

# Morphology and Mechanical Properties of Natural Rubber and Styrene-Grafted Natural Rubber Latex Compounds

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

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

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

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**ABSTRACT:** The mechanical properties of natural rubber latex (NRL) modified with styrene-grafted natural rubber (styrene-GNR) latex were investigated. Styrene-GNR was first synthesized via emulsion copolymerization using cumene hydroperoxide/tetraethylene pentamine as an initiator. The styrene-GNR latex produced was mixed with NRL with various latex compounding contents and then prevulcanization was carried out. The mechanical properties and heat, weathering, and ozone resistance of the natural rubber (NR) and styrene-GNR latex compounds were investigated as a function of the grafted NR content. The results indicated that the tensile and tear strength were decreased, whereas Young's modulus and hardness were increased at high content of styrene-GNR. Addition of sty-

rene-GNR improved the resistance of the compounds to heat and weathering ageing. The ozone resistance of the compound containing styrene-GNR is superior to that of the NR-rich compound. The results indicated that NR/styrene-GNR latex compounds maintained good antiageing properties required for outdoor applications. The tensile fracture surface examined by scanning electron microscopy confirmed a shift from ductility failure to brittle with an increase of the styrene-GNR content in the compounds. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 1395–1402, 2008

**Key words:** natural rubber; latex; graft copolymer; styrene; compound; ageing resistance

## INTRODUCTION

Graft copolymerization has attracted much attention and is applicable to a new class of specialty polymers with an expanded useful range. Graft copolymers are produced when a vinyl monomer is polymerized in the presence of preformed polymer containing double bonds to give chemical bonding to that polymer. Natural rubber (NR) obtained from *Hevea brasiliensis* is classified as one of the most important natural resources used industrially, as it is well-known to be the most excellent rubbery material, having outstanding mechanical properties while it is weak in oil-resistance, weather-resistance, and ozone-resistance. The chemical modification of NR by grafting with vinyl monomers combines the properties of both NR and the polymer of the monomer grafted. It has gained considerable importance as it leads to polymers with altered and improved properties for the production of new materials.<sup>1</sup> The

most promising graft copolymer based on NR, thus far obtained, is that derived from methyl methacrylate (MMA) and styrene (ST). The graft copolymer may be prepared by graft copolymerization of NR in latex form, since the NR, an unsaturated elastomer having the existence of double bonds in its chains, can be readily grafted with a variety of monomers, using the well-established technique of seeded emulsion polymerization.<sup>2–7</sup> Natural rubber latex (NRL) has a broad size distribution of particles having an average size of about 0.7  $\mu\text{m}$ .<sup>8</sup> Styrene-grafted natural rubber (styrene-GNR) latex is a kind of specialty latex produced by chemical modification of NRL.<sup>1,9,10</sup> ST monomer is graft copolymerized with NRL under the action of a free-radical catalyst to produce graft copolymer. Because the rigid chains of polymer are grafted onto the flexible chains of NR, this characteristic molecular geometry gives grafted NR having high resistance to the outdoor environment. However, grafted NR is poor in film-forming properties and processability. NRL possesses excellent film-forming properties and has been widely used in the manufacture of dipping products such as gloves, condoms, and catheters, but the hardness of this film is lower, and the tear strength of this film is comparatively poor. Lu et al.<sup>11</sup> incorporated methyl methacrylate grafted natural rubber latex

Correspondence to: W. Arayapranee (wanvimon@rsu.ac.th).

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(MGL) to increase the modulus and hardness of the film and improved its antiageing properties. The prevulcanized blend of NRL and production of NRL and MGL possessed excellent film-forming properties. However, the systematic study on latex compounds of NR with graft copolymers and the properties of latex compounds seems to be scarce. For the first part of this work, an investigation was directed to the synthesis of the grafted NR with a small amount of polystyrene (PST) by using redox initiator for core-shell type of structured particles. Subsequently, an investigation was carried out on the mechanical properties, effect of heat and weathering ageing on tensile properties, ozone resistance, and morphology studies of the tensile fracture surfaces of films by latex compounding NR with different amounts of styrene-GNR. A systematic study on the property changes of the latex compounds of NR and styrene-GNR was also carried out.

