Natural Rubber-*g*-Methyl Methacrylate/Poly(methyl methacrylate) Blends

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Received 26 May 2000;18 August 2000

ABSTRACT: The grafting of the methyl methacrylate (MMA) monomer onto natural rubber using potassium persulfate as an initiator was carried out by emulsion polymerization. The rubber macroradicals reacted with MMA to form graft copolymers. The morphology of grafted natural rubber (GNR) was determined by transmission electron microscopy and it was confirmed that the graft copolymerization was a surface-controlled process. The effects of the initiator concentration, reaction temperature, monomer concentration, and reaction time on the monomer conversion and grafting efficiency were investigated. The grafting efficiency of the GNR was determined by a solvent-extraction technique. The natural rubber-*g*-methyl methacrylate/poly(methyl methacrylate) (NR-*g*-MMA/PMMA) blends were prepared by a melt-mixing system. The mechanical properties and the fracture behavior of GNR/PMMA blends were evaluated as a function of the graft copolymer composition and the blend ratio. The tensile strength, tear strength, and hardness increased with an increase in PMMA content. The tensile fracture surface examined by scanning electron microscopy disclosed that the graft copolymer acted as an interfacial agent and gave a good adhesion between the two phases of the compatibilized blend. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 428–439, 2001

Key words: natural rubber; graft copolymerization; methyl methacrylate; thermoplastic elastomer

INTRODUCTION

Natural rubber (NR), commercial grade of *Heave brasiliensis*, contains 93–95 wt % of *cis*-1, 4-polyisoprene, with the double bonds in NR undergoing the usual chemical reaction.[1] The modification of NR via graft copolymerization is to prepare a product that has some better properties than those of the unmodified one (NR). In addition, it is conceivable that the graft copolymer shows novel properties due to the highly ambivalent nature of the rubber backbone and grafted side chains. The graft copolymerization of methyl methacrylate (MMA) onto NR using various initiator systems was studied by several investigators. Sandardi and Kadariah[2] investigated the method of radiation grafting of MMA onto NR latex. Lenka et al.[3] presented the kinetics and mechanism of graft copolymerization of MMA onto NR using the acetylacetonate complex of

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Contract grant sponsor: Thailand Research Fund.

Journal of Applied Polymer Science, Vol. 81, 428–439 (2001)

Mn(III). They also studied the graft copolymerization of MMA onto NR using vanadium ions as the initiator.[4] Graft copolymerization of the MMA monomer onto crepe NR using a potassium peroxydisulfate initiator and catalyzed by silver ions was carried out for various concentrations of the monomer and initiator.[5] They found that the grafting reaction was temperature-dependent. Enyiegulam and Aloka[6] reported the graft characteristics and solution properties of the NR-*g*-MMA copolymer in MEK/toluene using benzoyl peroxide as the initiator. Oommen and Thomas[7,8] prepared the graft copolymer by polymerization of MMA onto NR latex using the cumene hydroperoxide–tetraethylene pentamine redox system.

In recent years, materials with the excellent processing properties of thermoplastics and the elastic characteristics of rubbers have become technologically interesting in their use as thermoplastic elastomers (TPEs). TPEs of NR and poly(methyl methacrylate) (PMMA) blends combine the excellent processability characteristics of PMMA and the elastic properties of NR. In addition, they can be successfully used for the fabrication of automobile components. Even though blending looks very attractive for the preparation of TPEs, the NR and PMMA blend components are highly incompatible and, hence, exhibit poor mechanical properties. The technological compatibilization of the immiscible pairs is necessary to improve the mechanical properties of the blends for commercial uses. The properties of blends of NR and PMMA can be improved by the addition of a compatibilizer that can interact with both blend components. Therefore, the compatibilizer can be a graft copolymer with segments that are chemically identical to NR and PMMA.

In this research, an attempt was made to prepare graft copolymers of MMA–NR using potassium persulfate as the initiator. The effects of the initiator and monomer concentrations, reaction temperature, and time on the grafting properties were studied. Graft copolymers were used for compatibilizing the blends of NR and PMMA. Blends of MMA-grafted NR and PMMA were prepared. The effects of the grafting properties and the MMA-grafted NR/PMMA blend ratio on the mechanical properties of the blends (tensile, tear, and impact properties) were investigated. The failure behavior of the samples was examined using the scanning electron microscopy technique.

EXPERIMENTAL

Materials

NR latex containing 61.2% dried rubber was supplied by Thai Rubber Latex Ltd. (Rayong, Thailand). MMA, supplied by the Siam Chemical Industry Co. Ltd. (Pratumthanee, Thailand), was washed with a 10 wt % aqueous sodium hydroxide solution followed by washing with distilled water until its pH was neutral. It was then dried using anhydrous sodium sulfate and passed through an activated aluminum oxide column to remove the residual inhibitor. PMMA, grade Crystallite MF#001 (specific gravity 1.19), supplied by the TPI Polyacrylate Co. Ltd. (Rayong, Thailand), was used as the thermoplastic matrix.

Preparation of the Grafted NR

The NR latex (DRC 61.20%) was placed in a 500-cm^3 glass vessel containing 100 cm^3 of distilled water. A potassium hydroxide solution containing 0.25 wt % of the dry rubber content (phr) was added as a buffer and 1.0 phr of sodium dodecylsulfate, an emulsifier, was then added while stirring. The mixture was deoxygenated by the bubbling of nitrogen gas for approximately 30 min at room temperature. The MMA monomer was then added continually while stirring for 15 min to allow the latex particles to attain swelling. The potassium persulfate initiator was added when the reaction was carried out at the desired temperature. The reaction was then allowed to proceed for 8 h under continuous stirring to complete the polymerization. The graft copolymer latex was cast at room temperature in open trays. Once dry, the sheets were removed from the trays and transferred to an oven at 70°C for approximately 24 h to remove any trace of the residual monomer. The dried sheet was then leached with distilled water to remove any water-soluble impurities from the rubber. Finally, the sheet was then dried again in the oven until it was thoroughly dry.

