

Blends of Poly(Vinyl Chloride) (PVC)/Natural Rubber-g-(Styrene-co-Methyl Methacrylate) for Improved Impact Resistance of PVC

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ABSTRACT: To improve the mechanical properties of poly(vinyl chloride) (PVC), the possibility of combining PVC with elastomers was considered. Modification of natural rubber (NR) by graft copolymerization with methyl methacrylate (MMA) and styrene (St) was carried out by emulsion polymerization by using redox initiator to provide an impact modifier for PVC. The impact resistance, dynamic mechanical analysis (DMA), and scanning electron microscopy (SEM) of St and MMA grafted NR [NR-g-(St-co-MMA)]/PVC (graft copolymer product contents of 5, 10, and 15%) blends were investigated as a function of the amount of graft copolymer product. It was found that the impact strength of blends was increased with an increase of

the graft copolymer product content. DMA studies showed that NR-g-(St-co-MMA) has partial compatibility with PVC. SEM confirmed a shift from brittle failure to ductility with an increase graft copolymer content in the blends. The mechanical properties showed that NR-g-(St-co-MMA) interacts well with PVC and can also be used as an impact modifier for PVC. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 1666–1672, 2004

Key words: NR-g-(St-co-MMA); impact resistance; dynamic mechanical analysis; scanning electron microscopy; compatibility

INTRODUCTION

Polymer blends are of considerable importance, as blending could provide a means for improving the impact strength of fragile polymers. Poly(vinyl chloride) (PVC) belongs to a major class of engineering plastics that possess many unique properties that are suitable for a wide variety of technical and industrial products. It is available at a relatively low cost, is nonflammable, and has good chemical resistance and corrosion resistance. However, the stiff and brittle material is deficient for PVC expanded applications. PVC is blended with rubbery polymers to improve its impact strength, thus making it suitable for rigid application. It is well known that graft copolymers formed during the production of rubber-modified plastics serve to promote adhesion between the rubbery phase and glassy phase, together contributing to the high impact strength of the blend. Furthermore, the addition of block or graft copolymers in relatively small quantities further improves mechanical properties.^{1–7}

The chemical modification of rubber by grafting of vinyl monomers involves the creation of a free radical on the backbone of rubber, thus providing a reactive entity for the modifying properties of rubber.^{8–11} When monomers are polymerized in the presence of preformed polymer to give chemical bonding to that polymer, the result is graft copolymers; a rubber core-glassy shell particle, arising from combining rubber materials with nonrubber polymers, could lead to many technical applications. Latex particles with a soft core and a hard shell are modified as impact modifiers, whereas particles with a hard core and a soft shell are usually applied in the coating and adhesive fields.^{12,13} Usually, polymers such as polybutadiene (PB), styrene-butadiene rubber (SBR), and natural rubber (NR) are chosen as the soft components, whereas the polymers of methyl methacrylate (MMA), styrene (St), acrylonitrile (AN), vinyl chloride (VC), and so on are chosen as the hard components. Graft copolymers exist at the interface between the core and the shell. When incorporated into the PVC matrix, the rubber core serves as a toughening agent, whereas the glassy layer serves as a compatibilizing agent with the PVC phase; hence, grafting is necessary to bring about sufficient adhesion between the two phases. Such a modification was made on polystyrene (so-called high-impact polystyrene, or HIPS),^{14,15} where the grafted chain is compatible with the continuous ma-

