Grafting of Methyl Methacrylate and Styrene onto Natural Rubber

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The graft copolymerization of methyl methacrylate and styrene onto natural rubber in the emulsion process was carried out by varying the concentrations of methyl methacrylate and styrene monomers, emulsifier concentration, initiator concentration, and reaction temperature. The grafting efficiency, graft ratio, and monomer conversion were reported. The molecular weights of free S/MMA and the frequency of grafted chains on the rubber backbone were determined by the gel permeation chromatography (GPC) technique. The copolymer composition was determined by nuclear magnetic resonance spectroscopy (NMR) and elemental analysis (CHO). The optimum condition of graft copolymerization was found to be at 100 parts by weight of monomer per 100 parts by weight of natural rubber latex, 1.5 parts by weight of emulsifier, 1.5 parts by weight of initiator and at a temperature of 70°C for 8 hours. The grafted natural rubber product could be used as an impact modifier for PVC; the grafted natural rubber product and PVC blend were prepared. The effect of grafted natural rubber product on tensile properties, Izod impact strength, and hardness of PVC blends was investigated.

Key words: Graft copolymerization, natural rubber, methyl methacrylate, styrene, mechanical properties.

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งานวิจัยนี้ได้ศึกษาการกราฟต์เมทิลเมทาคริเลตและสไตรีนบนยางธรรมชาติด้วยกระบวนการอิมัลชัน โดยศึกษาปัจจัยต่างๆ ที่มีผลต่อปฏิกิริยาการกราฟต์โคพอลิเมอไรเซชัน อันได้แก่ ความเข้มข้นของมอนอเมอร์เมทิลเมทาคริเลต และมอนอเมอร์สไตรีน ความเข้มข้นของสารก่ออิมัลชัน ความเข้มข้นของตัวริเริ่ม และอุณหภูมิของปฏิกิริยา และศึกษาหาประสิทธิภาพการกราฟต์ สัดส่วนการกราฟต์ และการเปลี่ยนมอนอเมอร์ การหาน้ำหนักโมเลกุลของ S/MMA อิสระ และความถี่ของการเกิดโซ่กราฟต์บนโซ่หลักของยางธรรมชาติทำได้โดยเทคนิค GPC องค์ประกอบของโคพอลิเมอร์หาได้ด้วยนิวเคลียร์แมกเนติกเรโซแนนซ์สเปกโทรสโกปี และการวิเคราะห์หาธาตุ CHO จากการศึกษาพบว่าภาวะเหมาะสมในการเตรียมยางธรรมชาติกราฟต์ คือ มอนอเมอร์ 100 ส่วนโดยน้ำหนักต่อ 100 ส่วนโดยน้ำหนักของยางธรรมชาติ สารก่ออิมัลชัน 1.5 ส่วนโดยน้ำหนัก ตัวริเริ่ม 1.5 ส่วนโดยน้ำหนัก และอุณหภูมิ 70°ซ เป็นเวลา 8 ชั่วโมง งานวิจัยนี้มีการนำยางธรรมชาติกราฟต์มาใช้เป็นสารเสริมการทนแรงกระแทกในพีวีซี โดยการเตรียมพลาสติกผสมของยางธรรมชาติกราฟต์กับพีวีซี ศึกษาผลของยางธรรมชาติกราฟต์ต่อความทนแรงดึง ความทนแรงกระแทกไอซอด และความแข็ง

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INTRODUCTION

Graft copolymers are important technological materials in that they can greatly influence the interfacial region in polymer blends and composites. The graft copolymerization would effectively combine the desirable properties of natural rubber with vinyl monomer in order to produce tough, hard, and impact resistant materials with easy processibility. The core-shell emulsion copolymerization is a well-known process used to control latex particle morphology. According to the polymer particle morphology, there are two main kinds of core-shell copolymers: soft core-hard shell and hard core-soft shell. Usually, polymers such as polybutadiene (PB), styrene-butadiene rubber (SBR), and natural rubber are chosen as the soft components, whereas the polymers of methyl methacrylate (MMA), styrene (S), acrylonitrile (AN), and so on are chosen as the hard components. Graft polymers exist on the interface between the core and the shell. Polymers with a soft core and a hard shell are used as an impact modifier, for plastics toughening, and as damped oscillation materials, whereas polymers with a hard core and a soft shell are usually applied to the coating and adhesive fields. The grafting of methyl methacrylate and styrene onto natural rubber can be used as an impact modifier in rigid PVC. The influences of the graft copolymerization process parameters such as emulsifier concentration, initiator concentration, monomer content, and polymerization temperature on the grafting efficiency and graft ratio have been investigated.(1, 2)

