

Use of Natural Rubber-g-Polystyrene as a Compatibilizer in Casting Natural Rubber/Polystyrene Blend Films

S. Chuayjuljit, S. Moosin, P. Potiyaraj

Department of Materials Science, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand

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ABSTRACT: Natural rubber/polystyrene (NR/PS) blend films with weight ratios of 70/30, 60/40, and 50/50 were prepared using polystyrene grafted natural rubber copolymers (NR-g-PS) as the compatibilizer. Copolymers with molar ratios of 90/10, 80/20, and 70/30 were synthesized via emulsion copolymerization using *tert*-butyl hydroperoxide/tetraethylene pentamine as an initiator. The copolymers were subsequently added into the blends at 0, 5, 10, 15, 20, 25, and 30 phr. The mixtures were cast into films by the solution-casting method using toluene as the casting solvent. Mechanical and morphological properties of the prepared films were investigated. The film prepared from

80/20 NR-g-PS showed higher tensile and tear strength, as well as finer domain size of the dispersed phase, than those prepared from 90/10 and 70/30 NR-g-PS. However, the mechanical properties of the films were decreased at high loading of the copolymers. In addition, thermogravimetric analysis revealed that weight loss was decreased upon introduction of the compatibilizer. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 95: 826–831, 2005

Key words: graft copolymers; blending; compatibilization; natural rubber; polystyrene

INTRODUCTION

Thermoplastic elastomers prepared from blends of natural rubber and polystyrene (NR/PS blends) combine the excellent elastic properties of rubbers and the superior processability of thermoplastics. Earlier works pointed out that these blends are immiscible, resulting in poor mechanical properties. To improve the compatibility, various techniques were employed. One involves the introduction of a homopolymer or copolymer that is miscible with the two phases.

Asaletha and Thomas¹ studied the compatibilizing activity of polystyrene grafted natural rubber (NR-g-PS) in NR/PS blends. Various ratios of NR/PS blends were prepared by the solution-casting technique. Prior to casting, NR-g-PS copolymers were added to the blends. The copolymers were prepared by the emulsion polymerization of styrene in rubber latex using γ -ray as the initiator. Morphological studies revealed that copolymer addition reduced the domain size of the dispersed phase and finally leveled off at higher concentrations. The results also indicated that the tensile strength and modulus increased with the addition of the copolymers and subsequently leveled off at higher concentrations. The impact strength increased up to 3% compatibilizer loading and then decreased at higher concentrations. The improvement of these me-

chanical properties was due to the enhanced interfacial bonding between PS and NR through the graft copolymers. In related research, Asaletha and Kumaran² found that casting solvents had a major influence on the morphology and properties of the dispersed phase of NR/PS blends. Carbon tetrachloride-cast film had a fine domain distribution compared to chloroform-cast film, and the domain size is much less in the former case. In both cases, the domain size is decreased by the addition of a few percentages of copolymer, followed by a leveling off at higher concentrations. The differences were associated with the preferential interaction of the solvent with the component polymers. Melt rheology and morphology of physically compatibilized NR/PS blends by the addition of NR-g-PS were studied.³ Blends were prepared by both melt-mixing and solution-casting techniques. In both cases, the shear viscosity decreased with the increase of shear stress, indicating a pseudoplastic nature. The viscosity of the system was increased with the increase of the rubber content. The melt-mixed blends showed lower viscosity compared to solution-cast blends due to mechanical degradation of both NR and PS at high temperature and shear rate. Morphology analysis revealed that the dispersed domain size was reduced significantly at high shear rate. Melt viscosity of the blends increased upon the addition of a few percentages of NR-g-PS followed by a decrease at higher loading.

Omman and colleagues^{4,5} investigated the rheological properties of natural rubber and poly(methyl

Correspondence to: P. Potiyaraj (pranut@sc.chula.ac.th).

