

Grafting of Natural Rubber for Preparation of Natural Rubber/Unsaturated Polyester Resin Miscible Blends

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ABSTRACT: Graft copolymers of natural rubber and polystyrene were synthesized by free-radical grafting of styrene monomer onto natural rubber in latex form. The obtained graft copolymers and unsaturated polyester (UPE) resin were mixed and cast at room temperature using methyl ethyl ketone peroxide as an initiator and Co-octoate as an accelerator. The samples prepared from ungrafted natural rubbers exhibited the aggregation of the rubber component, whereas the samples prepared from grafted natural rubbers showed good dispersion of the rubber component in a glassy matrix of UPE resin. It was found that the amount of polystyrene grafted onto natural rubber and the graft copolymer content in polymer blend significantly affect the

mechanical properties of the blend samples. An increase in the amount of hard and brittle polystyrene in glassy matrix of UPE resin overshadowed the impact-absorbing ability of the rubber component, causing the impact strength of the blend samples to be lower than that of pure UPE resin. On the other hand, an increase in easily elongated uncrosslinked rubber molecules, as the graft copolymer content in blend samples increased, resulted in a decrease in their flexural strength. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 1496–1503, 2004

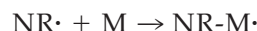
Key words: graft copolymer; natural rubber; unsaturated polyester; resin; polymer blend; miscibility

INTRODUCTION

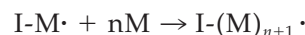
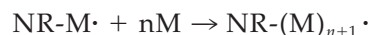
Unsaturated polyester resin (UPE resin), a resin prepared from a polyester synthesized by esterification of glycol, unsaturated acid, and saturated acid dissolved in styrene monomers, is widely used in many applications, such as electronic equipment, containers, automobiles, and cultured marble because of its clarity, because of its excellent chemical and corrosive resistance. However, the major disadvantage of this polymer is its brittleness. It has been found that the dispersion of rubber particles within the glassy matrix can improve this property because the rubber particles can absorb and disperse the energy.^{1–3} Therefore, in previous studies, both synthetic and natural rubbers were blended with UPE resin.^{4–6} However, because of the difference in chemical structures of UPE resin and these rubbers, especially natural rubber, the immiscibility of the two components was observed. In general, many methods can be applied to increase the miscibility of polymer blends. One method is to modify the chemical structure of one component of polymer blends by grafting of the segments, which can react or interact with other components. This is normally done

by free-radical-initiated reactions, including thermal initiation, redox initiation, and high energy irradiation.^{7–11} In the case of natural rubber, it can be grafted with synthetic polymers such as poly(methyl methacrylate) and polystyrene by several initiation methods.^{12–15} The following grafting scheme details the formations of graft copolymer and also homopolymer by-product. (The abbreviations used are as follows: NR, natural rubber; M, monomer; and I, initiator.)

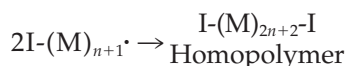
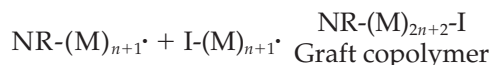
Initiation



Propagation



Termination

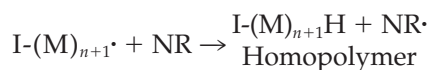
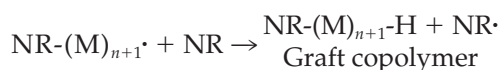


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TABLE I
Amounts of Materials Used in the Main Reactor and Feeding Tank

No.	NR : SM (mol %)	Main reactor			Feeding tank			
		NR (60%DRC) (g)	TEPA (g)	Distilled water (mL)	SM (g)	<i>t</i> -BHPO (g)	PL (g)	Distilled water (mL)
1	95 : 5	155.10	1.0	50	7.5	1.0	5.0	50
2	90 : 10	146.95	1.0	50	15	1.0	5.0	50
3	80 : 20	130.61	1.0	50	30	1.0	5.0	50
4	70 : 30	114.28	1.0	50	46	1.0	5.0	50

Chain-transfer reaction



In this research, styrene monomers were grafted onto natural rubber backbone to form natural rubber/polystyrene graft copolymer. It is expected that polystyrene in copolymer would interact with styrene monomers in UPE resin, which results in an increase in the miscibility of UPE resin and grafted natural rubber blends. The effects of the amount of polystyrene grafted on natural rubber and the amount of graft copolymer in polymer blend on morphology and mechanical properties were investigated.