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trix to impact adhesion between the rubbery phase and the glassy polystyrene phase. Shaw and Singh,¹⁶ using graft copolymer of ethylene-propylene-diene (5-ethylidene-2-norbornene) rubber with St and MMA to blend with polystyrene, found an improvement in impact strength with a subsequent decrease in tensile strength. St and MMA copolymer were grafted on polybutadiene to achieve impact modification of PVC.^{17,18} The adhesion between the PVC matrix and St-MMA-grafted chain is possible as it provides a partially miscible blend. This work focused on the influence of the NR-based core-shell. NR as the core polymer in latex particle has an overall balance of properties that are unmatched by synthetic rubbers. Because of its biological origins, NR is clearly more challenging to synthetic impact modifiers. However, because NR has a low glass transition temperature (T_g) and lightly tacky nature, NR cannot be adopted directly in polymer blends. It has to be adapted to facilitate the melt mixing and to be effective for rubber toughening. NR-based latex particles with a sufficiently thick shell, comprising an inner soft polymer sphere, the core, and an outer hard polymer the shell, give a free-flowing powder that is usually employed in continuous extrusion processes for the preparation of polymer blends. In the first part of this work, the present investigation is directed to the synthesis of graft copolymers of NR by using redox initiator for core-shell type of structured particles. Later on, the applicability of graft copolymers as a possible impact modifier for PVC will be evaluated and investigated. This will also provide insight into how PVC blends with the prepared graft copolymers influence the thermal and mechanical properties.

EXPERIMENTAL

Materials

Suspension PVC (OxyVinylsTM 225P, K-value = 65) produced by Oxy Vinyl, LP was used for blending purposes. The commercial high-ammonia NR latex used had 60% dry rubber content (DRC) and is composed almost entirely of *cis*-polyisoprene. Reagent-grade St (Aldrich, purity ~ 99%) and MMA (Aldrich, purity ~ 99%) monomer were prepared free of inhibitor by washing with 10% sodium hydroxide solution, followed by deionized water and then by distillation under reduced pressure. Used as received were the chain-transfer agent *n*-dodecyl mercaptan (nDM, Aldrich); the emulsifier sodium dodecyl sulfate (SDS, Aldrich, purity ~ 98%); the stabilizer isopropanol; the buffer potassium hydroxide (KOH, Aldrich); the initiators: redox initiator system, cumene hydroperoxide (C₉H₁₂O₂, CHPO, Aldrich, purity ~ 80%); and the activator agent tetraethylenepentamine [HN(CH₂CH₂NHCH₂CH₂NH₂)₂, TEPA, Aldrich]. Lead sulfate (stabilizers, Aldrich) and polyethylene oxides (lubricant, Aldrich) were used to prepare

TABLE I
Recipe for Graft Copolymers Synthesis

Ingredients	Quantities (g)
Natural rubber (60% DRC)	50
Water	70
Stabilizer	3
Buffer	0.12
Redox initiator amount (CHPO : TEPA = 1 : 1)	0.3
Emulsifier amount	0.6
Chain-transfer agent amount	0.15
Styrene	15
Methyl methacrylate	15

polymer blends. Deionized water was used throughout the work.

Preparation of graft copolymers

The graft polymerizations were carried out by using a 300-mL Parr reactor, equipped with a condenser. NR latex and an aqueous solution of additive were charged to the reactor and dissolved oxygen present in the ingredients was removed by purging nitrogen gas for at least 30 min through the mixture, providing a still stable latex. If necessary, buffer was added to maintain the pH of the system at 10. The monomer mixture with mercaptan was fed to the reactor and TEPA was then added. The NR seed latex was swollen with the monomer mixture for 1 h at the reaction temperature before adding the redox initiator. The polymerization reaction was performed at a stirring speed of 200 rpm at 50°C for 8 h. The posttreatment included the coagulation of polymer latex and washing with deionized water. The gross polymers were recovered and dried to constant mass in a vacuum oven at 40°C. The recipes for the graft copolymerization are shown in Table I.

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

Grafting efficiency (GE, %)

$$= \frac{\text{weight of monomers grafted}}{\text{weight of monomers polymerized}} \times 100 \quad (1)$$

¹H-NMR spectra were obtained by using a Bruker AC 250 MHz NMR spectrometer, which was found to combine accuracy and reproducibility (± 2 wt %) with

