had a higher modulus value compared to GNR containing low polarity functional groups. The Young modulus arising from filler-rubber interactions can be increased when a good dispersion of the filler is possible within the rubber, which is dependent on the chemical nature of the rubber [32]. Similar results have been observed for grafting of methyl methacrylate onto natural rubber latex by gamma irradiation for improving the mechanical properties of dry films [11].

Figure 5 shows that all of the composites, after thermal aging at 100°C for 72 h in air, exhibited a reduction in tensile strength, compared to before aging, indicating thermal degradation of the matrixes of the rubbers. The decline in tensile strength for these materials could be attributed to the rubber which can react with oxygen, thus leading to chain scission or reduced crosslink formation between the rubber chains. The silica filled NBR composite possessed the highest retention in tensile strength, followed by GAN, GMA, SBR,

GST, and then the NR composites. The results reveal that the NR composite was affected by thermal oxidative aging more than synthetic and grafted rubbers as it contained non-polar functional groups. On the other hand, the double bonds in NR were more reactive to thermal oxidative degradation than synthetic and grafted rubbers and therefore possessed the lowest retention value. Furthermore, excessive main chain scission resulted in a reduced tendency to crystallize with increasing temperature. As discussed earlier, the polarity of the rubber matrix provided a relatively strong interaction between the silanol group on the silica surface and polar functional groups of GNR being a polar rubber; thus, the distribution of the silica in the rubber matrix may be an easier process. This led to good thermal stability.

The effect of molecular polarity in a rubber matrix on the percentage of retention in tensile strength of the composites after being immersed at 100°C for 72 h in a low polar hydrocarbon oil (IRM 901) and in a more polar hydrocarbon oil (IRM 903) is shown in Figure 5. There was a remarkable difference in their retention strength. The percentage retention for silica filled NBR was larger, whereas it was smaller for silica filled SBR, GNR, and NR composites, respectively. However, NBR showed the highest retention followed by SBR, GAN, GMA, GST, and NR. The filler-rubber interaction was more remarkably improved in the case of the silica filled NBR composite (due to the presence of the nitrile group) compared with the silica filled SBR composite, so the percentage retention of the first was considerably higher than the second. The filler-rubber interaction caused limitations in the ease of penetration of oil into the rubber chains. This also implies that the presence of polarity of the rubber is believed to play a significant role in raising a good filler-rubber interaction which resisted the penetration of the oil into the voids between the rubber chains. NBR displayed less resistance in IRM903 oil than IRM901 oil, whereas other composites showed a different result between both oils. This agrees with the discussions mentioned earlier. NBR with a strong molecular polarity, in the more polar hydrocarbon oil (IRM 903), showed a lower retention than in the low polar hydrocarbon oil (IRM 901) and became more penetrable by the high polar hydrocarbon oil (IRM 903) and less penetrable by the low polar hydrocarbon oil (IRM 901). As expected, retention of tensile strength on oil resistance was higher in silica filled GNR composites compared with the silica filled NR composite due to the poor interaction between the NR matrix and silica particles because of the differences in polarity. This indicates that rubber with strong molecular polarity showed a good interaction with silica, which helped to improve the restriction extensibility of the rubber chains and made it more difficult for oil to diffuse into the voids between the rubber chains and increased the percentage retention. The presence of polar functional groups within the rubber matrix was found to improve aging resistance of the rubber composites.

The results of percentage retention of Young's modulus based on the changes in tensile modulus after thermal aging and oil immersion at 100°C for 72 h are presented in Figure 6. All the vulcanizates showed an increase in tensile modulus

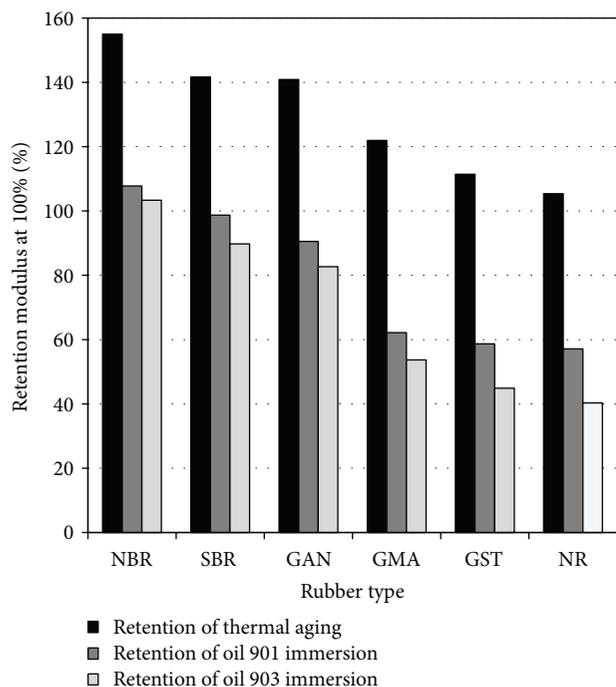


FIGURE 6: Percent retention of Young's modulus at 100% of various rubber matrices filled with 40 phr silica after aging at 100°C for 72 h.