EXPERIMENTAL

Materials

Styrene monomer and natural rubber latex were donated from Dow Chemical Company (Midland, MI) and Thai Rubber Latex Corp. (Samutprakam, Thailand), respectively. Tetraethylene pentamine was purchased from A.S.C. Xenon Limited Partnership (Thailand). Petroleum ether, *tert*-butyl hydroperoxide, sodium hydroxide, methanol, and potassium laurate were purchased from Merck (Darmstadt, Germany). Sodium sulfate anhydrous and methyl ethyl ketone were purchased from Fluka (Buchs, Switzerland).

UPE resin, methyl ethyl ketone peroxide, and cobalt octoate were donated from Siam Chemical Industries Co. (Thailand).

Styrene monomer was purified by washing initially three times with 10% aqueous sodium hydroxide solution, followed by distilled water, until the pH of monomer reached 7. Then sodium sulfate anhydrous was added to the monomer. The mixture was kept in a refrigerator at 4°C overnight and then sodium sulfate anhydrous was removed by filtration. The purified monomer was stored in a refrigerator until use. Other materials were used as received without further purification.

Methods

Synthesis and characterization of natural rubber/polystyrene graft copolymers^{14,15}

Natural rubber latex (NRL), tetraethylene pentamine (TEPA), and distilled water were mixed in main reactor equipped with a mechanical stirrer, a thermometer, a condenser, a N₂ gas inlet, and a feeding tank containing a mixture of purified styrene monomer (SM), *tert*-butyl hydroperoxide (*t*-BHPO), and potassium laurate (PL) in distilled water. The mixture in the main reactor was stirred at the rate of 100 rpm at 50°C. After the mixture in the feeding tank was stirred for 30 min, it was continuously charged to the main reactor within 1 h. After that, the mixture was stirred at this temperature for another 2 h and the graft copolymer latex was obtained (see Table I).

For characterization, the graft copolymer latex was coagulated with 10 wt % calcium chloride solution and the coagulum was dried at 50°C and weighed. The dried product was then subjected to Soxhlet extraction for 24 h using petroleum ether as a solvent for extracting ungrafted natural rubber for another 24 h using methyl ethyl ketone as a solvent for extracting homopolystyrene. Finally, the remaining graft copolymer was removed, filtered, washed with methanol, dried in an oven at 50°C for 24 h, and weighed. All data were used to calculate %conversion, %grafting efficiency, and %homopolystyrene formation of the system by the following equations:

%Conversion

$$= \frac{\text{Weight of HPS} + \text{weight of GPS}}{\text{Weight of SM}} \times 100$$

%Grafting efficiency

$$= \frac{\text{Weight of GPS}}{\text{Weight of HPS} + \text{weight of GPS}} \times 100$$

%Homopolystyrene formation

$$= \frac{\text{Weight of HPS}}{\text{Weight of HPS} + \text{weight of GPS}} \times 100$$