Soxhlet extraction procedures were carried out to assess the amounts of the free NR and graft copolymer in the final product. The free NR was extracted in a Soxhlet extractor by light petroleum ether for 24 h and free PMMA was treated with acetone for 24 h.[6] After each extraction, the grafted NR was determined by the residual weight. The grafting efficiency is defined as the weight of MMA-grafted rubber divided by the total weight of polymers produced (the free PMMA and the grafted rubber):

$$\text{Grafting efficiency} = \frac{\text{weight of grafted copolymer} \times 100}{\text{total weight of polymer formed}} \quad (1)$$

Transmission Electron Microscopy (TEM)

The grafted NR latex was diluted 400 times with distilled water. Then, 1–2 drops of a 2% aqueous solution of osmium tetroxide was used to stain the rubber particles in 200 cm^3 of diluted latex for 1 day. A drop of the diluted latex was placed on a carbon-coated Formvar film deposited on a grid and dried in a dessicator. Ruthenium tetroxide (0.2 g) was dissolved in 10 cm^3 of 5% aqueous sodium hypochlorite. The ruthenium tetroxide staining solution was used to stain the rubber domain but the PMMA domain was not stained. The morphology of the grafted NR latex was examined by TEM (TEM Model JEM-200CX) at 120 kV.

Dynamic Mechanical Property Measurements

The dynamic mechanical properties of the grafted NR were measured on a dynamic mechanical analyzer (Perkin–Elmer 7e) with a liquid nitrogen cooling system. The dual-cantilever mode of deformation geometry, known as three-point bending, was used in a temperature range of -110 to $+165$°C at a heating rate of 10°C min^{-1} and at a frequency of 1 Hz. The test specimen dimensions were 12 mm in length, 4 mm in width, and 3 mm in thickness.

Preparation of Grafted NR (GNR)/PMMA Blends

The thermoplastic blends were prepared at various ratios of GNR and PMMA by a melt-mixing system. The PMMA pellets were fed into a two-roll mill for 3 min and then blended with the GNR for 4 min. The mixing-roll temperature was kept constant at 165°C. The milled sheets were cut and fed into the mill again at 165°C for 4 min until the surface of the blend was smooth. Thin sheets from the two-roll mill were then pressed by a compression-molding machine at 170°C and a pressure of 120 kg cm^{-2} for 10 min.

Mechanical Property Testing

Tensile properties of the blends were determined according to ASTM D638 using a dumbbell-shaped specimen. A Lloyd universal testing machine was used at a crosshead speed of 50 mm min^{-1}. The tear strength of the specimens was determined according to ASTM D624 using 90°-angle test pieces at a crosshead speed of 500 mm min^{-1}. The Shore hardness of the specimens was measured according to ASTM D22 using a type D Durometer. The impact energy was determined by an impact tester (ITR-2000), in which the flat plate anvil consists of a 350-mm-square plate with a central 50-mm-diameter aperture. The plate is provided with tapped holes on a 50-mm-square grid layout, designed to take M6 × 1.0-mm bolts. This enables test specimens to be clamped and bolted to the anvil and also for installation of various supports and locating structures provided by the users. The dimensions of the specimens used were $15.0 \times 15.0 \times 0.3$ cm^3. The operating pressure for the impact cylinder was 480 kPa. The reported value is the average of five replicates of each property test.

Scanning Electron Microscopy (SEM) Studies

SEM was used to investigate the fracture surface of the GNR/PMMA blends after the tensile property test. The fracture surfaces of test samples were carefully cut, mounted on an SEM stub using double-sided tape, sputter-coated with gold, and then examined under an electron microscope, Model JSM-6400, operated at 20 kV.

RESULTS AND DISCUSSION

The graft copolymerization of MMA in NR latex by the emulsion polymerization technique was studied using potassium persulfate as an initiator. The dependence of the percentage conversion and grafting properties on the initiator concentration, reaction temperature, monomer concentration, and reaction time was examined.

Effect of the Initiator Concentration

The effect of the initiator concentration on the monomer conversion and grafting properties is shown in Table I. In Figure 1, the conversion increases with an increase of the initiator concentration in a low concentration range, and it hardly changes in the range of a high initiator concentration. Initially, increases in the initiator concentration produce more free radicals to increase the conversion. At the higher initiator concentrations, an abundance of the initiator radicals is produced and the radical recombination can only slightly increase the conversion.

Table I Effect of the Initiator and Monomer Concentrations on Graft Copolymerization at 55°C for 8 h

				Graft Properties			
Sample	Initiator Concentration (phr)	Monomer Concentration (phr)	Conversion (%)	Grafted NR (%)	Free NR (%)	Free PMMA (%)	Grafting Efficiency (%)
A	0.50	100	67.4	56.4	27.9	15.7	60.9
B	0.75	100	75.9	57.9	26.6	15.4	64.1
C	1.00	100	79.9	54.0	28.1	17.8	59.9
D	1.50	100	82.1	45.5	32.4	22.1	51.0
E	2.00	100	82.3	45.3	32.5	22.2	50.7
F	0.75	40	56.0	23.1	64.1	12.8	30.2
G	0.75	60	64.9	37.4	46.5	16.1	42.6
H	0.75	80	74.3	51.2	31.4	17.5	53.0
I	0.75	120	75.7	44.2	32.0	23.8	49.9

With an increasing initiator concentration, the number of graft points and the grafting efficiency increase. From Figure 1, increasing initiator concentrations up to 0.75 phr are accompanied by a significant increase in grafting efficiency. Beyond this concentration, the grafting efficiency decreases markedly. When higher concentrations of the initiator are used, excessive radicals react with each other, leading to a faster rate of termination or primary termination. Up to this point, the grafting efficiency does not increase at all. Instead, it decreases slightly as in the results reported by Lenka et al.[3–5] and Enyiegbulam and Aloka.[6] From Table I, the homopolymer (PMMA) content increases when the initiator concentration is higher than 0.75 phr, with homopolymerization preferred to graft copolymerization at high initiator concentrations. One interesting point was anticipated to increase the weight of the grafted copolymer: Since the emulsifier of sodium dodecylsufate was added before the drying of the grafted latex, during heat drying, the unused double bonds of NR could form crosslinking with those of the GNR. These crosslinked portions could therefore not be extracted by petroleum ether. The highest grafting efficiency was observed at the initiator concentration of 0.75 phr.