Some investigators studied the grafting of vinyl monomer onto synthetic and natural rubber. For the graft copolymerizations of styrene/methyl methacrylate (75/25) onto polybutadiene seed latex using an oil-soluble (cumene hydroperoxide) initiator performed over a range of emulsifier concentrations, the emulsifier-free polymerization showed a very high degree of grafting while neither secondary nucleation nor coagulation was observed.(3) For the graft copolymerization of styrene and methyl methacrylate on SBR latex particles in the core-shell emulsion process with the benzoylperoxide-Fe^{2+} redox initiator, the effects of the principal factors such as the polymerization temperature, monomer-to-polymer ratio, and the frequency of monomer addition and conversion on the grafting degree and the grafting efficiency were studied.(4) The graft copolymerization of methyl methacrylate onto natural rubber using potassium peroxydisufate catalyzed by the silver ion was carried out by varying the concentration of monomer, initiator, thiourea and silver ion; the grafting reaction was temperature dependent the energy of activation was determined.(5) The grafting of methyl methacrylate and styrene onto natural rubber has never been investigated.

The purpose of this work is to prepare the graft copolymer of methyl methacrylate and styrene onto natural rubber, and to study the influences of initiator concentration, emulsifier concentration, and polymerization temperature on conversion, grafting efficiency, graft ratio, and grafting frequency. The grafted natural rubber was used as an impact modifier in PVC, and the mechanical properties of the blend were measured.

EXPERIMENTAL

Materials

NR latex containing 60.05% dried rubber was the product of Thai Rubber Latex Co., Ltd. and it was used as received. The methyl methacrylate and styrene monomers were supplied by Aldrich. The methyl methacrylate and styrene monomers were scrubbed with 5 wt% NaOH to remove the inhibitor and distilled prior to use. Potassium persulfate, sodium dodecyl sulfate, dodecyl mercaptan, and isopropanol were from Fluka and they were used as received. PVC resin (K value = 66), MBS (methyl methacrylate and styrene graft onto polybutadiene), lead sulfate, and stearic acid were supplied by the Thai Plastic and Chemical Public Co., Ltd. and used as received.

Graft Copolymerization of Methyl Methacrylate and Styrene onto Natural Rubber

The graft copolymerization was performed in a 1 liter glass vessel under nitrogen with a three-curved blade impeller and at a stirrer speed of 180 rpm. Natural rubber latex and an aqueous solution of additives were fed to the reactor and the dissolved oxygen in the reaction mixture was removed by bubbling nitrogen gas through the mixture before polymerization. The mixture of 25 wt% styrene and 75 wt% methyl methacrylate and dodecyl mercaptan was charged to the reactor and the polymerization reaction was performed at the desired polymerization temperature for 8 hours. Then, phenol was added to stop the reaction. The grafted NR latex was coagulated. The resulting crumb was filtered, washed, and dried at 70°C in a vacuum oven.

Determination of Grafting Efficiency and Graft Ratio

The free S/MMA copolymer was extracted by using acetone for 24 hours at 55°C while free NR was extracted by light-petroleum ether for 24 hours at 70°C. The grafting efficiency (GE) and graft ratio (GR) were calculated by the following equations.(6)

$$\mathrm{GE} = \frac{\text{weight of grafted S/MMA}}{\text{weight of free S/MMA + weight of grafted S/MMA}} \qquad (1)$$

$$\mathrm{GR} = \frac{\text{weight of grafted S/MMA}}{\text{weight of backbone, } \textit{cis}\text{-1,4-polyisoprene}} \qquad (2)$$

Characterization of Grafted Natural Rubber

The infrared (FT-IR) spectra of grafted natural rubber were taken on a Nicolet infrared spectrometer model Impact 410 with KBr cell, the grafted natural rubber was dissolved in chloroform. The ^{1}H-NMR spectroscopy was carried out with the rubber samples either being dissolved or swollen in $CDCl_3$. A Bruker model AC-F200 NMR spectrometer was used. The copolymer composition of grafted natural rubber was also determined by an elemental analyzer (Perkin-Elmer model PE2400).

Determination of Morphology

The latex was diluted 400 times with distilled water to a concentration of 0.05 wt%. To this solution, 1 cm^3 of a 2% aqueous OsO_4 solution was added, and allowed to stain the natural rubber in the grafted polymer for 1 hour. The stained latex was placed on a 400 mesh grid and dried. The morphology was examined by TEM (JSM 200CX).