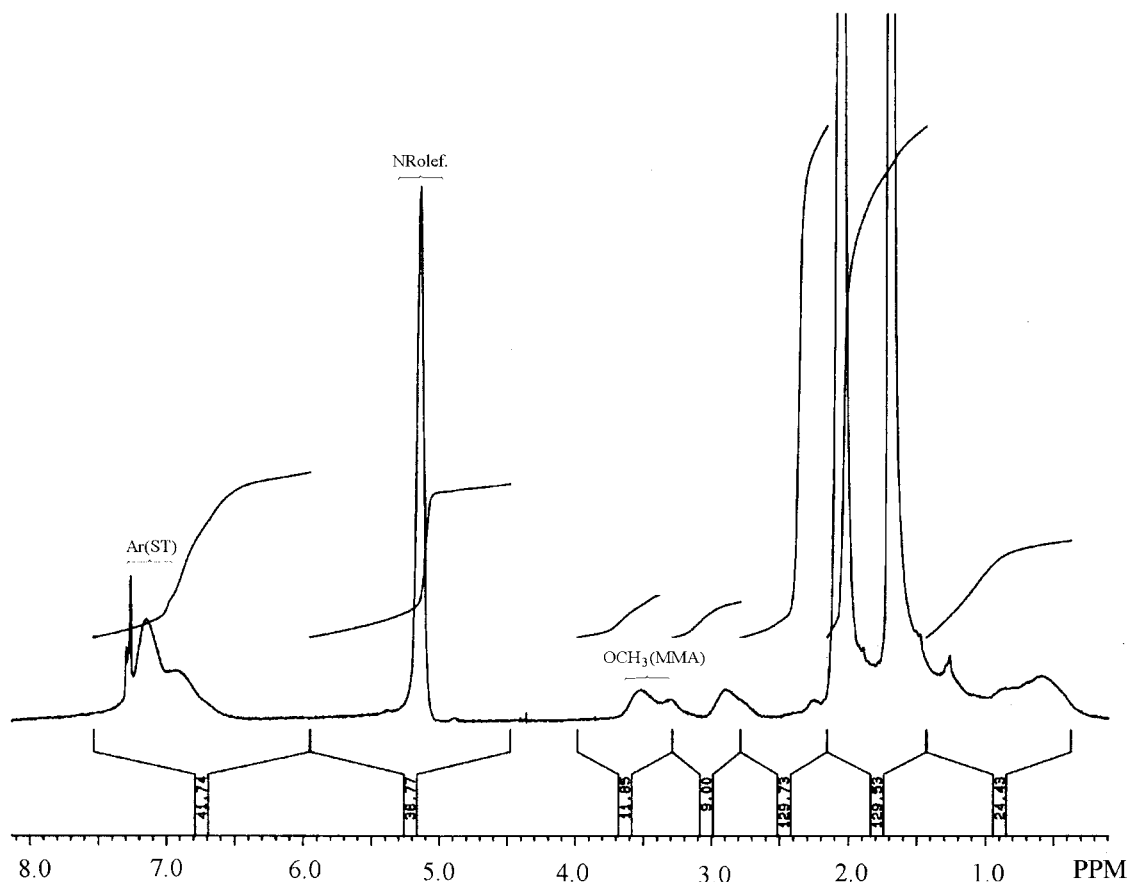


Figure 1 250-MHz $^1\text{H-NMR}$ spectra of graft copolymers. Ar(ST) represents the resonance of the aromatic protons of the styrene unit, NRolef. represents the resonance of the olefinic protons of the natural rubber unit, and $\text{OCH}_3(\text{MMA})$ represents the resonance of the methoxy protons.

ease of analysis. Analysis was carried out, using 5–10% (w/v) solution in deuterated chloroform (CDCl_3).

The morphology of the copolymers was examined by using a JEM-200CX transmission electron microscope (TEM) at 120 kV. The grafted latex was diluted 400 times with deionized water to a concentration of 0.025 wt %. To this solution, 1 mL of a 2% aqueous OsO_4 solution was added and allowed to stain the NR in the graft copolymers overnight.