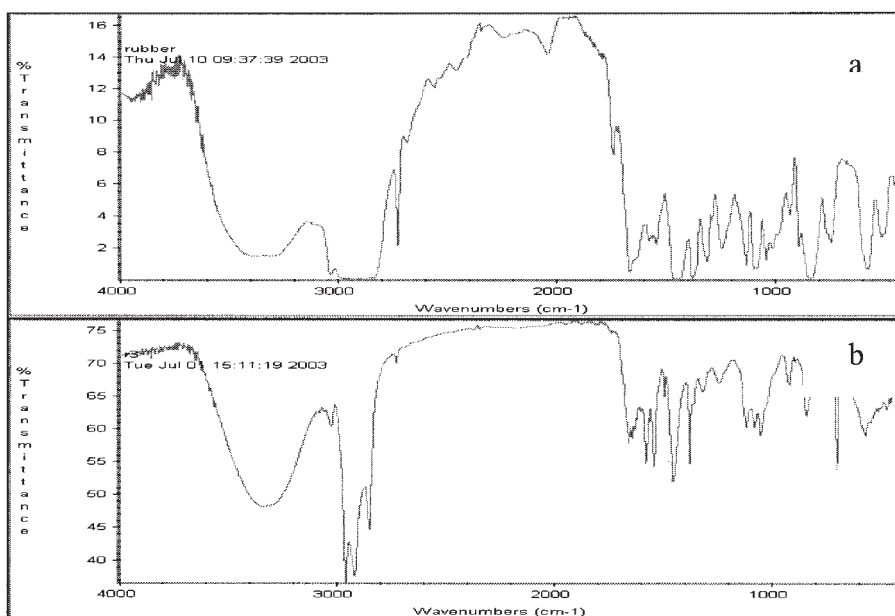


Figure 1 FTIR spectra of ungrafted natural rubber (a) and grafted natural rubber at NR : SM ratio of 80 : 20 (b).

where GPS represents polystyrene grafted onto natural rubber and HPS represents the homopolystyrene byproduct.

Chemical structures of graft copolymers were analyzed using a Nicolet-Impact 400 FTIR spectrophotometer (Nicolet Analytical Instruments, Madison, WI).

Preparation of natural rubber/polystyrene graft copolymers and UPE resin blends

UPE resin (100 g) was stirred at 300 rpm at room temperature. Graft copolymer latex from the synthesis just described, the amount of which was varied from 5, 10, 20, and 30 to 40 g, was added to the resin and the mixture was stirred for 30 min. After that, cobalt octoate (0.1 mL) and methyl ethyl ketone peroxide (MEKPO, 1 mL) were added to the mixture, which was stirred for 2 min then poured into silicone molds. After 18 h, the samples were removed from the molds and baked in an oven at 60°C for 1 h.

Morphology and mechanical properties of polymer blends

The flexural test and impact tests on the samples were used based on ASTM D 790M and ASTM D 356-93A, respectively. Morphology of the samples, after being subjected to impact testing, was characterized using a JSM 5800 LV scanning electron microscope (SEM; JEOL, Tokyo, Japan).

RESULTS AND DISCUSSION

An example of FTIR spectra of natural rubber-*g*-polystyrene copolymers (NR-*g*-PS), as shown in Figure 1,

exhibits peaks corresponding to C—H bending, C=C stretching, and =C—H stretching of aromatic rings of polystyrene at wavenumbers of 3026, 1601, and 695 cm^{-1} , respectively. Furthermore, it was found that with increasing styrene content in the graft copolymer, the intensity of these peaks increases, especially for the peak at 695 cm^{-1} . This observation is in good agreement with %grafting efficiency and %homopolymer formation, as given in Table II. These results suggest that grafting is more favorable than homopolymerization as the amount of styrene monomers increases.

When ungrafted and grafted natural rubbers were blended with UPE resin, it was observed that the samples prepared from ungrafted natural rubbers exhibited the aggregation of the rubber component, whereas the samples prepared from grafted natural rubbers showed good dispersion of the rubber component in the glassy matrix of UPE resin, as shown in Figure 2. This indicates that polystyrene grafted onto the main chain of natural rubber increases the miscibility between natural rubber and UPE resin.

Even though the grafted natural rubbers are well dispersed in UPE resin, the impact strength of blend

TABLE II
Grafting Characteristics of natural rubber-*g*-polystyrene copolymers

No.	NR : SM (mol %)	%Conversion	%Grafting efficiency	%Homopolystyrene formation
1	95 : 5	87.45	12.67	87.33
2	90 : 10	91.60	35.05	64.95
3	80 : 20	85.30	79.20	20.80
4	70 : 30	90.79	87.73	12.24

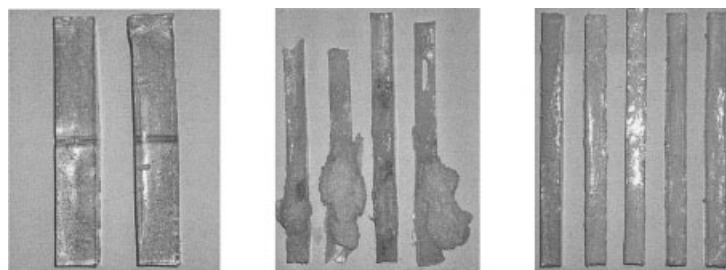


Figure 2 Samples of pure UPE resin (a), ungrafted NR/UPE resin blend (b), and grafted NR/UPE resin blend (c).