G.P.C.

Molecular weights of the free S/MMA chain length were studied using a Waters liquid chromatography apparatus with the UV and IR detectors. Terahydrofuran was the eluant and a flow rate of 10 cm^3 min^{-1} was used. The apparatus was calibrated by mono-dispersed PS calibration standards. The graft frequency and free S/MMA chain length were determined.

Blend Preparation

The powder blends of the PVC compound and the grafted natural rubber product were prepared at room temperature. The PVC blend was composed of 100 parts by weight of PVC, 10 or 15 phr grafted natural rubber product, 3.5 phr lead sulfate (heat stabilizer), and 1.0 phr stearic acid (lubricant). The mixture was roll milled at 180°C for 5 min. The thin sheets from the two-roll mill were then pressed by compression molding at 190°C for 10 min, and the sheet thickness was 3 mm.

Mechanical Property Testing

The tensile properties were determined according to ASTM D638, the type of test specimen was type I, and the speed of testing was 5 mm min^{-1}. The notched Izod impact strength was determined according to ASTM D256, and the energy of the hammer was 21.6 J. The shore hardness of the specimens was determined according to ASTM D2240, the type D Durometer was used.

RESULTS AND DISCUSSION

Preparation of Grafted Natural Rubber

The graft copolymerization was carried out by preparing natural rubber as the core and styrene and methyl methacrylate as the shell monomers. The grafted natural rubber particles consisting of a polyisoprene core and compatibilizing styrene and methyl methacrylate polymer shell were prepared by emulsion polymerization. The natural rubber latex was used as a seed latex of *cis*-1,4-polyisoprene from which the isoprene monomers were polymerized first, and the mixture of styrene and methyl methacrylate monomers was subsequently added to continue the polymerization within the seed particle. The key process lies in the grafting of a significant portion of the growing styrene-methyl methacrylate random copolymer radicals onto the double bonds of the existing elastomeric components. The grafting between the plastic and elastomer components led to the compatibility of the system, resulting in a favorable state of dispersion and also bonding the phases together. Upon the graft copolymerization, the second monomers were mixed to give a phase separation to yield the complex inner morphology.(7) Emulsion grafting to small particles exhibited a closed shell of graft copolymer on their surfaces, and no inclusion was visible in the images either before or after the mixing process. If the closed shell of grafted rubber latex were formed incompletely, coagulation in the acid solution would occur.

Figure 1. Transmission electron micrograph of the completed closed shell of the graft natural rubber latex (x 45,000).

The amount of mixed monomer solution per 100 g of rubber content was varied at 50, 75, 100, 125 and 150 g. Graft copolymerization was performed with 1.5 parts by weight of emulsifier and 1.5 parts by weight of initiator per 100 parts of natural rubber at 50°C for 8 hours, and a complete formation of the core-shell structure was produced. Such a complete formation of the core-shell structure was confirmed by the coagulation reaction of grafted latex in an acid solution. As mentioned above, if the formation was complete, the coagulation could not occur. The result indicated that the complete closed shell indeed formed at above 100 parts by weight of monomers. The morphology of core-shell formation and the dispersion of particles of grafted natural rubber latex are shown in Figures 1 and 2, respectively.

Figure 2. Transmission electron micrograph of the grafted natural rubber (x 30,000).

Effect of the Emulsifier Concentration

The seeding polymerization in our work is emulsion polymerization during interval III. The majority of monomers swell or reside inside the latex particles during interval III and the emulsifier charge is just sufficient to maintain colloidal stability of the particles. The effect of emulsifier concentration on the monomer conversion, grafting efficiency, and graft ratio is presented in Table 1 and Figure 3. The monomer conversion increased with an increase in the emulsifier concentration. At concentrations higher than 1.0 part by weight of emulsifier, the monomer conversion increased slightly. In Figure 3, the grafting efficiency increased with increasing emulsifier concentration, reached a maximum value (57.1%) at 1.5 parts by weight, and then decreased with emulsifier concentration. As a result of the decrease in emulsifier concentration, the coagulation occured. If the coagulation takes place with the decreasing emulsifier concentrations, the decreasing total surface area imposes a direct effect on the grafting efficiency and graft ratio. Above the maximum value of 57.1%, the grafting efficiency and graft ratio decreased, due to the presence of more free micelles in the water phase. These micelles can be initiated to form a new crop of particles, so there will be fewer monomers left for grafting.(3) The appropriate emulsifier concentration of 1.5 parts by weight was found.