## EXPERIMENTAL

### Materials

The commercial high-ammonia NRL comprised almost entirely of *cis*-polyisoprene had 60% by weight dry rubber content and was produced by Yala Latex Industry (Thailand). Reagent-grade ST ( $C_8H_8$ , purity  $\sim 99\%$ ; Fluka, Switzerland) monomer was destabilized in the conventional way by washing with a 10% aqueous solution of NaOH and then with deionized water until neutral. It was then stored in a refrigerator until required. The emulsifier sodium dodecyl sulfate (purity  $\sim 90\%$ ; BDH, England), the stabilizer isopropanol (BDH), the buffer potassium hydroxide (Aldrich, Milwaukee, WI), the initiators, redox initiator system, cumene hydroperoxide ( $C_9H_{12}O_2$ , CHPO, purity  $\sim 80\%$ ; Fluka, Germany), and the activator agent tetraethylene pentamine [ $HN(CH_2CH_2NHCH_2CH_2NH_2)_2$ , TEPA, purity  $\sim 85\%$ ; Fluka, Switzerland] were used as received. Sulfur (commercial; Chemmin, Thailand), zinc diethyl dithiocarbamate (accelerator, Naftocit DI 7; Chemetall, Germany), and zinc oxide (activator, commercial; Gradmann, Thailand) were used as aqueous dispersions. Deionized water was used throughout the work.

### Preparation of styrene-GNR

The graft copolymerization reaction of ST with NR was carried out in a 2000-mL four-necked, round-bottomed flask equipped with stirrer, thermometer, reflux condenser, and gas inlet tube. Deionized water, emulsifier, stabilizer, and NRL were charged to the reactor and the dissolved oxygen in the ingredients was removed by purging with nitrogen gas for at least 30 min through the mixture, providing

TABLE I  
Graft Copolymerization Recipe

Ingredients	Amount
Water	500 g
60% Natural rubber latex	250 g
Potassium hydroxide	0.60 g
Isopropanol	15 g
Sodium dodecyl sulfate	2.25 g
Initiator amount (CHPO : TEPA = 1 : 1)	$3.3 \times 10^{-2}$ mmol/g rubber
Styrene amount	3.00 mmol/g rubber

still a stable latex. If necessary, buffer was added to maintain the pH of the system at 10. The redox initiation system, consisting of CHPO and TEPA (molar ratio of 1 : 1), was used. The monomer and TEPA as an activator agent were fed to the reactor. The NR seed latex was swollen with the monomer mixture for 1 h at the reaction temperature before adding the initiator. The polymerization reaction was performed at a stirring speed of 400 rpm at 50°C for 5 h. The post treatment included the coagulation of polymer latex and washing with deionized water. The gross polymers were recovered and dried to constant mass in a vacuum oven at 40°C. The recipes for the graft copolymerization are shown in Table I.

The gross polymers were resolved into graft copolymers, free NR, and PST by Soxhlet extraction. A 60–80°C boiling point petroleum ether and a methyl ethyl ketone (MEK)/acetone (50 : 50, v/v) mixture were used for extracting free rubber and PST for 24 h, respectively. The weight difference between the initial sample and extracted samples was used to calculate the measure of grafting efficiency (GE) according to the following relationship:

$$\text{Grafting efficiency (GE, \%)} = \frac{\text{weight of monomers grafted}}{\text{weight of monomers polymerized}} \times 100$$

The presence of functional groups of the graft copolymer was verified using a Bruker (Model Tensor 27, Germany) Fourier transform infrared spectrometer.

The morphology was examined by using a JEOL JEM-1220 transmission electron microscope (Tokyo, Japan) at 120 kV. The grafted latex was diluted 400 times with deionized water to a concentration of 0.025% by weight. To this solution, 1 mL of a 2% aqueous  $OsO_4$  solution was added and allowed to stain the rubber in the graft copolymer overnight.

### Latex compound preparation

Latex compounds of varying composition (0–50%) at 10% intervals by weight were prepared as graft copolymer products. Dispersion (50%) of commercial

**TABLE II**  
**Formulation of the NR Latex Compound**

Ingredients	Dry (parts by weight)
60% Natural rubber latex	Variable 100, 90, 80, 70, 60, 50
24% Grafted natural rubber latex	Variable 0, 10, 20, 30, 40, 50
50% ZDEC dispersion	1.0
50% Sulfur dispersion	1.5
50% Zinc oxide	2.0

chemicals was prepared by using a ball mill. The latex was mixed with the compounding ingredients according to the formulation given in Table II. The latex compounds were prevulcanized in a water bath at 60°C and stirred well for 2 h providing a homogeneous mixture. The compounded latex was then matured (keeping overnight to facilitate the diffusion of added chemicals), which ensures latex films of uniform properties. The compounded latex, after removing residues and coarse particles by filtering through a sieve (opening: 250  $\mu\text{m}$ ) is then cast on raised glass plates having a dimension of 13 cm  $\times$  13 cm  $\times$  2 mm. The cast film was then allowed to dry in air until transparent and then vulcanized at 70°C for 4 h in an air circulated oven. The vulcanized samples thus obtained were kept in a desiccator prior to mechanical testing.

### Mechanical properties

Tensile properties were determined on an Instron universal testing machine (model 4466; Instron, Canton, MA) using C-type Dumbbell-specimen, according to ASTM D 412. The tear strength was measured in an Instron universal testing machine according to ASTM D 624 (Die C). Hardness measurement of samples was done according to ASTM D 2240 (Shore A) using a Bajeiss Serial DTE 5205/03 instrument (MEGA Advance, Berlin, Germany).