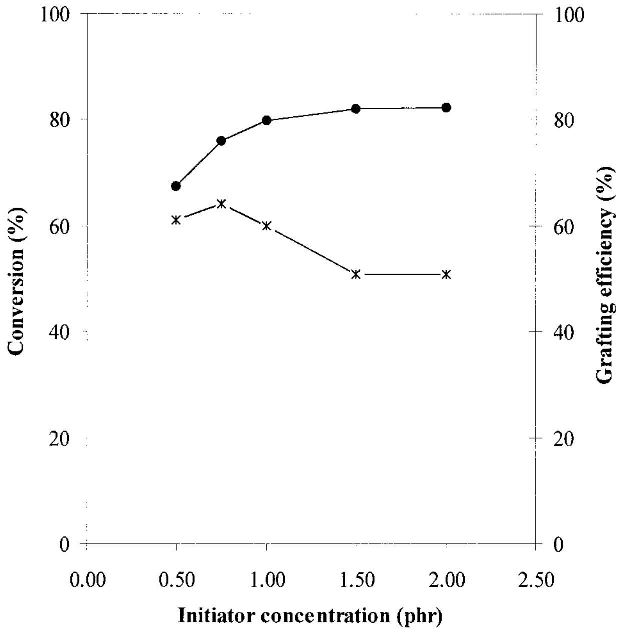


Figure 1 Effect of the initiator concentration on graft copolymerization (MMA 100 phr, 55°C, 8 h): (●) conversion; (×) grafting efficiency.

Effect of the Monomer Concentration

The NR latex used as the backbone polymer of *cis*-1, 4-polyisoprene was grafted with MMA monomers. NR particles were swollen with the monomers, which were then polymerized onto the swollen NR latex particles. The effects of the monomer concentration on the conversion and percentage grafting efficiency were investigated. Experiments were performed in the monomer concentration range of 40–120 phr based on the dry rubber content. The conversion increases with increasing monomer concentration as shown in Figure 2.

As the monomer concentration increases, the grafting efficiency increases and reaches a maximum at the monomer concentration of 100 phr. Thereafter, it decreases. At higher monomer con-

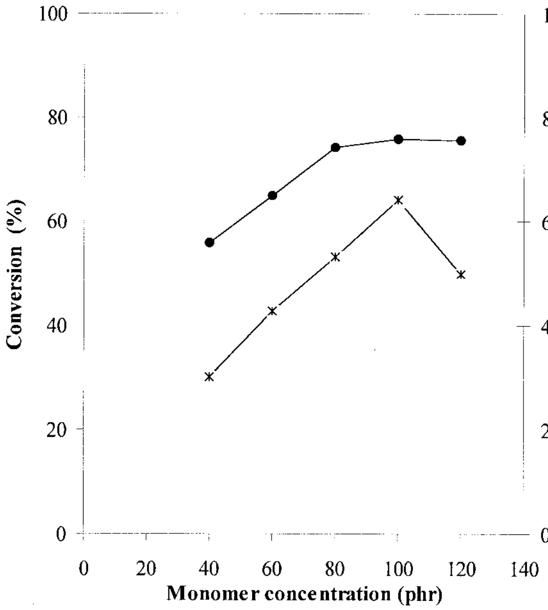


Figure 2 Effect of the monomer concentration on graft copolymerization (initiator 0.75 phr, 55°C, 8 h): (●) conversion; (×) grafting efficiency.

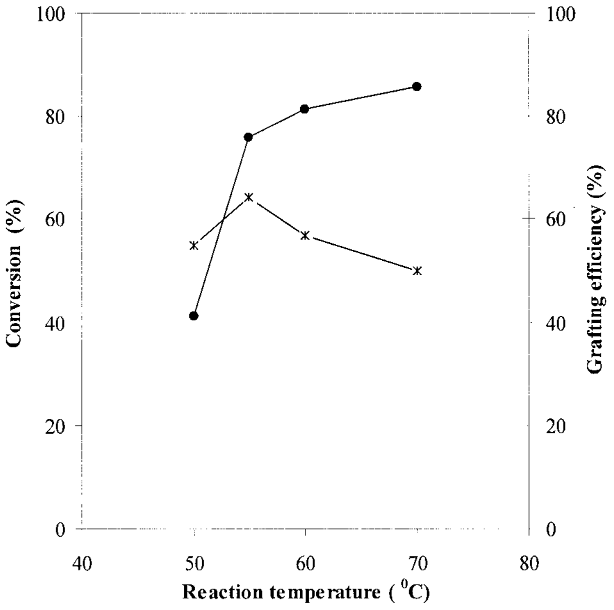


Figure 3 Effect of the reaction temperature on graft copolymerization (MMA100 phr, initiator 0.75 phr, 8 h): (●) conversion; (×) grafting efficiency.

centrations, many reactions, which probably compete with the grafting reaction, take place in the solution. This means that homopolymerization is more pronounced than is graft copolymerization at higher monomer concentrations. Another explanation is that there were no new active sites on the rubber molecule, so the grafting efficiency thus decreased at high monomer concentrations. Owing to the *cis*-1, 4 configuration, the grafting sites on the *cis* positions might not be available after a certain percentage of grafting had taken place. The newly arriving monomers are sterically hindered, resulting in limiting grafting at high monomer concentrations.

Effect of the Reaction Temperature

The graft copolymerization was carried out at four different temperatures ranging from 50 to 70°C. In Table II and Figure 3, we see that a higher temperature results in a higher conversion. Transfer of radicals to the rubber chains produces grafts. Decomposition of the initiator increases with an increasing reaction temperature; it causes an increase in both the number of free radicals and the rate of polymerization. When the polymerizing temperature was higher than 55°C, the grafting efficiency decreased because of the radical recombination. The initiator

Table II Effect of the Reaction Temperature and Time on Graft Copolymerization

				Graft Properties[a]			
Sample	Temperature (°C)	Time (h)	Conversion (%)	Grafted NR (%)	Free NR (%)	Free PMMA (%)	Grafting Efficiency (%)
B	55	8	75.9	57.9	26.6	15.4	64.1
J	50	8	41.2	57.4	32.1	13.1	54.8
K	60	8	81.3	52.9	27.8	19.3	56.9
L	70	8	85.8	48.1	28.9	23.0	50.1
M	55	4	67.9	30.4	41.7	23.9	40.9
N	55	6	74.5	53.8	29.0	17.2	59.8
O	55	10	74.9	50.6	31.3	18.1	57.8

[a] MMA in the feed = 100 phr; initiator = 0.75 phr.