Figure 3. Effect of the emulsifier concentration on the monomer conversion and grafting efficiency.

Effect of the Initiator Concentration

The effects of initiator concentration on the monomer conversion, grafting efficiency, and graft ratio are shown in Table 1 and Figure 4. From Figure 4, the monomer conversion, grafting efficiency, and graft ratio increase rapidly with an increasing amount of initiator concentration initially, and increase slowly at high initiator concentrations.

Table 1. Effect of the emulsifier concentration, initiator concentration, and reaction temperature on the monomer conversion, grafting efficiency, and graft ratio. Latex:monomers = 1:1, polymerizing time = 8 hours.

Temperature (°C)	Emulsifier concentration (parts by wt)	Initiator concentration (parts by wt)	Monomer conversion (%)	Grafting efficiency (%)	Graft ratio
50	0.5	1.5	48.1	23.5	0.38
50	1.0	1.5	72.2	49.7	0.77
50	1.5	1.5	74.9	57.1	0.89
50	2.0	1.5	76.2	51.5	0.81
50	2.5	1.5	76.9	36.6	0.63
50	1.5	0.5	48.0	18.3	0.26
50	1.5	1.0	65.5	49.7	0.81
50	1.5	2.5	78.1	59.9	0.94
40	1.5	1.5	54.1	41.1	0.41
60	1.5	1.5	76.3	61.0	0.97
70	1.5	1.5	79.5	65.3	0.99

Figure 4. Effect of the initiator concentration on the monomer conversion and grafting efficiency.

Initially, the increase of the initiator concentration produces more grafting sites for styrene/methyl methacrylate random copolymers or styrene, methyl methacrylate to graft onto. Therefore, the monomer conversion, grafting efficiency, and graft ratio can, of course, increase. At the higher initiator concentrations, excessive radicals will react with each other and shorten the chain length of the grafts. Beyond the limit of the initiator amount, therefore, the monomer conversion, grafting efficiency, and graft ratio do not increase but are almost constant. The same results were also reported by Zhao et al.(4) and Merkel et al.(7)

Effect of the Reaction Temperature

The reaction temperature imposes a strong effect on the grafted natural rubber product because the reaction temperature affects the reactivity ratios of monomers and ratio of styrene and methyl methacrylate monomers in the aqueous phase. Grafts are produced by transfers of radicals to the rubber chains. It is well known that the activation energy of the transfer reaction is greater than that of the propagation reaction. With increasing temperature, decomposition of the initiator increases, resulting in an increase in the number of free radicals and rates of polymerization and grafting. The monomer conversion, grafting efficiency, and graft ratio increase when the polymerization temperature increases. These results are illustrated in Table 1 and Figure 5. Only little variation of the monomer conversion, grafting efficiency, and graft ratio occurred when the temperature increased above 50°C, due to the very low activation energy of the decomposition of the initiator used in the experiment. The experimental results are in agreement with those of Zhao et al.(4)

The graft frequency and free S/MMA chain length were determined by a gel permeation chromatography method.(6) The free S/MMA was clearly evidenced in the low molecular weight peak, eluting at about 800-1,000 seconds. After appropriate peak fitting, this distribution was analyzed for molecular weight parameters using the MAXIMUM-820 software supplied with the chromatography unit and utilizing the results from column calibration with narrow distribution PS standards (Scientific Polymer Products). For the reaction temperature of 40°C, the average molecular weights of free S/MMA determined by the GPC method were as follows: $\bar{M}_n$ = 121,907, $\bar{M}_w$ = 677,630, $\bar{M}_z$ = 2,174,102, and $\bar{M}_w/\bar{M}_n$ = 5.55. The effect of the reaction temperature on the average molecular weight of free S/MMA is shown in Table 2. The free S/MMA chain length is proportional to the average molecular weights.

Table 2. Effect of the reaction temperature on average molecular weights of free S/MMA and graft frequency. Latex:monomers = 1:1, emulsifier concentration = 1.5 parts by weight, initiator concentration = 1.5 parts by weight, polymerizing time = 8 hours.

Temp.	MW of free S/MMA				Graft
($^\circ$C)	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_z$	$\bar{M}_w/\bar{M}_n$	Frequency
40	121,907	677,630	2,174,102	5.55	4,349
50	91,790	520,691	2,146,770	5.67	1,734
60	101,063	439,117	1,549,824	4.34	1,538

70	87,546	370,165	1,503,207	4.22	1,303

Table 3. Effect of the reaction temperature on the composition of grafted natural rubber. Latex:monomers = 1:1, emulsifier concentration = 1.5 parts by weight, initiator concentration = 1.5 parts by weight, polymerizing time = 8 hours.