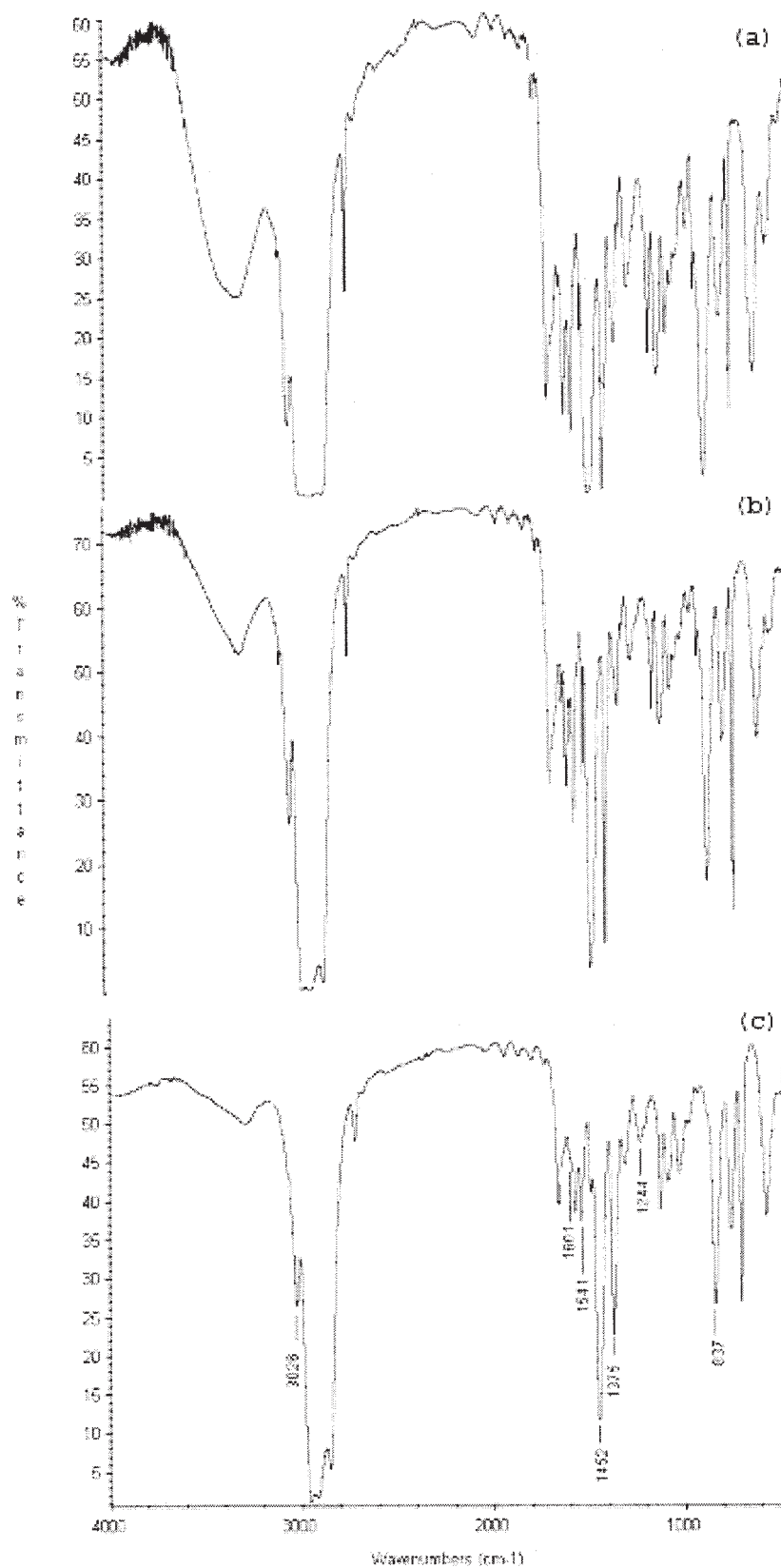


Figure 1 FTIR spectra of (a) NR-g-PS (NR/PS 90/10 mol %); (b) NR-g-PS (NR/PS 80/20 mol %); (c) NR-g-PS (NR/PS 70/30 mol %).