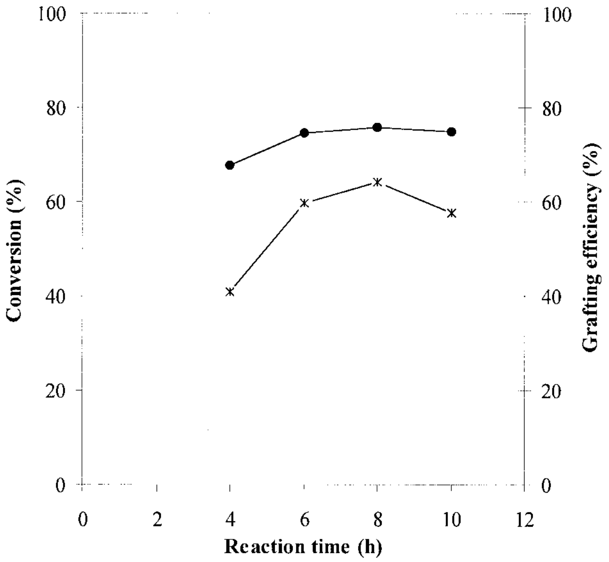


Figure 4 Effect on the reaction time on graft copolymerization (MMA 100 phr, initiator 0.75 phr, 55°C): (●) conversion; (×) grafting efficiency.

decomposition increased with the increasing reaction temperature to give an instantaneous abundance of free radicals. The radicals underwent either recombination or other side reactions; the initiator efficiency for grafting was thus reduced at higher temperatures. The decrease of grafting efficiency can be also explained by the increased formation of homopolymers of MMA and NR, in that the higher-temperature polymerization increases in polymer radical diffusion in the aqueous phase and encounters among themselves. This should promote an increased amount of homopolymers.

Effect of the Reaction Time

The effect of the reaction time on the grafting of MMA onto the NR is shown in Table II and Figure 4. It can be seen that as the reaction time increases there is an increase in the conversion and grafting efficiency in the lower reaction time range. At the reaction time of 8 h, its conversion and grafting efficiency reach a maximum value; thereafter, the grafting efficiency decreases slightly. At a long reaction time (10 h), the PMMA homopolymer is formed more readily than is the graft copolymer since there are no new, active grafting sites on the rubber molecules. The appropriate conditions for the preparation of GNR were found to be 100 parts by weight of the monomer per 100 parts by weight of the dry rubber content, 0.75 phr of the initiator concentration, and a reaction temperature of 55°C for 8 h, which gave a high monomer conversion and grafting efficiency.

Morphology of the Grafted NR

The grafting of MMA onto the NR is a core–shell-type emulsion copolymerization. The GNR particles consist of the NR core and the compatibilized MMA polymer shell. In graft copolymerization of the NR latex, the grafting reaction occurs largely on the surface of the rubber particles. This is true if the initiator used for the grafting reaction is a water-soluble initiator,[2] such as potassium persulfate (used in the present work). Radicals generated on the surface regime of the particles cannot diffuse inside the rubber particles due to the high viscosity of the NR particles. The radical concentration on the rubber surface is considerably higher than that in the center of the latex particle.[9]

Figures 5 and 6 show the morphology of the GNR-based core–shell particles synthesized from 4-, 6-, and 8-h polymerization. The NR seeds show mainly a spherical morphology of a core–shell configuration with the NR particles as the core and a thin PMMA film as the shell. A thin layer of the grafted PMMA covering the NR seed particles indicated the complete closed shell. The grafting between the plastic and elastomer components led to the compatibility of the two domains, resulting in a favorable state of dispersion and some possible chemical bonds linking the two phases together. Using different staining solutions allowed us to increase the contrast between the NR phase and the PMMA phase. The surface layer stained with RuO_4 appeared darker than when stained with OsO_4. Depending on the polymerization time, distinct differences in the polymer phase arrangement on the latex particles were revealed.

The core–shell morphology of the particles may be attributed to the effect of PMMA macromonomer graft copolymers partitioning on the surface of the seed particles. During the period of polymerization, the thickness of the graft copolymer layer on the surface of the seed particles increased with the increasing reaction time. After 8 h of polymerization, PMMA resided on the surface of the particles as a continuous shell and the seed particles had a complete closed shell.

Dynamic Mechanical Thermal Analysis (DMTA)

Thermal transition phenomena of the GNR were investigated by DMTA. The temperatures at

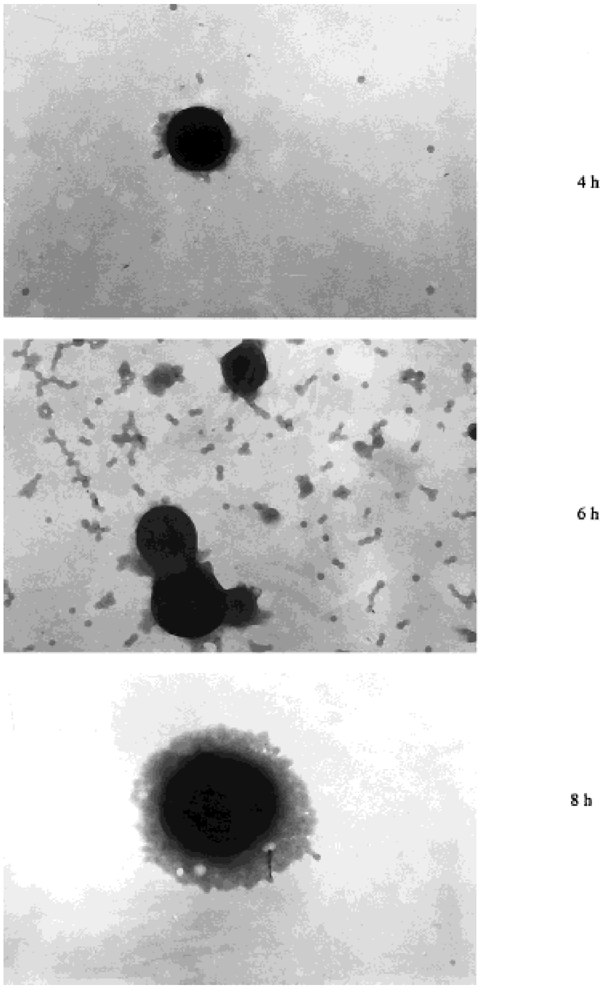


Figure 5 Transmission electron micrographs of the GNR latex (OsO_4 stain); MMA 100 phr, initiator 0.75 phr, 55°C, 4–8 h (×24,000).

which damping (tan δ) peaks were observed are quoted as glass transition temperatures. The dynamic mechanical properties of the GNR were measured at 1 Hz over the temperature range of -110 to $+165$°C. Figure 7 shows the dependence of the storage modulus on the temperature for the GNR prepared from different monomer concentrations. The storage modulus decreases with an increasing testing temperature. This is because the relaxation arising from local motions of the polymer chains is very stiff around the transition region. The storage modulus decreases with increasing MMA concentration, which is expected because an increase in the MMA concentration generally results in an increase in the chain stiffness of the GNR and contributes to improved mechanical properties.