samples were lower than those of pure UPE resin, as shown in Figure 3. Furthermore, from SEM micrographs in Figure 4, it is observed that with increasing graft copolymer contents, the amounts of rubber component in blend samples increase and this component is well dispersed in UPE matrices. Therefore, one should expect a higher impact strength at higher graft copolymer content. However, from Figure 3, it is clearly seen that only the blend samples prepared at the molar ratio of NR : SM = 95 : 5 (UPE/NR1Y, Y = graft copolymer content in blends) exhibit this trend. On the other hand, at the molar ratios of NR : SM = 90 : 10 (UPE/NR2Y), 80 : 20 (UPE/NR3Y), and 70 : 30 (UPE/NR4Y), the impact strength of the blend samples tends to decrease as the amount of graft copolymer in the blends increases from 5, 10, 20, and 30 to 40 g. This may be attributable to an increase in the amount of hard and brittle polystyrene grafted onto natural rubber molecules; therefore, the blend samples contained a higher content of low impact resistant glassy matrix than that of pure UPE resin. The results suggest that this effect of polystyrene component overshadows the effect of the rubber component.

The effect of the molar ratio of NR : SM on the impact strength of grafted NR/UPE resin blends when the graft copolymer content in blends is constant can be divided into two cases: at low and high graft copolymer contents. For the former case (5, 10, and 20 g), it was found that at lower NR : SM molar ratios of 95 : 5 and 90 : 10, the blend samples exhibited

lower impact strength than that of the samples prepared at higher NR : SM molar ratios of 80 : 20 and 70 : 30. This may be because, at lower amounts of polystyrene grafted onto natural rubber molecules, good dispersion of the rubber component in UPE resin could not be achieved, thus causing defects at the interface of these two components. Therefore, if the load was applied at these areas, the impact strength decreased. For the latter case (30 and 40 g), it was found that at NR : SM molar ratio of 95 : 5, the blend samples exhibited higher impact strength than that of the samples prepared at higher NR : SM molar ratios of 90 : 10, 80 : 20, and 70 : 30. This may be a result of the effect of increasing the amount of hard and brittle polystyrene from graft copolymer in the blended matrix, as previously described, and an increase in these glassy matrices is also clearly seen from SEM micrographs, as shown in Figure 5. The voids present in SEM micrographs from both Figures 4 and 5 indicate the lack of the rubber component after impact testing when each sample broke into two parts and some domains of the rubber component were separated by impact force and embedded in both parts, whereas some domains were pulled and embedded in only one part, causing the formation of voids in the other part.

From Figure 6, it can be seen that the flexural strength of blend samples is lower than that of pure UPE resin. This may be attributable to the presence of the flexible and easily elongated natural rubber mol-

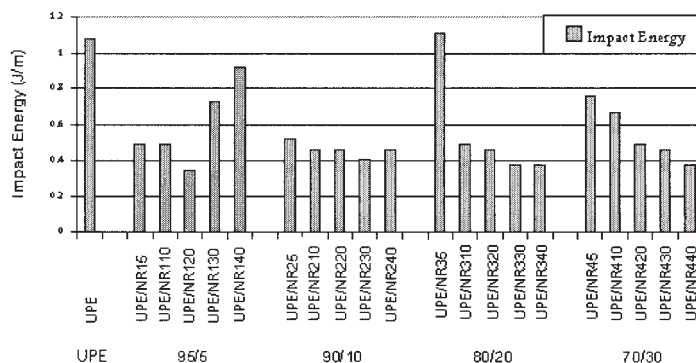


Figure 3 Impact strength of pure UPE resin and grafted NR/UPE resin blends.