Blend preparation

Blends of varying compositions (0–15%) at 5% intervals by weight were prepared as graft copolymer products. The powder of PVC and the graft copolymer products were prepared by a melt-blending technique. The mixture of polymeric materials along with a 2.5 parts per hundred (phr) lead sulfate (thermal stabilizer) and 2.0 phr polyethylene oxide (lubricant) for PVC was hand mixed thoroughly, followed by melt-blending by using a single-screw extruder with a barrel and die temperature of 165°C. Extrudates were then chopped into granules in a granulator. The granules thus obtained were molded into sheets (about

3-mm-thick) with a hot-press molding machine at 170°C and 100 atm for 5 min.

Izod impact tests were carried out with a Pendulum Impact Tester in accordance with ASTM D256. The dimensions of the specimen used were $64.0 \times 12.7 \times 3.0$ mm. The impact energy was obtained by the difference of the potential energy of the falling hammer before and after impact. Impact energy per unit breadth of the sample is expressed as the impact strength. The results shown were the average of a minimum of five specimens.

The measurement of dynamic mechanical properties of the blends was carried out in a Dynamic Mechanical Analyzer (Perkin-Elmer 7e). The dual cantilever mode of deformation geometry, known as three-point bending, was used over a temperature range of 25 to 170°C at a heating rate of 10°C per min and at a frequency of 0.8 Hz. Test specimen dimensions were 12 mm in length, 4 mm in width, and 3 mm in thickness.

To observe the fracture surface of PVC/NR-g-(St-co-MMA) blend, the specimens were fractured under cryogenic conditions by using liquid nitrogen. A Hitachi X-60 scanning electron microscope (SEM) was

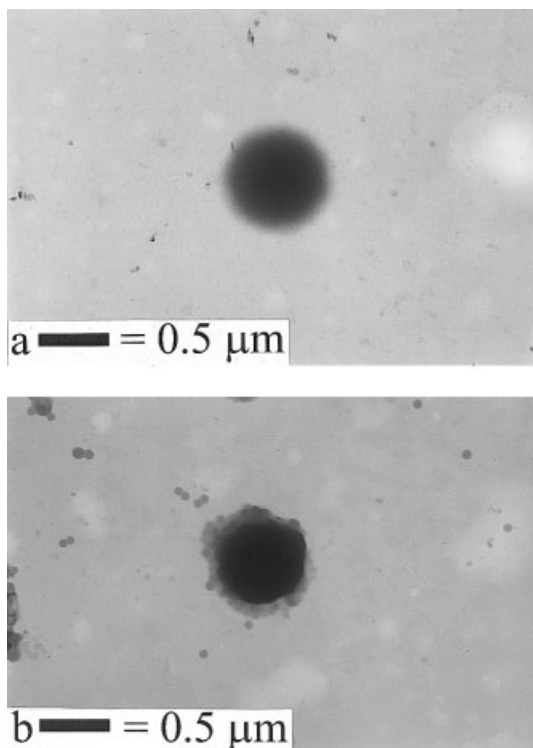


Figure 2 Transmission electron micrographs of polymers ($\times 30,000$): (a) Natural rubber; (b) Graft copolymers.

used for observations, before which the surfaces were coated with thin layers of gold.

RESULTS AND DISCUSSION

Graft copolymer characterization

Free rubber and copolymers (PSt/MMA) are removed by using petroleum ether and the mixture of acetone and MEK, respectively. The amount of grafting efficiency was 56.9%. This value was obtained gravimetrically as reported earlier. After solvent extraction, the graft copolymers were analyzed by $^1\text{H-NMR}$. Figure 1 illustrates the $^1\text{H-NMR}$ spectrum of the polymers. The peaks at 5.15 ppm are assigned to the olefinic proton content in the NR. The signals at 6.5–7.5 ppm are attributed to the phenyl group of PSt. The peaks observed at 3.5–3.7 ppm are attributed to the methoxy group of PMMA. These $^1\text{H-NMR}$ analyses confirm that the latex prepared in this emulsion polymerization contained graft copolymers. The proton NMR of NR-*g*-(St-*co*-MMA) was used to calculate the amount of constituents by standard integration method. The percent of St and MMA grafted onto the NR backbone was found to be 10.7 and 6.5%, respectively.