The effect of the MMA concentration on the value of the loss factor (tan δ) is shown in Figure 8. The tan δ value shows a maximum around the transition region. We can then locate the glass transition temperature (T_g) of the NR-grafted PMMA. It is apparent that the large energy loss peaks are associated with the large changes in the modulus. This may result from the high-energy input used for a joint motion of parts of the main polymer chains in the transition region. We also found that tan δ decreased as a consequence of increasing the MMA concentration, and the higher interaction between the NR and MMA moieties of the GNR occurred at a high MMA concentration of 120 phr. However, tan δ also decreased as a consequence of the decrease of the rubber phase, which was substituted by the PMMA phase. Therefore, tan δ decreased with increase of the grafting efficiency since the rubber chain was partially immobilized by grafting.

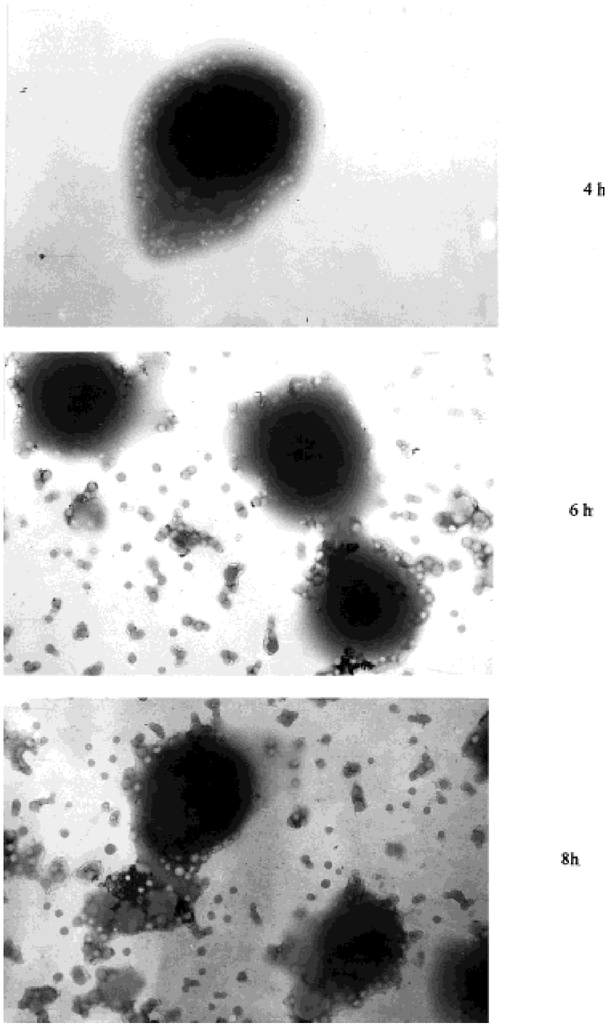


Figure 6 Transmission electron micrographs of the GNR latex (RuO_4 stain); MMA 100 phr, initiator 0.75 phr, 55°C, 4–8 h (×24,000).

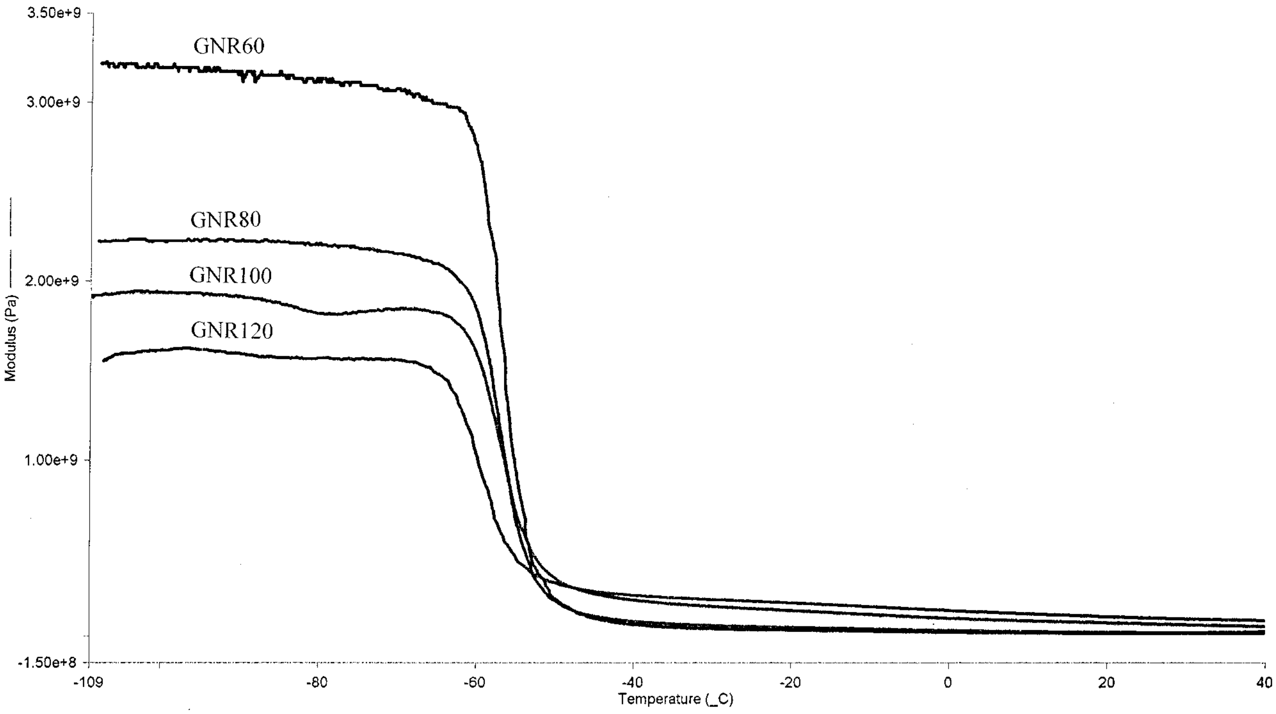


Figure 7 Storage modulus of the GNR at different MMA concentration.