TABLE I
Glass Transition Temperatures of NR-g-PS

Glass transition temperature (°C)	NR/PS (mol %)		
	90/10	80/20	70/30
Onset temperature	-64.5	-64.0	-63.8
Midpoint temperature	-61.8	-61.3	-61.1
Inflection point temperature	-61.0	-60.5	-60.6

methacrylate) blends using poly(methyl methacrylate) grafted natural rubber as a compatibilizer. Chlorobenzene and toluene were used as the casting solutions in the solution casting of the blends. Domain size of the dispersed phase was greatly reduced with the small addition of the compatibilizer.

In this research, the NR/PS blend films were prepared by the solution-casting technique using toluene as the casting solvent. NR-g-PS synthesized via emulsion polymerization using *tert*-butyl hydroperoxide/tetraethylene pentamine (TBHPO/TEPA) as an initiator. The effects of compositions of blends and polymers as well as copolymer concentration on the morphology and properties of the blends were investigated.

EXPERIMENTAL

Preparation and analysis of NR-g-PS

Styrene monomer, provided by Pacific Plastics Ltd. (Thailand), was initially purified by removing the exist inhibitor. It was then reacted with natural rubber latex, which was supplied by Thai Rubber Latex Corp. Public Co., Ltd. (Thailand). Emulsion polymerization was conducted in a reactor under nitrogen atmosphere with TBHPO/TEPA as the organic redox initiators and water as the medium. NR-g-PS with molar ratios of 90/10, 80/20, and 70/30 were synthesized. A Fourier transform infrared spectrophotometer (FTIR, Nicolet Impact400D) and a differential scanning calorimeter (DSC, Netzsch DSC200) were used for analyzing chemical structures of the polymerization products. The grafting efficiency was calculated. Gel permeation chromatography (Waters 150-CV) was used to determine the molecular weight of the prepared copolymers.

TABLE II
Grafting Efficiency of NR and PS Copolymerization

Copolymerization results (%)	NR/PS (mol %)		
	90/10	80/20	70/30
Grafting efficiency	49.33	52.33	56.33
Grafted NR	49.33	52.33	56.33
Undgrafted NR	2.00	5.34	9.00
Undgrafted styrene	48.67	42.33	34.67

TABLE III
Molecular Weight of PS Grafting onto NR

NR/PS (mol %)	\bar{M}_n	\bar{M}_w	Polydispersity index
90/10	4.2×10^4	9.9×10^4	2.4
80/20	3.5×10^4	8.1×10^4	2.3
70/30	1.5×10^4	3.0×10^4	2.0

Preparation and analysis of NR/PS blend films

Natural rubber latex of 60% dry rubber content, also obtained from Thai Rubber Latex Corp. Public Co., Ltd., was precipitated by calcium chloride, washed, and then dried at room temperature. The dried rubber and polystyrene (supplied by Siam Polystyrene Co., Ltd., Thailand) were mixed with weight ratios of 70/30, 60/40, and 50/50. Toluene was poured over the mixtures of dried rubber and polystyrene. Then NR-g-PS was added with 0, 5, 10, 15, 20, 25, and 30 phr. The toluene was added to obtain 3% w/v solution. The mixing was done for 8 h. The mixtures were then poured over glass plate molds and left to dry at room temperature. Films were removed from the glass plates and dried in an oven at 70°C for 24 h.

The prepared films with thickness less than 0.25 mm were cut into test specimens for tensile and tear tests. Based on ASTM D412, the tensile test was performed using a universal testing machine (Lloyd LR5K) equipped with a 500 N load cell. The test speed is 500 mm/min with 25-mm gauge length. Tensile strength, modulus of elasticity, and elongation at break of test specimens were determined. Tear strength was investigated according to ASTM D624 using the same universal testing machine and the same conditions were reported.