Reaction Temperature (°C)	Copolymer composition, MMA: I: S[b]	
	NMR method	EA method[a]
40	13.9 : 75.8 : 10.3	13.6 : 78.0 : 8.3
50	16.0 : 73.5 : 10.5	18.0 : 69.4 : 12.7
60	20.7 : 66.3 : 13.0	21.8 : 65.3 : 12.9
70	29.4 : 55.1 : 15.5	24.6 : 57.4 : 18.0

[a] Elemental analysis.

[b] Methyl methacrylate : Isoprene : Styrene

Figure 5. Effect of the polymerization temperature on the monomer conversion and grafting efficiency.

The graft frequency is the number of backbone polymer repeating units between graft chains. The graft frequency was calculated by the total number of graft chains per backbone chain, both derived from the molecular weight analysis. The effect of the reaction temperature on the graft frequency is shown in Table 2. The value of the graft frequency decreased with increasing reaction temperature because the initiator could easily decompose to form free radicals at high temperatures. These newly-formed free radicals are very active in abstracting hydrogen radicals on the natural rubber backbone. Many active sites are then produced with fewer repeating units between two chains. Therefore, the repeating units between grafted chains decreased with increasing reaction temperature.

The process of graft copolymerization of methyl methacrylate and styrene onto natural rubber in the core-shell emulsion process is very complicated and there are many effective factors. The influences of the principal factors on the monomer conversion, grafting efficiency, and graft ratio are listed in Table 5.

Table 5. Effect of various factors on the monomer conversion, grafting efficiency (GE), and graft ratio (GR).

Factors	Conversion	GE	GR
Emulsifier content ↑	↑	↓	↓
Initiator content ↑	↑	↑	↑
Reaction temperature ↑	↑	↑	↑

↑ : increase ↓ : decrease

Copolymer Composition of Grafted Natural Rubber (NR-*g*-S/MMA)

An FT-IR spectrum obtained from the insoluble portions after extraction with petroleum ether and acetone is shown in Figure 6. The spectrum obtained compares favorably to those in literature.(8) It exhibits the characteristic absorption bands of $R_2C{=}CHR$ of isoprene at 810 cm^{-1} and a C=O stretching vibration at 1750 cm^{-1} and C═C stretching vibration at 1510 cm^{-1}. The peaks of the grafted natural rubber appeared at 1750 and 1510 cm^{-1}, due to the carbonyl group (C=O stretching) of methyl methacrylate and C═C stretching of the benzene ring of styrene, respectively. This confirms the existence of grafting of methyl methacrylate and styrene onto the natural rubber backbone.

The copolymer composition of grafted natural rubber was determined by ^{1}H-NMR. The grafted natural rubber samples were dissolved with $CDCl_3$. The methyl methacrylate/isoprene/styrene ratio of grafted natural rubber was determined by the signal areas of ^{1}H-NMR spectra. The signal areas at 7.0 ppm, 5.2 ppm, and 3.6 ppm are the aromatic protons of styrene, the C=CH proton of isoprene, and the OCH_3 protons of methyl methacrylate, respectively.

From the different signal areas, the methyl methacrylate/isoprene/styrene ratio can be calculated by using the following equations:(3)

$$\text{Styrene (S)} = A_{\delta = 7.0} / 5 \quad (3)$$

$$\text{Isoprene (I)} = A_{\delta = 5.2} / 1 \quad (4)$$

$$\text{Methyl methacrylate (MMA)} = A_{\delta = 3.6} / 3 \quad (5)$$

where A_δ is the total signal area. The ratios of styrene, isoprene, and methyl methacrylate in the grafted natural rubber are presented in Table 3.

The elemental analyzer was also used to determine the copolymer composition. The ratios of styrene, isoprene, and methyl methacrylate were calculated by using the number of moles in the grafted natural rubber obtained from the analysis.(9) The copolymer composition determined by elemental analysis is shown in Table 3. The methyl methacrylate content in grafted natural rubber increased with increasing reaction temperature. The maximum methyl methacrylate content was determined to be 24.6% (elemental analysis) or 29.40% (NMR method) at the polymerization temperature of 70°C. The styrene content of the grafted natural rubber also slightly increased with increasing reaction temperatures from 40 to 70°C. The styrene content at 70°C was 15.5% and 18.0% by the NMR method and elemental analysis, respectively. These results imply that high reaction temperatures accelerated the less bulky species to polymerize them to graft onto the rubber backbone. The high content of methyl methacrylate and styrene corresponds to the high grafting efficiency and graft ratio.