The morphology of NR and the graft copolymers are shown in Figure 2. The grafting of St and MMA onto the NR is a core-shell type, emulsion copolymerization. The graft copolymer particles consist of the NR core and the compatibilized PSt/MMA shell. The

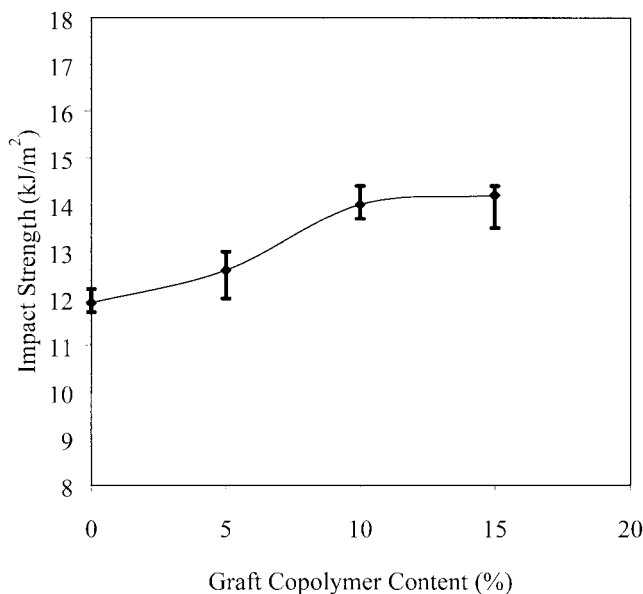


Figure 3 Izod impact strength of PVC/[NR-*g*-(St-*co*-MMA)] blends.

darker areas represent the NR core regions, while the lighter areas are PSt/MMA film as shell. The surface of the NR latex particle is smooth [Fig. 2(a)]. The presence of nodules on the surface of the graft copolymers may be due to the growing macroradical chains, which are grafted onto the surface of the NR particle and continue to propagate to form the shell layer. The second-stage polymer shells onto the core particle produce heterogeneous structures (core-shell structures), which are formed by phase separation of incompatible polymers during polymerization. This is also confirmed by the results shown in Figure 2(b) in that the NR core was encapsulated by a poly(St-*co*-MMA). Emulsion polymerization processes were adapted for preparation of NR seed latex. A bipolar redox initiator (cumene hydroperoxide/tetraethylpentamine) and low temperature promoted the forma-

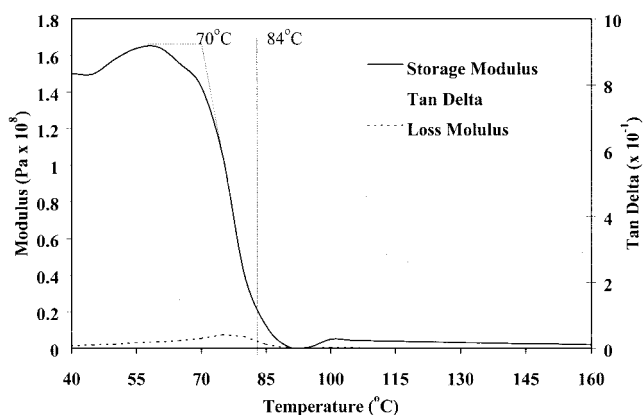


Figure 4 DMA curves for PVC as a function of E'/E'' and $\tan \delta$.