Thermal properties of the prepared blends were investigated using a thermogravimetric analyzer (TGA, Netzsch STA 409C) and a DSC (Netzsch DSC 200). Morphology of films was studied under an op-

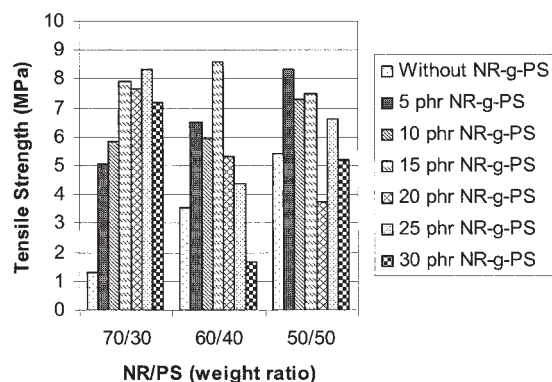


Figure 2 Tensile strength of NR/PS films compatibilized with NR-g-PS (NR/PS 80/20).

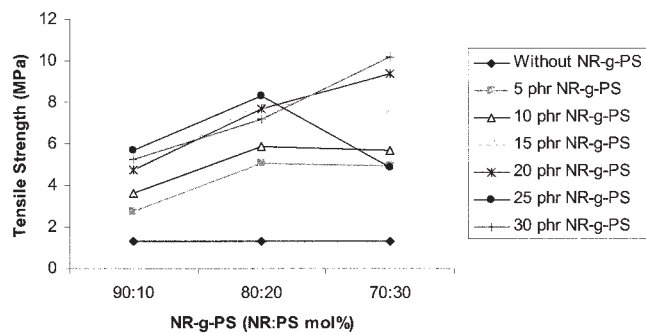


Figure 3 Tensile strength of NR/PS films (NR/PS 70/30) compatibilized with NR-g-PS.

tical microscope (Olympus BH2-UMA) with 160 \times magnification.

RESULTS AND DISCUSSION

Properties of NR-g-PS

NR-g-PS copolymers were successfully synthesized as evidenced by FTIR and DSC analyses. The grafting products were characterized by FTIR. An FTIR spectrum of 80/20 NR-g-PS is shown in Figure 1 as an example. The spectrum shows the absorption peaks corresponding to various stretching in the molecule. Peaks at 837 and 1244 cm^{-1} correspond to C=C and C-C stretching of NR, respectively. The peak at 1375 cm^{-1} corresponds to C-H stretching of NR. The aromatic structure of PS is pronounced clearly with the peak at 3026 cm^{-1} corresponding to the aromatic C-H stretching, the peaks at 1541 and 1601 cm^{-1} corresponding to aromatic C=C stretching, and the peak at 1452 cm^{-1} indicating aliphatic C-H stretching. According to DSC analysis reported in Table I, a single T_g was observed for each graft product, suggesting the presence of a single-phase polymer. In addition, as the amount of styrene monomer increased, glass transition temperatures were insignificantly changed.

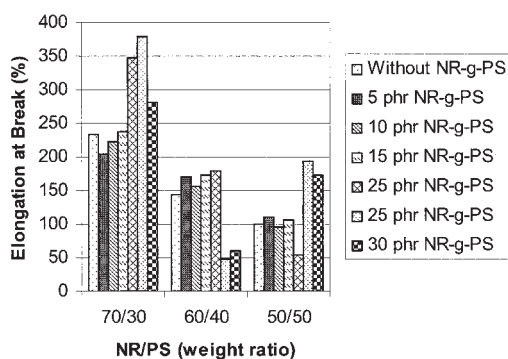


Figure 4 Elongation at break of NR/PS films compatibilized with NR-g-PS (NR/PS 80/20).

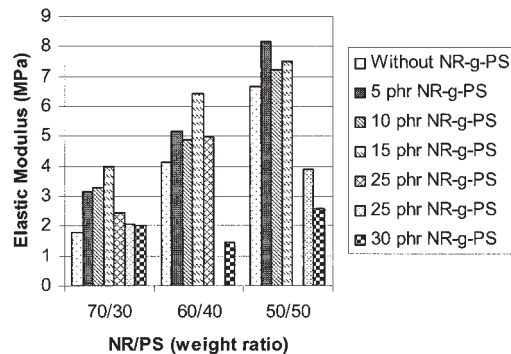


Figure 5 Modulus of NR/PS films compatibilized with NR-g-PS (NR/PS 80/20).