The appropriate condition for preparation of grafted natural rubber was at 70°C for 8 h. which gave high monomer conversion, grafting efficiency, graft ratio, and styrene/methyl methacrylate content.

Blending of Grafted Natural Rubber and PVC

MBS (Methyl methacrylate-Butadiene-Styrene terpolymer) is widely used as an impact modifier in PVC. This work has successfully produced an impact modifier from natural rubber similar to MBS for PVC improvement. The grafted natural rubber was prepared by emulsion polymerization for 8 hours at 70°C. The basic formulation was 100 parts by weight of monomer per 100 parts by weight of natural rubber, 1.5 parts by weight of emulsifier and 1.5 parts by weight of initiator. Table 4 illustrates the effect of the grafted natural rubber product and MBS on tensile properties, Izod impact strength, and hardness of the PVC blend. The increases of impact strength of the PVC with the grafted natural rubber product and MBS were 38.4% and 65.3%, respectively. For the comparison between the grafted natural rubber product and MBS impact modifier, the impact strength of the PVC/MBS blend was somewhat higher than that of the PVC/grafted natural rubber product. Therefore, the grafted natural rubber product is more or less acceptable as an impact modifier in rigid PVC.

Impact strength is essentially a function of how readily cracks can propagate within the matrix. When the grafted NR product and MBS are included as impact modifiers for PVC, they stretch as the crack passes by, thus dissipating much of the energy necessary to develop the new surface of the growing crack. The effect of the high impact modifier content is to dissipate a large amount of energy. This makes crack propagation more difficult, leading to increased impact strength.(10-11) The higher the grafted NR product and MBS content, the higher the impact strength of the blends. The appropriate grafted natural rubber products used for this purpose were for 10 and 15 phr.

CONCLUSION

The grafting of methyl methacrylate and styrene onto natural rubber seed particles was prepared by core-shell emulsion polymerization. The rubber macroradicals reacted with methyl methacrylate and styrene monomers to form graft copolymers. The particle structure of grafted natural rubber is the core-shell type. The grafted natural rubber properties were strongly influenced by the reaction temperature. The grafted natural rubber prepared using 100 parts by weight of monomer per 100 parts by weight of natural rubber, 1.5 parts by weight of emulsifier, and 1.5 parts by weight of initiator at 70°C showed a high grafting efficiency and graft ratio. The maximum percent grafted natural rubber, monomer conversion, grafting efficiency, and graft frequency were 57.6, 79.5, 65.3, and 1,303 respectively, at a reaction temperature of 70°C.

The copolymer composition of grafted natural rubber (NR-*g*-S/MMA) was determined by the NMR method and elemental analysis. At the reaction temperature of 70°C, the ratios of styrene, isoprene, and methyl methacrylate in the grafted natural rubber were 15.5 : 55.1 : 29.4 (by NMR method) and 18.0 : 57.4 : 24.6 (by elemental analysis). The grafted NR product could be used as an impact modifier for PVC resin to form PVC/grafted NR product blends by mechanical blending and compression molding. The good mechanical properties of were obtained at 10 and 15 phr of the grafted NR product.

Figure 6. The infrared spectrum of grafted natural rubber.

Figure 7. The NMR spectrum of grafted natural rubber.

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Property	PVC	PVC + 10 phr impact modifier		PVC + 15 phr impact modifier	
		grafted NR	MBS	grafted NR	MBS
Tensile strength (MPa)	48.9 ± 0.39	40.2 ± 0.36	37.9 ± 0.15	38.8 ± 0.25	37.5 ± 0.44
Elongation at break (%)	61.4 ± 0.40	71.9 ± 0.24	73.5 ± 0.48	88.2 ± 0.24	92.3 ± 0.45
Modulus (MPa)	20856.2 ± 6.07	13455.5 ± 4.16	14285.0 ± 2.88	10236.5 ± 2.87	11755.9 ± 2.76
Izod impact strength (kJ/m^2)	270.2 ± 0.17	303.9 ± 0.18	423.1 ± 0.13	374.0 ± 0.12	446.6 ± 0.08
Hardness (N)	37.7 ± 0.20	36.0 ± 0.10	36.1 ± 0.20	35.3 ± 0.12	35.1 ± 0.20

Table 4. Effects of grafted NR product and MBS on the mechanical properties of PVC blends.