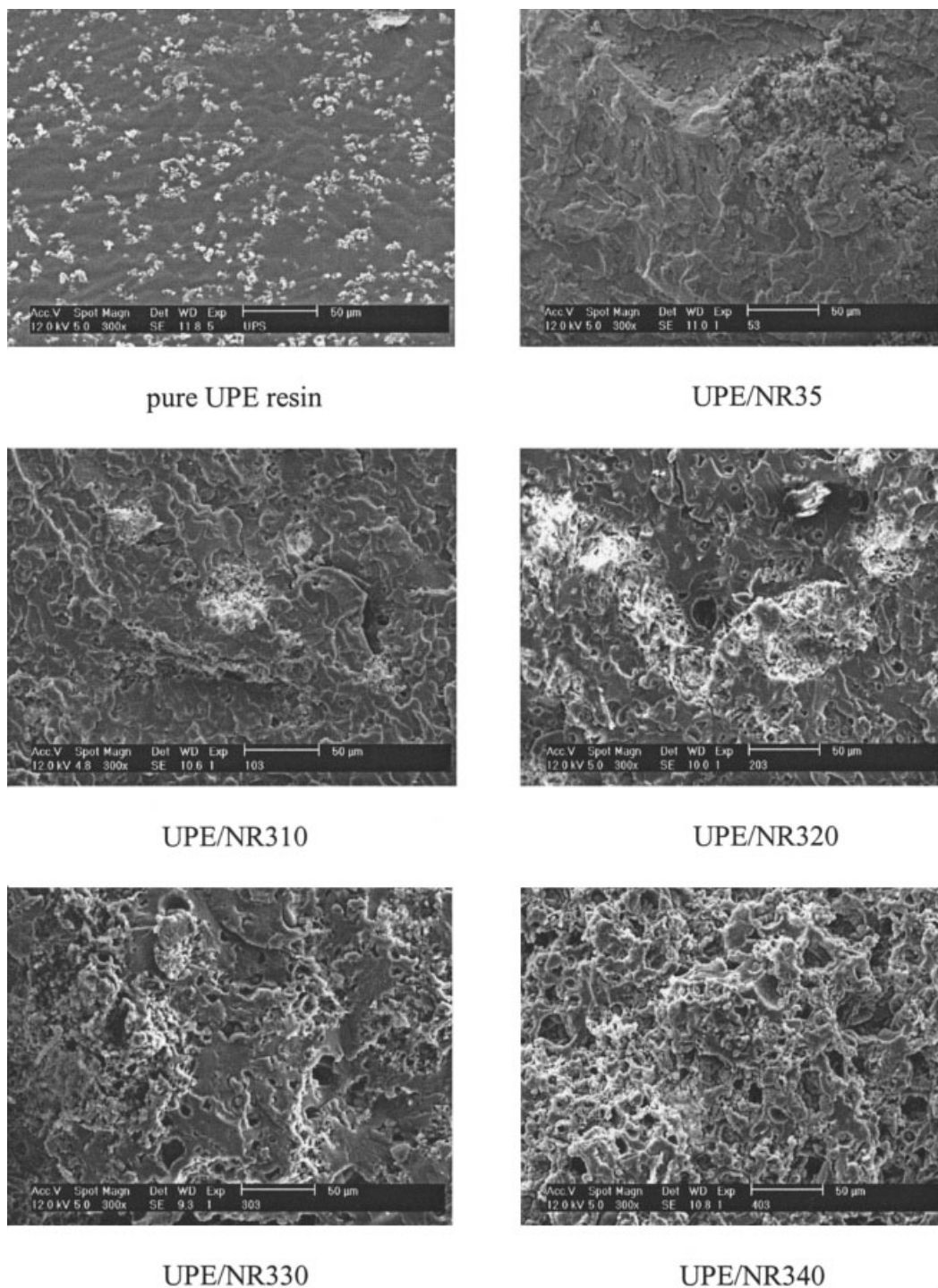


Figure 4 SEM micrographs at $\times 300$ of pure UPE resin and grafted NR/UPE resin blends with molar ratios of NR : SM = 80 : 20 (UPE/NR3Y, Y = graft copolymer content in blends).