after thermal aging. It was found that NR possessed lower modulus than those of synthetic and grafted rubbers. Rubbers reacted with oxygen resulted in chain scission or the oxidative breakdown during thermal aging. This resulted in the generation of rubber macroradicals, which in recombination with the rubber macroradicals formed rubber chains with some degree of branching. Thus, the composites would become stiffer resulting in higher tensile modulus. From Figure 6 it can be seen that the retention of the tensile modulus of NBR showed a higher value than SBR, GNRs, and NR. This is likely due to the strong interaction between silica and polar rubber which tended to restrict the flexibility of the rubber chains.

Unlike thermal aging, the 100% modulus showed a significant decrease as shown in Figure 6. The reduction in retention of modulus of the composites, after being immersed in both oils, may be due to the diffusion of oil molecules through the rubber phase. Thus, the composites will become softer. As expected, the lowest retention of tensile modulus is found for NR, and the highest retention value is found for NBR. The order of maximum retention of tensile modulus was NBR > SBR > GAN > GMA > GST > NR. As discussed before, this was due to the polarity of rubber and better interaction of silica in the polar rubber matrix, which consequently resulted in less oil penetration into the rubber matrices.

Optical photographs of the surfaces of the vulcanized rubbers of ozone exposed samples are presented in Figure 7. The nature and intensity of cracks due to ozone attack are different for the various rubbers. In the case of the NBR composite, the crack density was less and the composite showed fine cracks which were not open as represented by the horizontal lines (Figure 7(a)), which confirms that the crack growth was retarded. Generally, no serious deterioration was

detected during the indicated period of ozone aging. Longer fine cracks propagated in a straight manner as was observed for the SBR composite (Figure 7(b)). Compared with the filled GAN and GMA composites, both showed long and wide cracks without much deviation as seen in Figures 7(c) and 7(d), but the crack density was less. However, for silica filled GST composite (Figure 7(e)), a high density of short and wide ozone cracks were found on the specimen surface. The cracks found in synthetic rubber composites were less severe, compared to the GNR composites. This implies a lower reactivity of double bonds to ozone attack and a strong interaction between silica and polar rubber which led to less ozone cracking on the surface of the rubber specimen. In the case of the silica filled NR composite, which has highly reactive double bonds to ozone; the highest level of severe ozone cracks was deep, wide, and continuous in NR (Figure 7(f)). The growth of ozone cracks were initiated in the rubber matrix and the cracks grew over the critical length, resulting in brittleness and macroscopic cracks on the surface of the NR specimens. This is probably due to the poor filler-rubber interaction between silica and nonpolar rubber and nonuniform dispersion of the filler in the matrix. The photograph clearly confirms that crack growths were stopped more effectively by the strong filler-rubber interaction between silica and the polar rubber. The strong interaction, giving rise to more finely dispersed filler particles, prohibited the growth of ozone cracks initiated in the rubber matrix before the cracks grow over a critical length for failure. Thus, the ozone resistance of the silica filled GNR composites improved slightly, whereas the ozone resistance of the silica filled NR composite was inferior.

Figure 8 shows the SEM micrographs of the tensile fractured surface of NBR (a), SBR (b), GAN (c), GMA (d), GST (e), and NR (f) composites taken at a magnification of 3000x. The smooth surface without matrix tearing lines observed in the NBR composite (Figure 8(a)) indicated a brittle material which contributed to a low tensile strength. The fractured surfaces showed poor dispersion and interaction in SBR (Figure 8(b)), whereby agglomeration occurred and many small pores indicated that the interaction between the silica and rubber was weak, leading to the lowest values in the tensile properties as compared to other materials. However, the failure mode changed in the presence of PAN, PMMA, and PST in the rubber matrix as shown in Figures 8(c), 8(d), and 8(e) which represent the grafting of NR with AN, MMA, and ST monomers, respectively. Figures 8(c) and 8(d) show a smoother surface with the presence of matrix tearing lines in both the samples indicating greater filler dispersion in the GAN and GMA matrices, respectively, and these had higher tensile properties compared to the GST composite. The SEM micrograph of the GST composite shows the presence of agglomeration and a few tiny holes which indicated the inhomogeneous distribution of silica (Figure 8(e)). This led to poor interaction between silica and the rubber. The micrograph of the fracture surface of the NR composite in Figure 8(f) shows more rough surfaces with many tearing lines indicating a typical feature of ductile failure which contributed to the highest tensile strength. These results correlated well with the interaction