### Ozone ageing

Ozone ageing studies under static conditions were conducted according to ISO 1431/1-1980 (E) in a Hampden (Model 1008-AH, Northampton, England) ozone test chamber at 40°C. Ozone concentration in the chamber was adjusted to 50 parts per hundred million (pphm). The ozonized oxygen generated in the ozonizer by a UV quartz lamp was collected in a separate chamber where the sample was exposed.

### Accelerated thermal ageing test

Tensile specimens were aged at 100°C for 72 h in an air-circulating ageing oven and the tensile properties of the aged samples were determined according to

ASTM D 573 (1994). Tensile test (ASTM D 412-99) was carried out on a tensile dumbbell test specimen before and after ageing to estimate ageing resistance.

### Weatherability

Tensile specimens were tested in the Q-U-V Accelerated Weathering Tester (Cleveland, OH) by exposing them to alternating cycles of light, using an UV lamp with 315 nm wavelength and 0.63 W/(m<sup>2</sup> nm) intensity at 60°C/4 h, and moisture, condensation in the dark at 50°C/4 h, for 14 days according to ASTM G 154-00a.

### Scanning electron microscopy

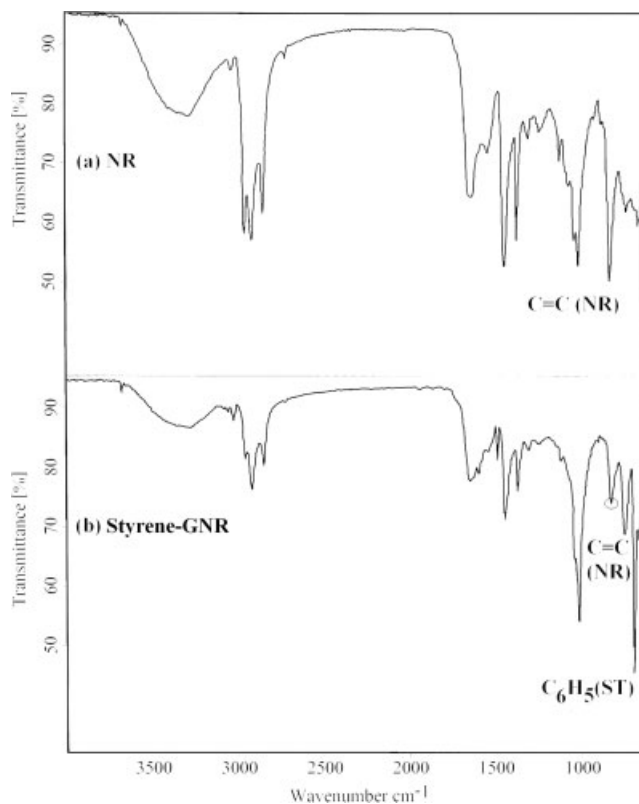
Scanning electron microscopic (SEM) studies of the compounds, after exposure to ozone, at a magnification of 50 and tensile fracture surfaces at a magnification of 3000 were carried out on gold-coated samples using a Joel Microscope (model JSM 5600 LV; Tokyo, Japan).

## RESULTS AND DISCUSSION

### Styrene-GNR characterization

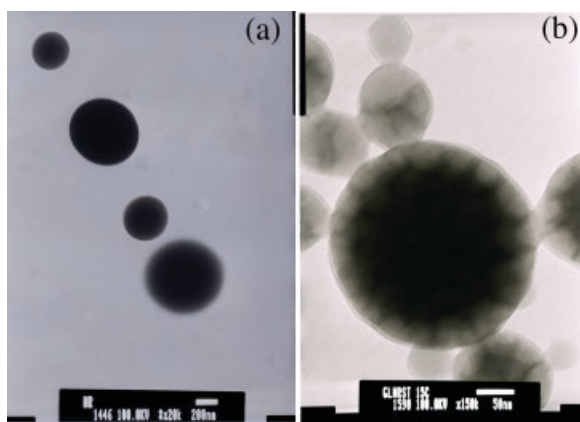
Styrene-GNR latex had 24% by weight dry solid content. Free rubber and PST are removed using petroleum ether and the mixture of acetone and MEK, respectively. The degree of GE was 89.09%. This value was obtained gravimetrically. For this work,  $\sim$  10% of the initial 3 mmol of ST remained unreacted at the end of the reaction and 0.26 mmol of the styrene was incorporated into rubber. The graft copolymer product was composed of 88.16 wt % graft copolymer, 2.52 wt % free polymer, and 9.32 wt % free rubber. After solvent extraction, the graft copolymer was analyzed by FTIR. Figure 1 shows the FTIR spectrum for the residue (the styrene-GNR). There are two characteristic peaks attributed to R<sub>2</sub>C=CHR of isoprene and the monosubstituted benzene ring of ST at wavenumbers of 837 and 698 cm<sup>-1</sup>, respectively. A similar type of observation in the IR spectra was also reported Asaletha et al.<sup>12</sup> and Xavier et al.<sup>13</sup> However, the spectra of ST-grafted chemically modified NR shows an additional peak of a monosubstituted benzene ring at 698 cm<sup>-1</sup>. This indicates the presence of the ST unit in the grafted NR and provides strong evidence of grafting.