ecules in the blend samples. These rubber molecules can easily move, even after a small flexural load was applied. Because the rubber molecules were not vulcanized, they continuously moved as the applied load increased until they separated from each other or from the UPE matrix, causing the breaking of the samples, as shown in Figure 7. Therefore, as the amount of graft

copolymer in the blend samples increases, indicating an increase in the rubber component, the flexural strength of the samples decreases, as was observed for the blend samples prepared at NR : SM molar ratios of 90 : 10 (UPE/NR2Y), 80 : 20 (UPE/NR3Y), and 70 : 30 (UPE/NR4Y). However, at NR : SM molar ratio of 95 : 5 (UPE/NR1Y), no specific trend is clearly ob-

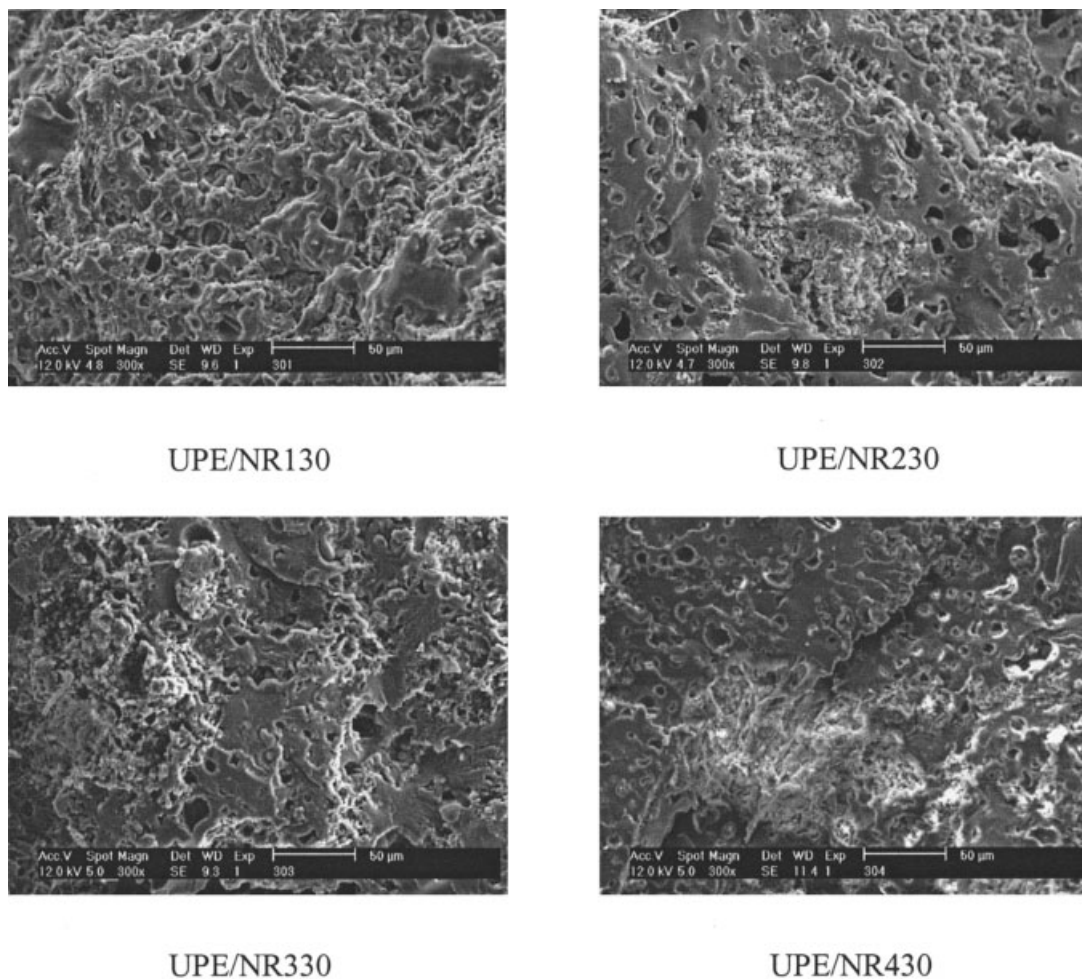


Figure 5 SEM micrographs at $\times 300$ of pure UPE resin and grafted NR/UPE resin blends with graft copolymer content in blends of 30 g (UPE/NRX30, X = formula no. of graft copolymer as indicated in Tables I and II).

served for flexural strength as the amount of graft copolymer in the blend increases from 5, 10, 20, and 30 to 40 g. This may be because at low content of polystyrene grafted onto natural rubber, a good dispersion of rubber component in UPE resin could not be achieved, thus causing defects at the interface of these

two components. Therefore, if the load was applied at these areas, the flexural strength decreased.