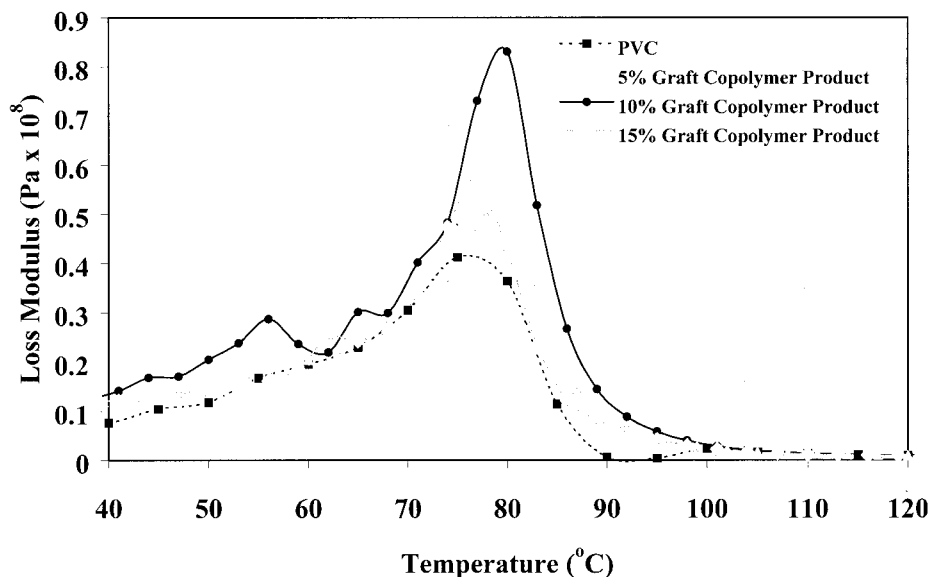


Figure 5 Loss modulus of PVC/[NR-g-(St-co-MMA)] blends.

tion of copolymers (PSt/MMA) shells around a NR core. Consequently, such core-shell latex particles disperse readily during melt blending and in the solid state adhere to many matrix polymers. Core-shell impact modifiers have a poly(St-co-MMA) outer shell. This shell composition is quite useful because poly(St-co-MMA) is thermodynamically miscible with or is wetted by a large number of polymers. Apparently, because of a satisfactory physical interaction between the vinyl monomer based shell and a number of matrix polymers, they have been widely used as toughening agents.

The effect of graft copolymer content on mechanical and morphological of polymer blends

The effect of graft copolymer content on Izod impact strength of the PVC blend is illustrated in Figure 3.

The impact strength of the blends was considerably increased with an increase of the graft copolymer product content up to 10%, where after, the impact strength increases marginally. Impact strength is essentially a function of how readily cracks can propagate within the matrix. When the graft copolymer product is included as an impact modifier for PVC, it stretches as the crack passes by, thus dissipating much of the energy necessary to develop the new surface of the growing crack. This makes crack propagation more difficult, leading to increased impact strength. The higher the grafted NR product, the higher the impact strength of the blends.

The results of dynamic mechanical measurements are given in Figures 4-6. Figure 4 represents the DMA

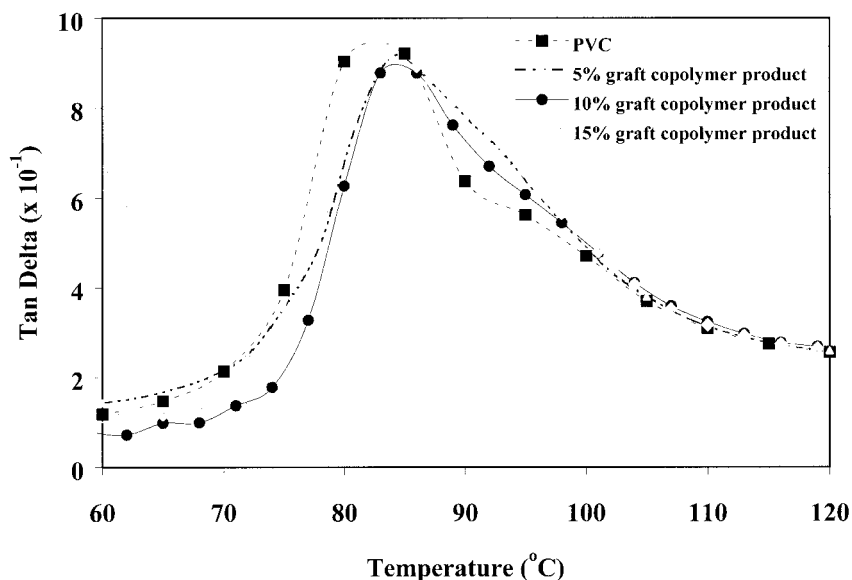


Figure 6 Tan δ of PVC/[NR-g-(St-co-MMA)] blends.