The morphology of NR and the graft copolymer is shown in Figure 2. The grafting of ST onto the NR is a core-shell type, via emulsion copolymerization. The graft copolymer particles consist of the NR core and the compatibilized PST shell. The darker areas represent the NR core regions, while the lighter



**Figure 1** FTIR spectrum of polymers: (a) NR and (b) Styrene-GNR.

areas are the PST film as shell. The surface of the NR particle is smooth [Fig. 2(a)]. The presence of nodules on the surface of the graft copolymer may be due to the growing macroradical chains, which are grafted onto the surface of the NR particle which continue to propagate to form the shell layer. The second stage polymer shell onto the core particle produces heterogeneous structures (core-shell structures), which are formed by phase separation of incompatible polymers during polymerization. This



**Figure 2** Transmission electron micrographs of polymers: (a) NR ( $\times 160,000$ ) and (b) Styrene-GNR ( $\times 150,000$ ). [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

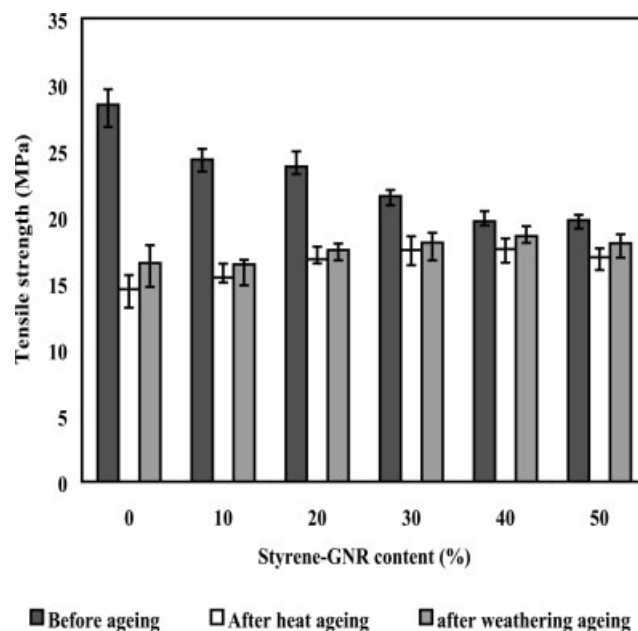
is also confirmed by the results shown in Figure 2(b) that the NR core of about 200 nm in diameter was encapsulated by PST with the thickness of the graft-copolymerized layer was less than 50 nm.

### Effect of GNR content on mechanical and morphological of latex compounds

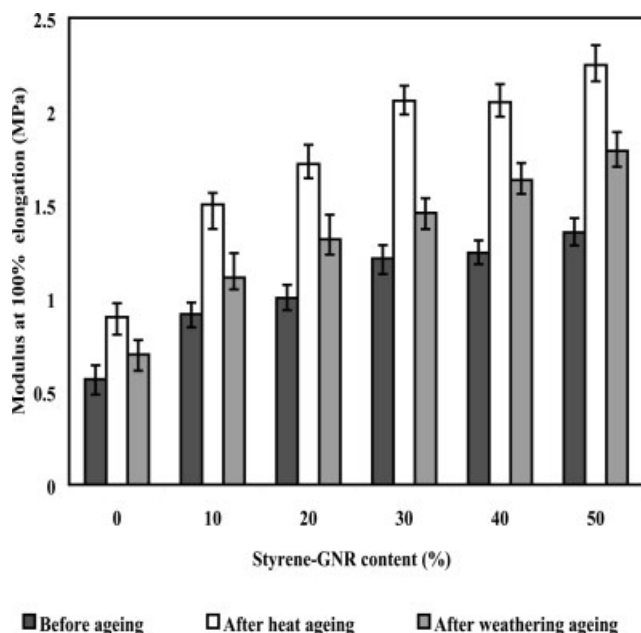
NRL possessed excellent film-forming properties and the film casted from NRL was soft and tacky. The styrene-GNR was poor in film-forming properties. When blending NRL with styrene-GNR latex, a combination of elastic properties of NR and hardness of styrene-GNR was obtained. The blend still possessed good film-forming properties similar to those of NRL. However, the film-forming properties were somewhat stiffer and less tacky than a NR film when the styrene-GNR content was increased.