From Figure 7 and Table III, we see that changing the MMA concentration from 60 to 120 phr causes a shift in the position of T_g and a change in the half-peak width. Regarding the overall width of the tan δ peaks, the peaks became clearly broadened at a low MMA concentration, indicating greater dynamic losses. The losses could be because more mechanical energy input

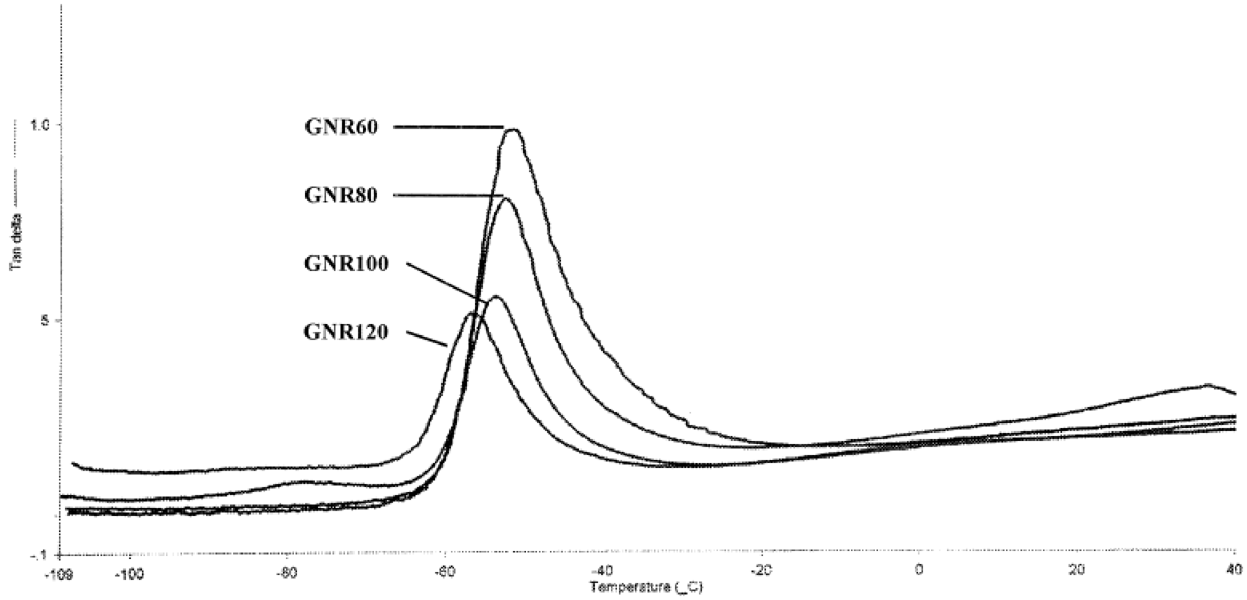


Figure 8 Loss factor (tan δ) of the GNR at different MMA concentrations.

Table III Glass Transition Temperature and Tan δ of the GNR Measured by the DMTA Technique

GNR	Monomer Concentration in the Feed (phr)	T_g (°C)	Tan δ
GNR60	60	−52.15	0.972
GNR80	80	−52.76	0.795
GNR100	100	−53.96	0.547
GNR120	120	−56.81	0.505

The number after GNR refers to the amount of MMA in the feed during graft copolymerization.

was converted to heat generated during the deformation, thus producing more energy losses in the movements of the polymer chains.

Blending of the GNR and PMMA

The GNR used henceforward is free from the free rubber and PMMA and it is aimed for applications in which a hard rubber segment with an optimum retention of properties, such as tensile properties and tear strength, is required. In this work, the graft copolymerization of MMA onto NR was carried out at 55°C for 8 h and the GNRs with MMA 60 and 100 phr were selected for the preparation of TPEs. The GNR and PMMA blends were prepared and the mechanical properties of the blends were investigated.

The mechanical properties of the blends are presented as a function of the blend ratio in Table IV. From Figure 9, we can see that PMMA enhances the hardness properties. The hardness increased with increasing PMMA content in the GNR/PMMA blends. The hardness of the GNR100/PMMA blend was higher than that of GNR60/PMMA. This is because the hard segments of PMMA-grafted chains in GNR100 are higher than in GNR60.

From Figure 9, the tensile strength of the GNR60/PMMA and GNR100/PMMA blends is seen to increase as the PMMA content is increased. For GNR100 blends, the tensile strength was higher than in GNR60 blends for the whole range of GNR/PMMA blend ratios, due to the higher percentage of GNR in GNR100. Therefore, an increase in the percentage of the GNR expressed in terms of the grafting efficiency improved the strength of the GNR/PMMA blends.

However, the elongation at break of the GNR/PMMA blends decreased with increasing PMMA content, due to the presence of the PMMA component as a brittle thermoplastic and the low strain at break, as shown in Figure 9. The break elongation of the GNR100 blends was less than that of the GNR60 blends for the whole range of GNR/PMMA blend ratios. Therefore, incorporation of PMMA yields a dramatic increase in the tensile strength with a very marked reduction in extensibility.

The effects of the blend ratio on the tear strength of GNR60 and GNR100 blends are shown in Figure 9. For the GNR60/PMMA blends, the tear strength considerably increased with an increasing content of PMMA. The increase in MMA content increased the proportion of hard segments in the MMA-grafted chains and the PMMA homopolymer. The tear strength of the GNR100/PMMA blends increased with the PMMA content and reached a maximum value at the GNR/PMMA ratio of 70/30. We anticipate that the continuous phase of the NR gives rise to the inferior tear strength. The high tear strength of the

Table IV Mechanical Properties of GNR/PMMA Blends

	GNR60/PMMA				GNR100/PMMA			
Properties	100/00	70/30	60/40	50/50	100/00	70/30	60/40	50/50
Tensile strength (MPa)	3.5	4.1	5.3	8.1	5.1	6.9	11.5	21.3
Elongation at break (MPa)	410.1	105.7	21.7	20.4	90.8	81.2	19.3	6.5
Stress at 100% modulus (MPa)	1.7	4.1	—	—	—	—	—	—
Tear strength (N/mm)	13.2	15.5	16.3	25.0	28.7	61.9	46.1	44.2
Hardness (Shore D)	15.0	21.6	35.8	47.8	31.4	49.8	56.1	60.9
Impact energy (J)	NA	NA	NA	1.21	NA	3.73	3.26	0.566

GNR60, the GNR prepared with MMA in the feed of 60 phr; GNR100, the GNR prepared with MMA in the feed of 100 phr. NA, not available due to too a high content of NR.