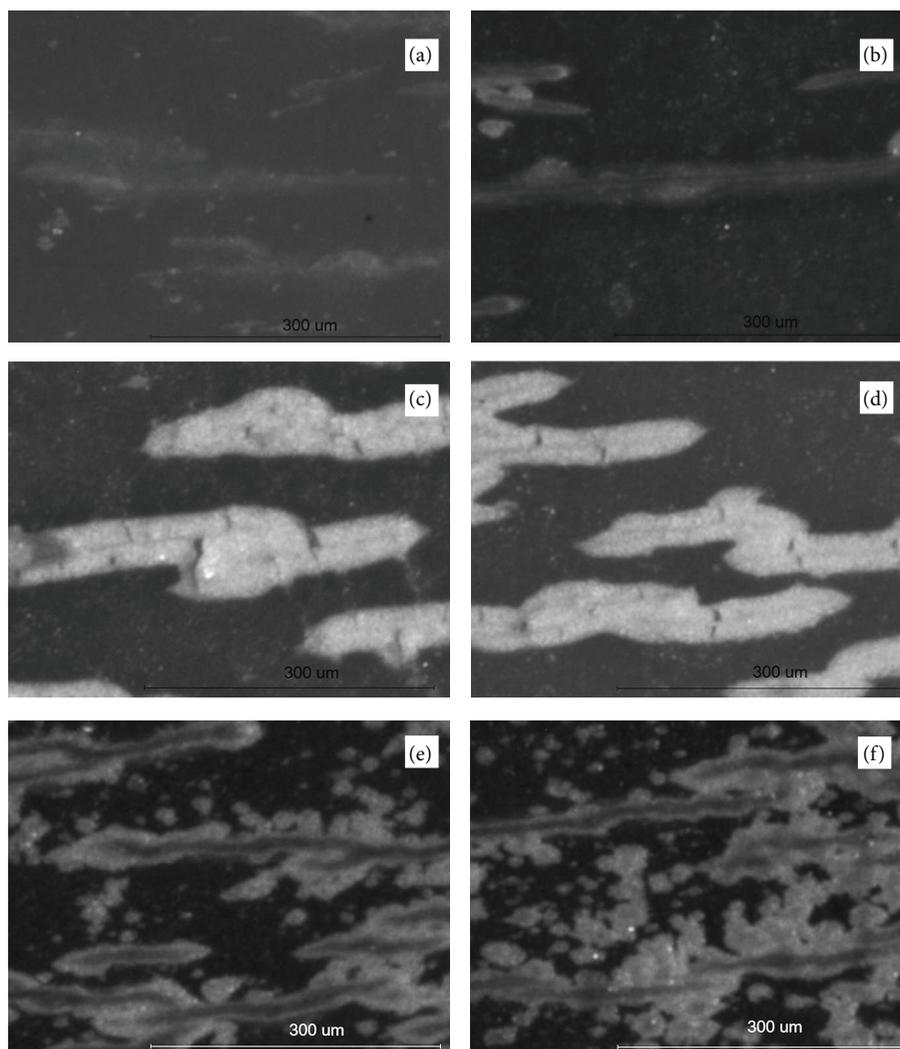


FIGURE 7: Optical photographs of ozone exposed: (a) NBR, (b) SBR, (c) GAN, (d) GMA, (e) GST, and (f) NR ( $\times 50$ ).

between the polar functional groups of rubber molecules and silica particles giving rise to a more homogeneous structure. Therefore, a better distribution of silica particles in the rubber matrix and an improvement in the tensile properties of the composites were observed.