### Tensile properties before ageing

Styrene-GNR latex was incorporated in different amounts of NRL up to 50% in the prevulcanized compounds to study the effect of styrene-GNR content on the tensile properties of the styrene-GNR/NR latex compounds. For this purpose, variation in the tensile properties of the compounds, such as tensile strength and modulus at 100% elongation with amounts of styrene-GNR are referred to in Figures 3 and 4, respectively. Tensile strength is an important characteristic of polymeric materials because it indicates the limit of final stress in most application. Fig-



**Figure 3** The effect of styrene-GNR content on tensile strength of compound before and after ageing.



**Figure 4** The effect of styrene-GNR content on modulus values at 100% elongation of compound before and after ageing.

Figure 3 shows the tensile strength of un-aged and aged styrene-GNR/NR latex compounds as a function of styrene-GNR content. Tensile strength of these compounds is primarily dependent on the styrene-GNR content in the compound. It can be seen that tensile strength of un-aged styrene-GNR/NR latex compounds decreased with an increase in the amount of styrene-GNR. The NR rich compounds possessed the highest tensile strength as expected, due to the NR crystallinity exhibited upon stretching. As more the rigid chains of PST were introduced into compound, the elasticity of the NR chains is reduced, leading to lower tensile strength at higher styrene-GNR content.

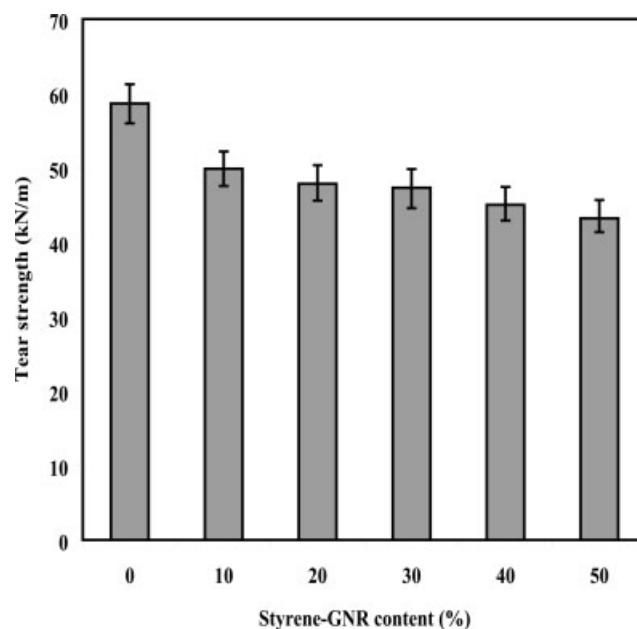
Young's modulus is an indication of the relative stiffness of the material. The effect of styrene-GNR content on modulus at 100% elongation of the compounds is illustrated in Figure 4. The modulus at 100% elongation showed an increase with an increase in the amount of styrene-GNR. As discussed earlier, the presence of styrene-GNR improved the rigid properties of the compounds, thus leading to the formation of compounds that exhibited higher modulus at 100% elongation at higher styrene-GNR content.

#### Tensile properties after ageing

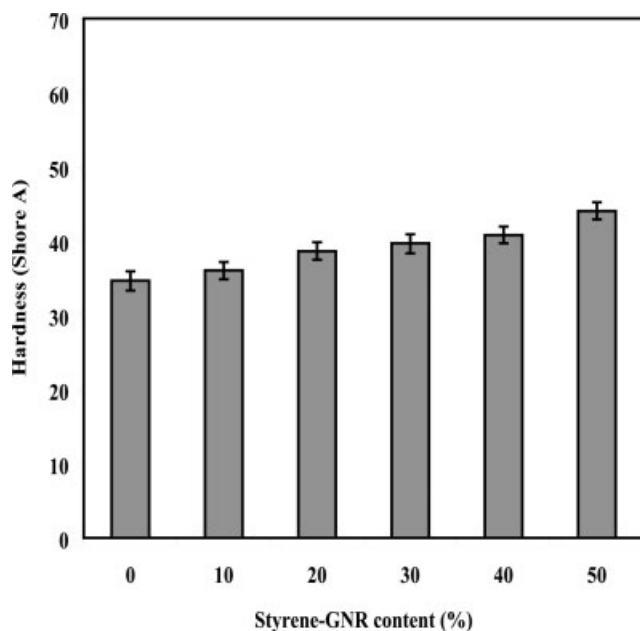
The influence of heat and weather ageing on the tensile properties of the compounds is shown in Figures 3 and 4. For all of the compounds after ageing showed a lower tensile strength but a higher