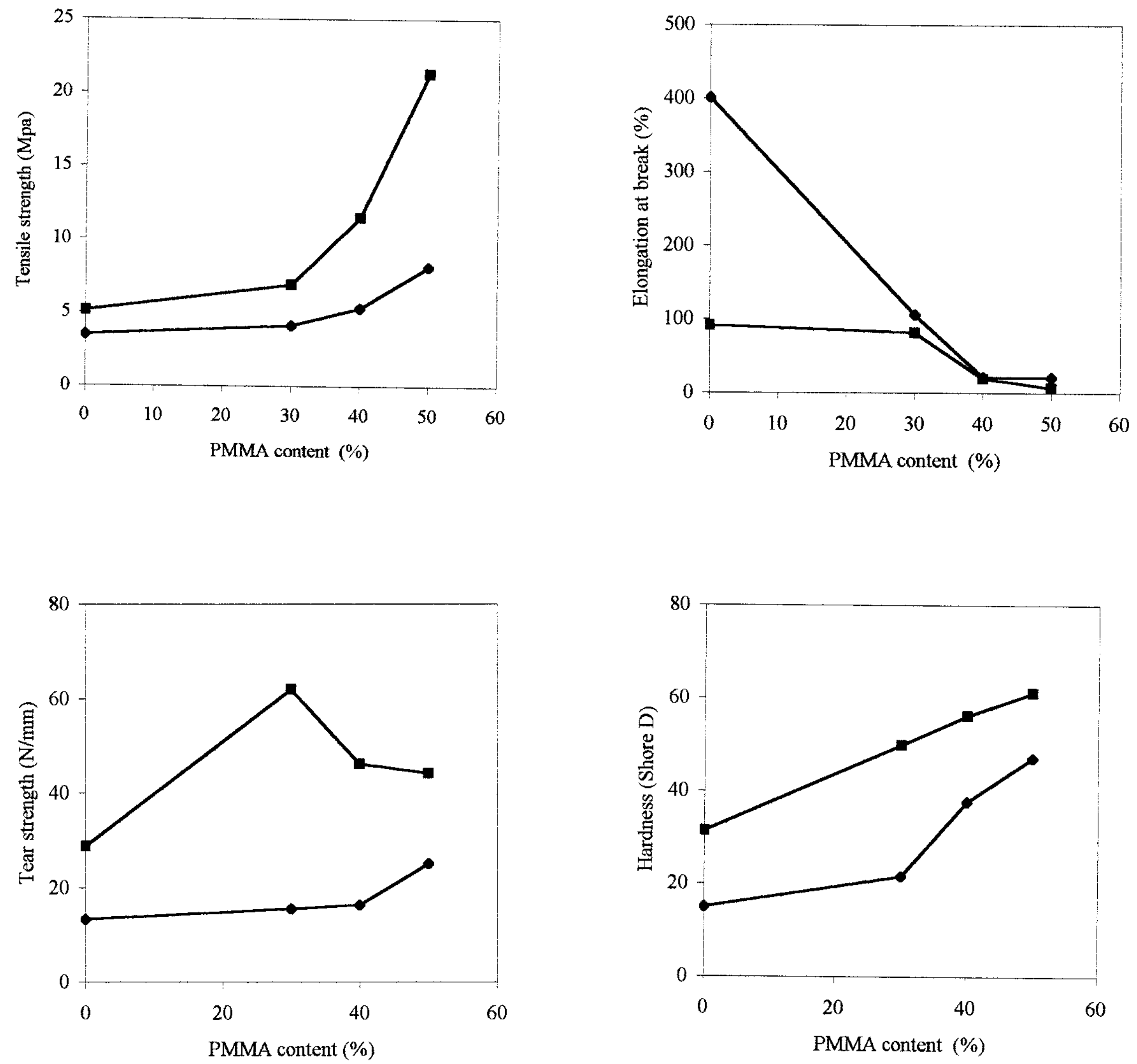


Figure 9 Effect of the PMMA content on mechanical properties of GNR/PMMA blends: (◆) GNR60; (■) GNR 100.

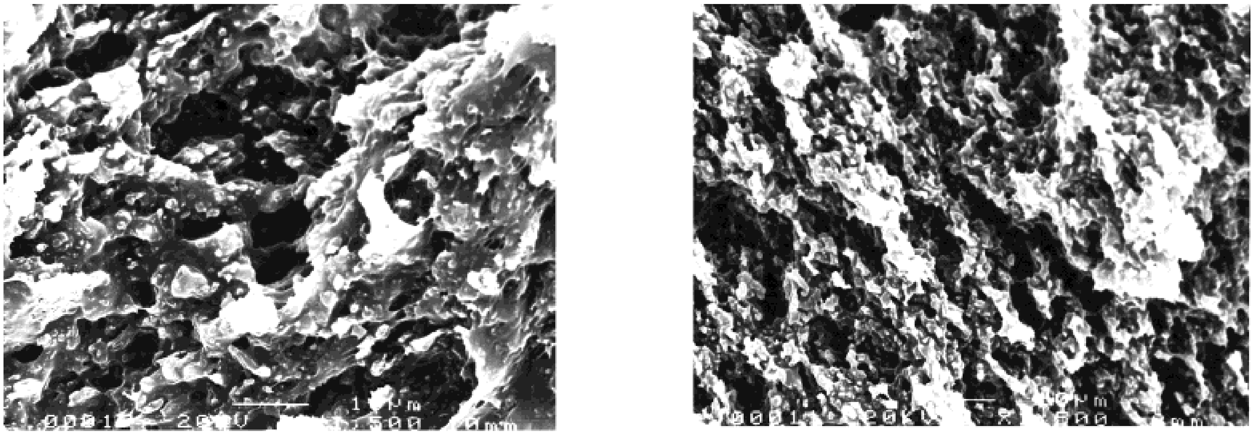
compatibilized system is provided by a good adhesion between the two components: the elastic and hard phases.

The impact energy of the GNR/PMMA blends is shown in Table IV. The impact energy of the GNR100/PMMA blends increased with the GNR content. The impact strength is essentially a function of how cracks can propagate within the matrix. When the GNR is present in a blend, it stretches as the crack passes by, thus dissipating much of energy necessary to develop the new surface of a growing crack. The effect of the highly GNR content is to dissipate a large amount of energy. This makes crack propagation more difficult, leading to an increased impact strength of the blend.[10,11] The higher the content of the GNR, the higher is the impact energy of the blend.

Comparing the blends, the GNR60/PMMA blends gave a low compatibility due to dissimilar characteristics as shown by the poor mechanical properties at all blend ratios. By increasing the grafting efficiency of the GNR, the mechanical properties of GNR100/PMMA blends were improved tremendously. Therefore, the effect of the graft copolymer is vital in increasing the adhesion between the immiscible polymers to provide a fine degree of wetting and dispersion.