Table II shows the grafting efficiency of natural rubber and styrene monomer at different ratios. Table III shows the molecular weight of polystyrene in the NR-g-PS system as revealed by GPC. The results indicated that, as the amount of styrene monomer increased, the grafting efficiency increased while the molecular weight of polystyrene decreased. It was then assumed that there were several short chains, rather than a few long chains, of polystyrene grafted on natural rubber molecules.

Mechanical properties of NR/PS blend films

Figure 2 shows the tensile strength of NR/PS blend films with various amounts of NR-g-PS (80/20 mol %). It was found that the addition of compatibilizer (NR-g-PS) improved the tensile strength of the blend films. However, with high loading of NR-g-PS, the tensile strength decreased. With the same amount of compatibilizer, the molar ratio of NR-g-PS affected mechanical properties of blend films, as illustrated in Figure 3. Generally, blends with 80/20 NR-g-PS yielded the films with the highest tensile strength. As the amount of polystyrene increased, the elongation at break of NR/PS blend films was reduced while the modulus at 100% strain increased. This was due to the hard brittle nature of polystyrene. According to Figures 4 and 5, the addition of NR-g-PS markedly improved the elongation at break and the modulus of elasticity. As in the case of tensile strength, the elongation at break and the modulus tended to be lower at high loading. The tear strength of blend films, shown in Figure 6, was affected by the compatibilizer in a similar manner as the tensile properties. The presence of water in the NR-g-PS grafting reaction probably accounts for the decrease in these mechanical properties at high loading. The difference in solubility parameter of water and toluene promoted phase separation between blends and the compatibilizer, resulting in poor mechanical properties at high loading.

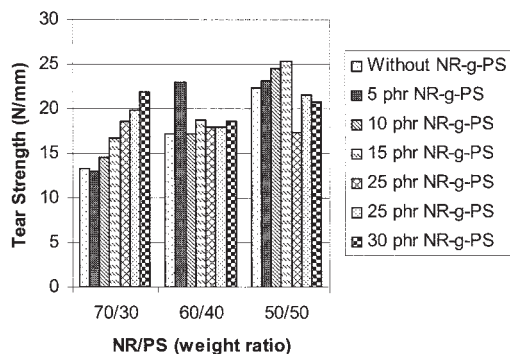


Figure 6 Tear strength of NR/PS films compatibilized with NR-g-PS (NR/PS 80/20)

Thermal properties of NR/PS blend films

From TG thermograms, the initial and final thermal decomposition temperatures of NR/PS blend films with and without NR-g-PS compatibilizer were determined as shown in Table IV. The addition of NR-g-PS resulted in a small change in initial decomposition temperatures as well as final decomposition temperatures. Table V shows the weight loss of films at 300 and 400°C and total weight loss. Weight loss was reduced as the amount of compatibilizer increased.

DSC thermograms of NR/PS blend films with and without NR-g-PS compatibilizer were analyzed. As shown in Table VI, two distinct T_g (midpoint) were observed in films with and without the compatibilizer. This was caused by the immiscibility of dispersed phase and continuous phase as also evidenced in the optical microscope (OM) micrographs explained later. As stated by Paul and Newman,⁶ if two polymers are immiscible, there are no compatibilizers that can blend these two polymers into one continuous phase. However, suitable compatibilizers would improve interfacial bonding between two phases, thus improving the dispersion of the dispersed phase in the continuous phase.

Morphology of NR/PS blend films

Figure 7 shows an example of the morphology of blend films under an OM. It could be clearly seen that,

TABLE IV
Decomposition Temperatures of NR/PS blends (70/30 wt %)

Amount of NR-g-PS (80/20) (phr)	Initial decomposition (°C)	Final decomposition (°C)
0	330.7	504.9
5	330.2	508.9
15	332.4	507.9
25	331.0	510.6

TABLE V
Weight Loss of NR/PS Blends (70/30 wt %)

Amount of NR-g-PS (80/20) (phr)	Weight loss (%) at 300°C	Weight loss (%) at 400°C	Total weight loss (%)
0	4.2	66.4	98.6
5	5.3	64.9	98.8
15	3.8	64.8	98.4
25	2.9	64.0	98.6

in the films without the compatibilizer, the domain size of dispersed phase is larger than that in the films with the compatibilizer. The results were agreeable with mechanical and thermal properties as discussed earlier.