Young's modulus than the compounds before ageing. Regardless of their composition and nature, all of the compounds exhibited a reduction in tensile strength, indicating a deterioration of their properties with accelerated ageing.<sup>14</sup> The accelerated ageing of rubbers that contain unsaturated bonds normally reduces their strength properties. Figure 3 shows the tensile strength of the compounds after accelerated ageing. The retention in tensile strength of the compounds increased with an increase in content of styrene-GNR. The superiority of compounds containing styrene-GNR, with respect to tensile after ageing was obvious. The result may be related to a decreasing of the unsaturated bonds in the compound by grafting ST onto NR, resulting in an improvement of the resistance of the compounds to heat and weather ageing. This indicates that the presence of styrene-GNR in compounds showed good antiageing properties. A similar observation has been made by Lu et al.<sup>11</sup> in the case of latex compounding NR with MMA-grafted NR.

The effect of heat and weather ageing on Young's modulus is illustrated in Figure 4. Young's modulus for all of the compounds containing styrene-GNR at a given loading shifted to a higher value after ageing. These increases are generally attributed to increases in the stiffness of the rubber matrix brought about by a reduction in the number of double bonds after ageing. On comparing these results, it is observed that the compounds after heat ageing mostly showed a higher 100% Young modulus than the compounds after weather ageing.



**Figure 5** The effect of styrene-GNR content on tear strength of compound.



**Figure 6** The effect of styrene-GNR content on hardness of compound.

### Tear strength

Tear strength, like tensile strength, is affected by the presence of styrene-GNR. Figure 5 shows the tear

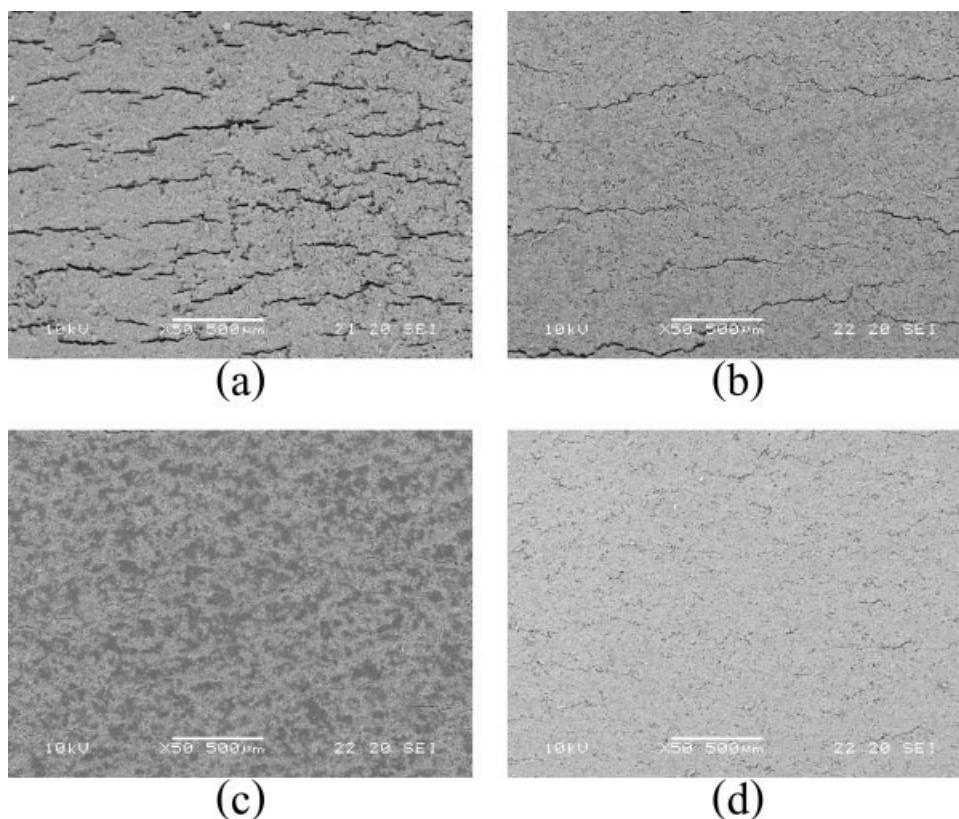
strength of the rubber materials. As can be seen, the addition of styrene-GNR decreased the tear strength of the rubber materials. This is mainly attributed to the presence of the rigid chains of PST in the rubber chains showing poor elasticity of the rubber chains, thus resulting in poor strength properties. For this reason, both tensile and tear strengths were decreased with increased loading of the styrene-GNR.