On the other hand, the effect of the molar ratio of NR : SM on the flexural strength of grafted NR/UPE resin blends, when the amount of graft copolymer in blend is constant (UPE/NRX5, UPE/NRX10, UPE/

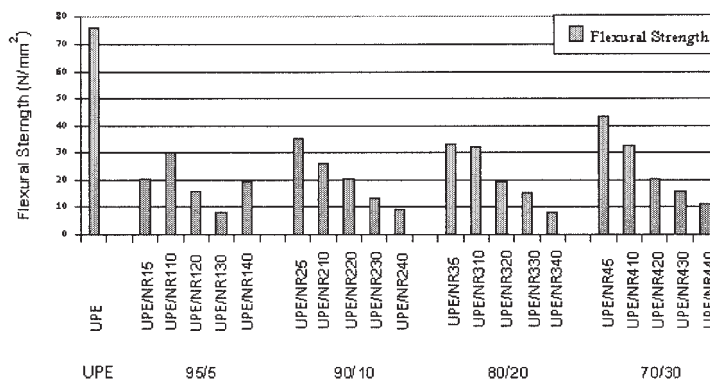


Figure 6 Flexural strength of pure UPE resin and grafted NR/UPE resin blends.

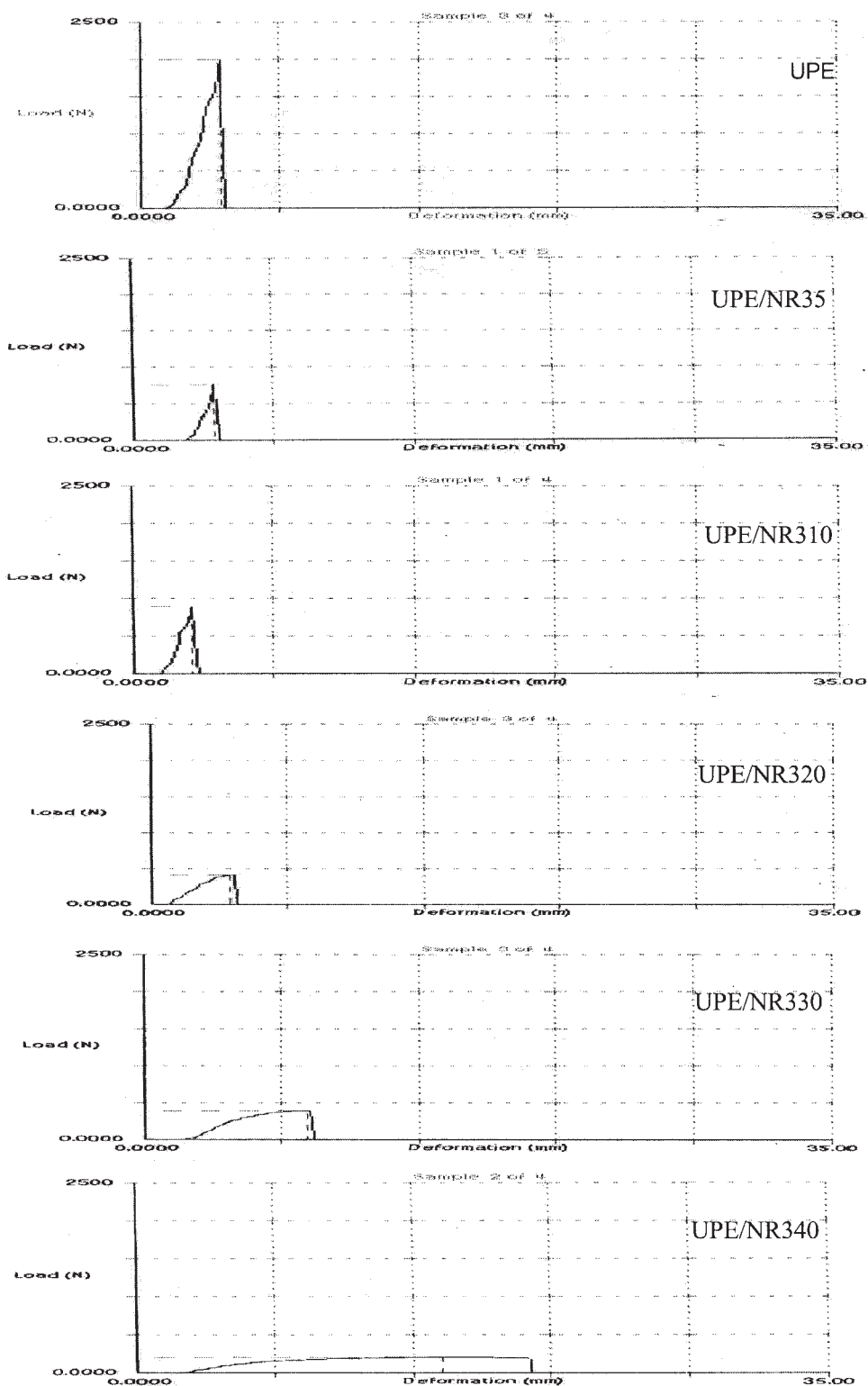


Figure 7 Flexural stress-strain curves of pure UPE resin and grafted NR/UPE resin blends with molar ratios of NR : SM = 80 : 20 (UPE/NR3Y, Y = graft copolymer content in blends).

NRX20, UPE/NRX30, and UPE/NRX40 when X = formula no. of graft copolymer, as indicated in Tables I and II), was not clearly seen. As the molar ratio of NR : SM increased from 95 : 5, 90 : 10, 80 : 20,

and 70 : 30, the flexural strengths of the samples were comparable. This suggests that the amount of polystyrene grafted onto natural rubbers at these ratios does not affect the flexural strength of the blend samples.

CONCLUSION

The results indicated that grafted polystyrene segments promoted good dispersion of natural rubber molecules in the glassy matrix of UPE resin. Although both impact strength and flexural strength of the blend samples were lower than those of pure UPE resin, the miscibility of the blend system was achieved. This suggests that by further improvement, the grafting of natural rubber can be possibly used as a method for preparation of miscible natural rubber/UPE resin blends.