#### 4. Conclusion

NR latex investigated in this study has been chemically modified by seeded emulsion polymerization; a NR particle was coated with a shell of various vinyl monomers such as AN, MMA, and ST to promote filler-rubber interaction. The physical properties of vulcanized GNRs were comparable to those of vulcanized NBR, SBR, and NR. The Mooney viscosity and  $t_{90}$  of NBR and SBR were found to be higher and longer than those of GNRs and NR, whereas the tensile properties of NBR and SBR were found to be lower. Tensile strength was slightly reduced by the presence of polar functional groups within the GNR materials whereas the Young modulus increased, as compared to NR. This can be

attributed to the good mechanical properties of NR due to strain-induced crystallization. Aging test results showed that the tensile strength decreased while the Young modulus may increase or decrease with accelerated aging. The presence of the polar polymer backbone structure resulted in an improvement in the resistance of the materials to thermal, oil, and ozone because of the presence of polar side chains on the backbone structure. Increasing the polarity of modified NR also improved resistance to attack by hydrocarbon oils and solvents. This may be attributed to the stiffness of the composites which made the rubber matrix less penetrable by hydrocarbon oils and solvent. Morphology studies of the compounds indicate that GNR has changed the fracture surface behavior from ductile behavior to brittle type. Overall, the grafting of an olefinic monomer onto NR gave it increased polarity and provided better aging resistance with slight reduction in tensile strength as compared to NR which was attributed to providing better reinforcement by polar silica filler with an improved resistance to accelerated aging.

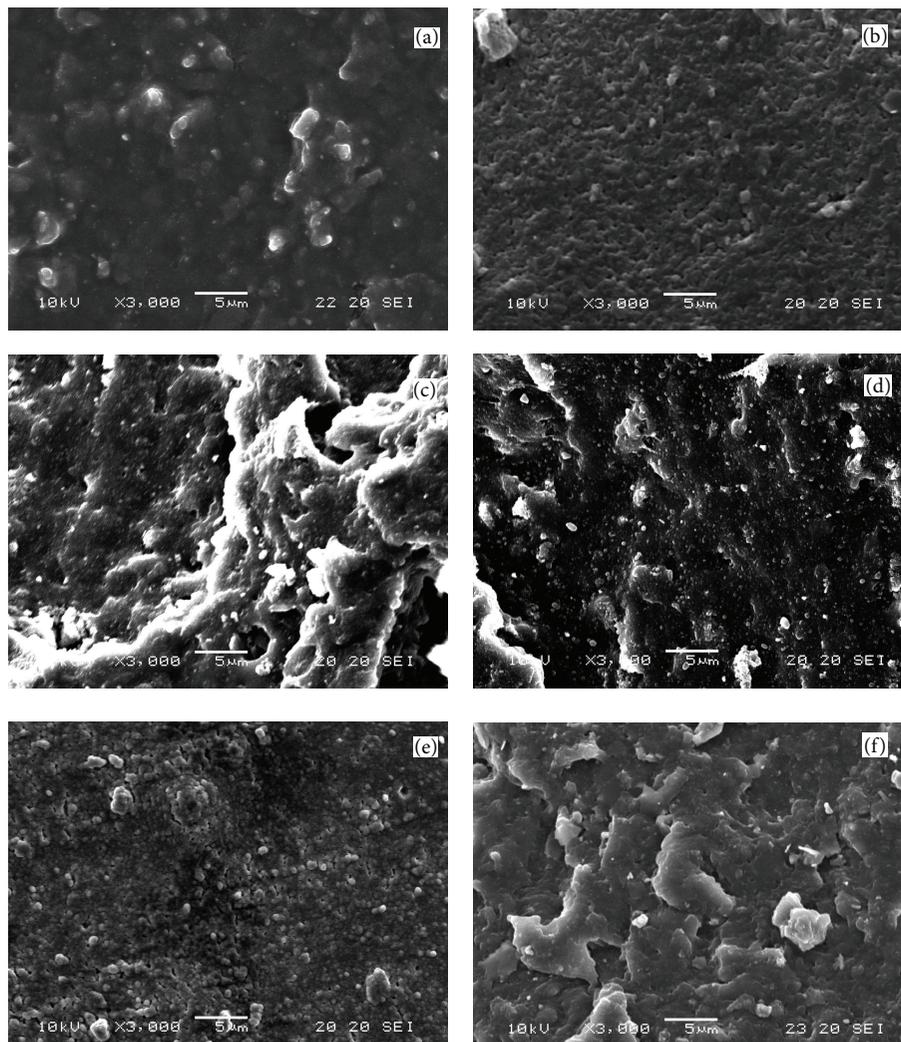


FIGURE 8: Scanning electron micrograph of tensile fracture surface of (a) NBR, (b) SBR, (c) GAN, (d) GMA, (e) GST, and (f) NR obtained at magnification of 3,000x.

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