### Hardness

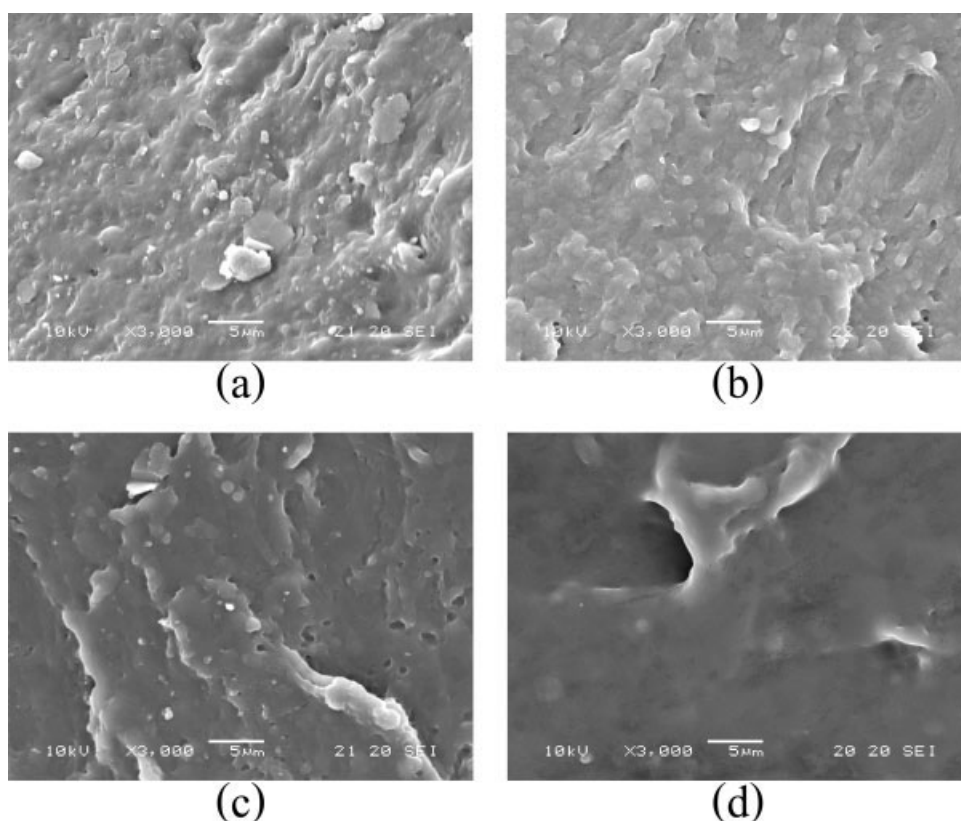
Figure 6 shows the effect of styrene-GNR content on hardness of rubber material. Hardness of the rubber materials increased with increasing styrene-GNR quantity. In addition, the trend of the results for hardness is similar to those for the Young's modulus. This is simply due to the fact that incorporation of more rigid chains of PST into rubber compound reduced elasticity of the rubber chains, thus enhancing stiffness properties.

### Ozone ageing

The interaction of rubber with ozone is best noted when the rubber is stressed or stretched in use. To assess the ozone resistance of the compounds, test



**Figure 7** SEM micrographs of ozone exposed: (a) NR-rich compound and NR compound with (b) 10% styrene-GNR, (c) 30% styrene-GNR, and (d) 50% styrene-GNR ( $\times 50$ ).



**Figure 8** SEM micrographs of tensile fracture surfaces: (a) NR-rich compound and NR compound with (b) 10% styrene-GNR, (c) 30% styrene-GNR, and (d) 50% styrene-GNR ( $\times 3000$ ).

samples having 20% strain were exposed to ozonized air of 50 ppm ozone concentration for 72 h at 40°C in the dark. However, the nature and intensity of cracks due to ozone attack are different for various contents of grafted NR. In the case of the NR compound, the ozone resistance of the compounds was inferior. NR is prone to be deteriorated by highly unsaturated polymer backbone.<sup>15</sup> The increase in the ozone resistance of the compounds containing styrene-GNR can be visualized using SEM technique. SEM micrographs of the surfaces of the ozone exposed samples are presented in Figure 7. The micrographs clearly show that the NR rich compound showed the wider and deeper cracks represented by the horizontal lines [Fig. 7(a)] while fine cracks were observed for the sample containing 10% styrene-GNR [Fig. 7(b)]. In the case of compounds that contained 30 and 50% of styrene-GNR, all showed fewer fine cracks as seen in Figure 7(c,d), which confirms that crack growths were stopped more effectively by the presence of styrene-GNR in the rubber matrix. This is due to the fact that the highly ozone resistant styrene-GNR is a functional polymer with lower double bond content in the backbone structure, which results in the protection of the weak NR against ozone attack. From the micrographs it is evident that the ozone resistance of

the compounds increased as the proportion of styrene-GNR in the compounds was increased. The ozone resistance of the compounds containing styrene-GNR is superior to the NR-rich compound. Results revealed that when styrene-GNR was added to the compound, it went more into the polymer phase. That is, higher amounts of PST in grafted rubber prohibit the growth of ozone cracks initiated in the rubber matrix before the cracks can grow to such a critical length leading to failure. Thus, the ozone resistance of the styrene-GNR added compounds improved remarkably. The effect of weather ageing on the appearance, especially yellowing, of the styrene-GNR compounds increased in the stiffness of the film. This clearly proves the suitability of the present compound system for outdoor applications.