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References

1. Merz, E. H.; Claver, G. C.; Baer, M. *J Polym Sci* 1956, 22, 325.
2. Vazquez, F.; Schneider, M.; Pith, T.; Lambla, M. *Polym Int* 1999, 41, 1.
3. Schneider, M.; Pith, T.; Lambla, M. *Polym Adv Technol* 2003, 6, 326.
4. Salamone, J. C. *Unsaturated Polyester Resins (Toughening with Elastomers)*, Polymeric Materials Encyclopedia; CRC Press: Boca Raton, FL, 0000; p. 8486.
5. Salamone, J. C. *Unsaturated Polyester Resins (Toughening with Liquid Rubber)*, Polymeric Materials Encyclopedia; CRC Press: Boca Raton, FL, 0000; p. 8489.
6. Maspoch, M. L. L.; Martinez, A. B. *Polym Eng Sci* 1998, 38, 282.
7. Sheng, J.; Hu, J. *J Appl Polym Sci* 1996, 60, 1499.
8. Sacak, M.; Oflaz, F. *J Appl Polym Sci* 1993, 50, 1909.
9. Liu, M.; Cheng, R.; Wu, J.; Ma, C. *J Polym Sci Part A: Polym Chem* 1993, 31, 3181.
10. Kiatkamjornwong, S.; Meechai, N. *Radiat Phys Chem* 1997, 49, 689.
11. Fanta, G. F.; Burr, R. C.; Doane, W. M.; Russell, C. R. *J Appl Polym Sci* 1977, 21, 425.
12. Fukushima, Y. *J Rubber Res* 1998, 1, 154.
13. Thiraphattaraphun, L.; Kiatkamjornwong, S.; Prasasarakich, P.; Damronglerd, S. *J Appl Polym Sci* 2001, 81, 428.
14. Schneider, M.; Pith, T.; Lambla, M. *J Appl Polym Sci* 1996, 62, 273.
15. Nakason, C.; Kaesaman, A.; Yimwan, N. *J Appl Polym Sci* 2003, 87, 68.