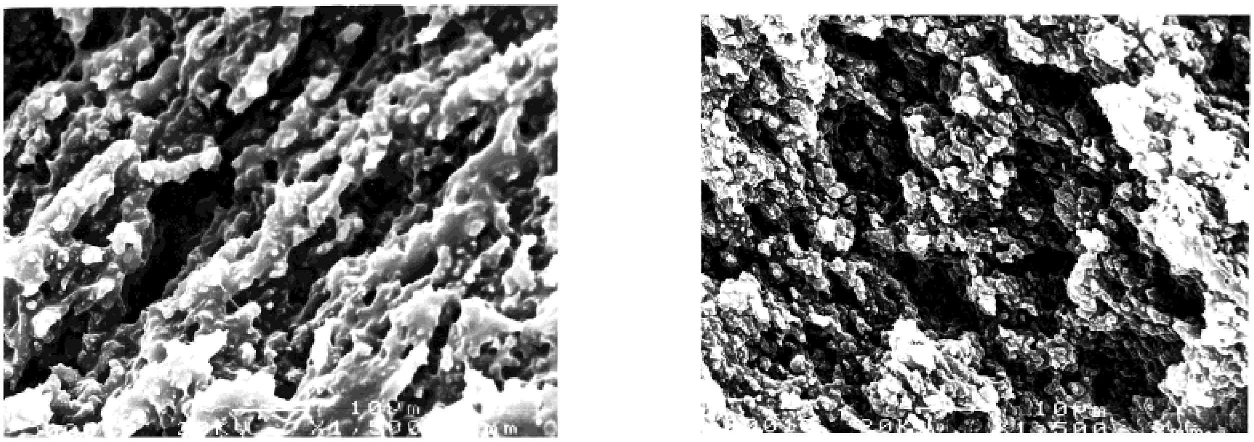
Morphology of the Blends

A scanning electron microscope was employed to investigate the fracture surfaces of the specimens after the tensile property test. Figure 10 shows the tensile fracture surfaces of the GNR60/PMMA



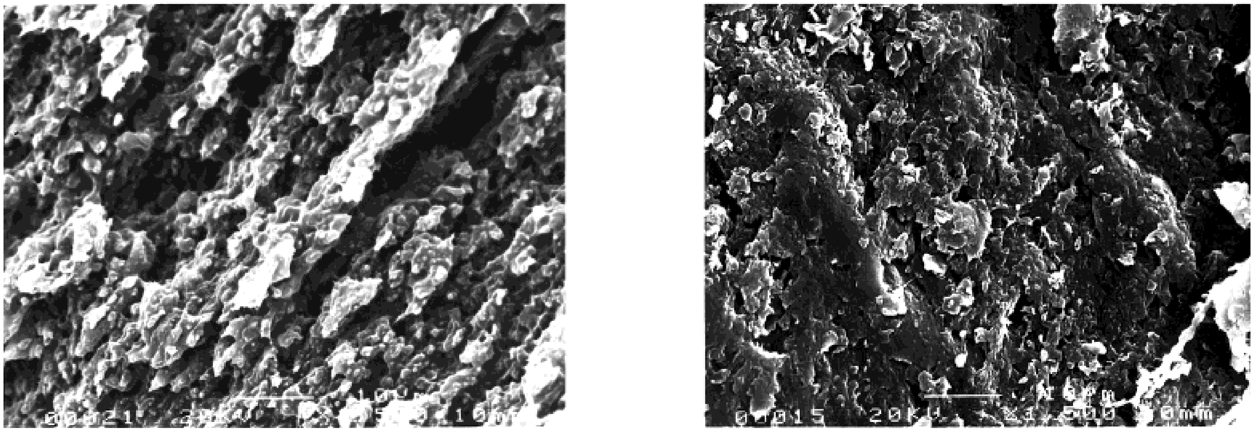
GNR60/PMMA (70/30)

GNR100/PMMA (70/30)



GNR60/PMMA (60/40)

GNR100/PMMA (60/40)



GNR60/PMMA (50/50)

GNR100/PMMA (50/50)

Figure 10 Fracture surfaces of GNR/PMMA blends (×1500).

and GNR100/PMMA blends at various blend ratios. We observe that cavitation of the specimens decreases with increasing PMMA content; the higher GNR content (70%) caused the increase of cavitation sites. A cavity may form and grow, but the growth was interrupted by adjacent growing cavities formed by neighboring particles. For GNR100/PMMA blends, the fracture surface was smoother than for GNR60/PMMA blends at the same blend ratio. Due to the better grafting properties of GNR100 than those of GNR60 (the higher percentage of GNR and grafting efficiency), the GNR100 blends give better interfacial adhesion between the two phases of the blends than that of the GNR60 blends. This observation indicates that the graft copolymer acts as an interfacial agent; therefore, increase of the percentage GNR and the grafting efficiency improves the mechanical properties of the GNR/PMMA blends. The high tensile strength values of the compatibilized blends are in agreement with our anticipations.

CONCLUSIONS

The graft copolymerization of the MMA monomer onto NR using potassium persulfate as the initiator was carried out by varying the initiator concentration, reaction temperature, monomer concentration, and reaction time. The grafting efficiency increased with increasing initiator concentration up to 0.75 phr. Then, it decreased, indicating that further increase in the initiator concentration favored homopolymerization rather than grafting. An increase in the concentration of MMA at a given benzoyl peroxide initiator concentration increased the grafting efficiency. The grafting efficiency decreased with an increase in temperature above 55°C. At 8 h of polymerization, the rubber seeds showed mainly a spherical morphology of a core–shell configuration with NR particles as the core and a thin PMMA film as the shell.

The morphology and mechanical properties of GNR/PMMA blends were studied as a function of the blend ratio and grafting copolymer composition. With an increase in the PMMA content, tensile strength and hardness increased but impact energy decreased. The mechanical properties of the blends showed considerable improvement upon the addition of the graft copolymer with a high grafting efficiency. Interfacial adhesion between the two homopolymers increased by the addition of the graft copolymer, and consequently, the mechanical properties improved. SEM studies of the fracture surface indicated better adhesion between the components in the compatibilized system.

Financial support of this research by the Thailand Research Fund is gratefully acknowledged by the authors. The authors thank Revertex (Thailand) Ltd. and the Siam Chemical Industrial Co., Ltd., for the material supply. The authors also thank the Rubber Research Institute of Thailand and the National Metal and Materials Technology Center of NSTDA for some research facilities.

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