CONCLUSION

In this research, thermoplastic elastomer films from natural rubber and polystyrene at various blending ratios were prepared by the solution-casting technique using toluene as the casting solution. The blends were compatibilized with various amounts of NR-g-PS copolymers. The prepared films were investigated for their mechanical, thermal, and morphological properties.

Polystyrene grafted natural rubber copolymers at different molar ratios were synthesized via emulsion polymerization using TBHPO/TEPA as initiators. When the amount of styrene monomer in the copolymerization system increased, the grafting efficiency increased while the molecular weight of PS was reduced. It was consequently assumed that there were a large number but short chains of PS grafting onto NR chains.

The tensile and tear strengths of NR/PS blend films were improved with the addition of NR-g-PS as the compatibilizer. Nevertheless, at higher loading these mechanical properties were decreased. At the same loading, films with 80/20 NR-g-PS showed the most superior tensile properties compared to those with other molar ratios.

The results were agreeable with those of the morphological study under the optical microscope. Films without the compatibilizer possessed a larger dispersed phase (polystyrene) than those with the com-

TABLE VI
 T_g (midpoint) of NR/PS blends (70/30 wt %)

Amount of NR-g-PS (80/20) (phr)	T_g (°C)
0	-63.4 and +104.6
5	-63.4 and +105.0
15	-63.3 and +105.9
25	-63.4 and +103.8

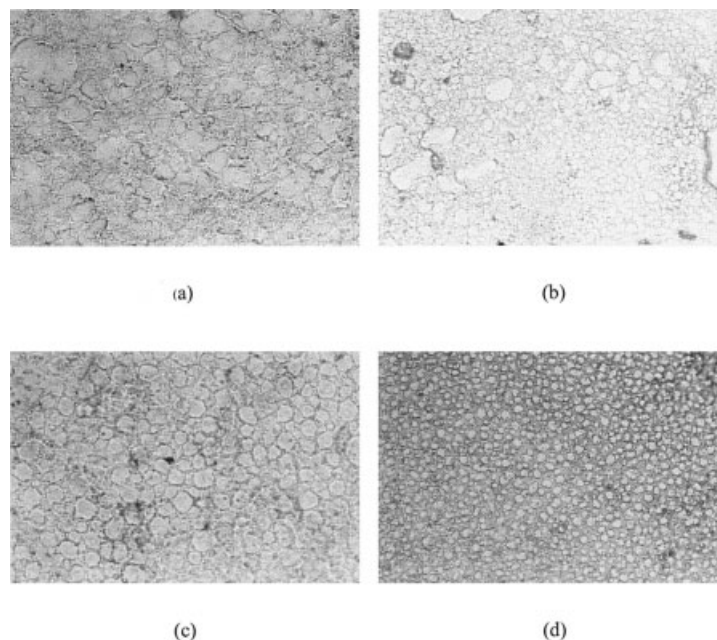


Figure 7 SEM micrograph (160 \times) of NR/PS films (70/30) compatibilized with NR-g-PS (80/20 mol %) at (a) 0 phr, (b) 5 phr, (c) 15 phr, and (d) 25 phr.

patibilizer. As the domain size of the dispersed phase decreased the miscibility increased, thus improving the mechanical properties of films.

Thermal stability of NR/PS blends was not improved with the addition of NR-g-PS compatibilizer. However, weight loss was reduced as the amount of the compatibilizer increased. The DSC analysis of NR/PS blends showed two distinct glass transition temperatures, which leads to the conclusion that complete miscibility of NR/PS blends with NR-g-PS compatibilizer was not achieved.

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