### Morphology

The morphology of latex compounds with and without styrene-GNR after tensile fracture is shown in Figure 8. The NR present is identified as fibrils, and the introduction of long fibrils has been related to the ductility of the material which indicates the higher tensile strength of NR-rich compound [Fig. 8(a)]. Arayaprane et al.<sup>16</sup> in the case of the incorpo-

ration of various fillers into NR compound reported that the rough surface with tear lines (fibrils) is a typical feature of ductile failure, which indicates the higher tensile strength and the scaly surface, which resulted in the brittle failure, hence the enhancement in the stiffness. The addition of styrene-GNR in rubber compounds is shown in Figure 8(b–d); it can be seen that the higher content of styrene-GNR caused more brittle and scaly surface showing microcharacteristics typical of a rigid and glassy type as evidenced by the absence of fibrils on the fracture surface. Consequently, the tensile was also low as shown by the experiments (compare with NR-rich compound).

### CONCLUSIONS

The preparation and characterization of polymer blends with structured NR-based latex particles are carried out by a batch emulsion polymerization process; a NR latex particle was coated with a shell of PST. The amount of GE was 89.09% determined by a solvent-extraction technique. By mixing NR uniformly with styrene-GNR and then carrying out prevulcanization, materials were produced via a latex compounding method. The prevulcanized blend of NRL and styrene-GNR latex possessed good film-forming properties. The amount of styrene-GNR strongly influenced the mechanical properties of the NR-based compound. Tensile and tear strength were reduced with increasing styrene-GNR content whereas the Young modulus and hardness increased. Ageing test results showed that the tensile strength decreased and Young modulus increased with accelerated ageing. Incorporation of styrene-GNR resulted in improvement of the resistance of the compounds to heat and weather ageing because of the presence of PST on the backbone chains in the compounds. The compounds containing styrene-GNR also had better resistance towards ozone exposure. On the other hand, the graft copolymer has

low carbon–carbon double bond content on the main chain which could undergo vulcanization; however, the functional polymer on backbone structure provides improved resistance to outdoor ageing. The study by Lu et al.<sup>11</sup> also reported similar observation. Morphology studies of the compounds indicate that the addition of styrene-GNR has changed the fracture surface behavior from ductile behavior to brittle type. Suitable application for the blends of NRL and styrene-GNR latex having high modulus and good ageing resistance could be the use in the production of NRL thread.

### References

1. Kawahara, S.; Kawazura, T.; Sawada, T.; Isono, Y. *Polymer* 2003, 44, 4527.
2. Anancharungsuk, W.; Tanpantree, S.; Sruanganurak, A.; Tangboriboonrat, P. *J Appl Polym Sci* 2007, 104, 2270.
3. Schneider, M.; Pith, T.; Lamba, M. *J Appl Polym Sci* 1996, 62, 273.
4. Hourston, D. J.; Romaine, J. *J Appl Polym Sci* 1990, 39, 1587.
5. Nakasorn, C.; Pechurai, W.; Sahakaro, K.; Kaseman, A. *J Appl Polym Sci* 2006, 99, 1600.
6. Mishra, S. N.; Lenka, S.; Nayak, P. L. *Eur Polym J* 1991, 27, 1319.
7. Okieimen, F. E.; Urhoghide, I. N. *J Appl Polym Sci* 2002, 84, 1872.
8. Saendee, S.; Tangboriboonrat, P. *Colloid Polym Sci* 2006, 284, 634.
9. Chuayjuljit, S.; Moolsin, S.; Potiyaraj, P. *J Appl Polym Sci* 2005, 95, 826.
10. Fukushima, Y.; Kawahara, S.; Tanaka, Y. *J Rubber Res* 1998, 1, 154.
11. Lu, G.; Li, Z.-F.; Li, S.-D.; Xie, J. *J Appl Polym Sci* 2002, 85, 1736.
12. Asaletha, R.; Groeninckx, G.; Kumaran, M. G.; Thomas, S. *J Appl Polym Sci* 1998, 69, 2673.
13. Xavier, T.; Samuel, J.; Kurian, T. *Int J Polym Mater* 2003, 52, 251.
14. Botros, S. H. *Polym-Plast Technol Eng* 2002, 41, 341.
15. Chang, Y.-W.; Shin, Y.-S.; Chun, H.; Nah, C. *J Appl Polym Sci* 1999, 73, 749.
16. Arayapranee, W.; Na-Ranong, N.; Rempel, G. L. *J Appl Polym Sci* 2005, 98, 34.