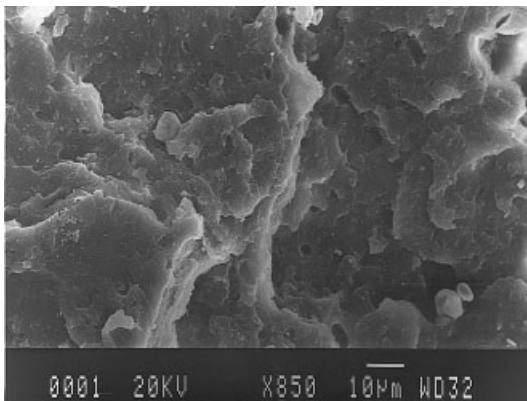


Figure 7 Scanning electron micrograph of fractured surface of PVC.

curves for PVC. The storage modulus curve E' shows an inflection point at 70°C that is attributed to the glass transition. At low temperature, the atoms in a polymer chain are restricted to isolated vibrational motions, and the bulk polymer is stiff and glassy in behavior. Above 70°C , the glass-rubber transition region, the inflection of the curve showed a decrease in modulus, which is generally associated with the onset of long-range coordinated rotational and translational motions, at which an amorphous polymer becomes much softer and rubberlike. Above the glass transition lies the rubbery plateau region where the flow of the rubbery region is hindered by physical entanglements of chains. At these higher temperatures, molecular motion is sufficiently rapid so that the molecules behave more nearly independently, and the modulus drops substantially due to the increasing role of viscous flow.

The damping (dissipation factor E''/E' or $\tan \delta$) curve goes through a maximum and then decreases as the temperature is raised. In the glass-rubber transition region, the internal friction ($\tan \delta$) curve goes

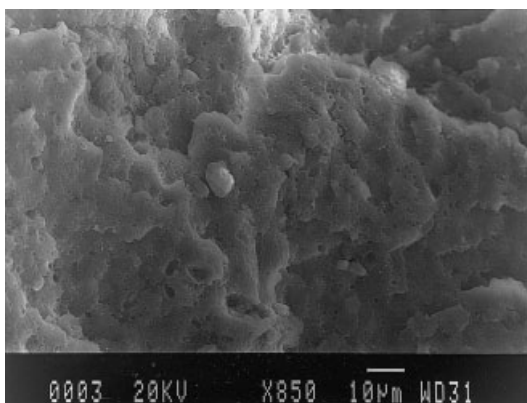


Figure 8 Scanning electron micrograph of fractured surface of PVC/NR-g-(St-co-MMA) (5% graft copolymer product).

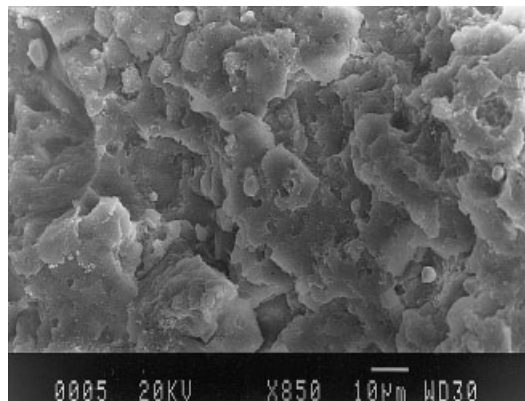


Figure 9 Scanning electron micrograph of fractured surface of PVC/NR-g-(St-co-MMA) (10% graft copolymer product).

through a maximum. The loss modulus E'' goes through a peak at a slightly lower temperature than does the dissipation factor E''/E' .

There was a difference in the transition behavior of blends when the graft copolymer product was added by increasing content of graft copolymer product in the PVC blend. The loss modulus versus temperature curves were obtained from DMA experiments. The loss modulus for PVC and PVC/graft copolymer product blends containing 5, 10, and 15 wt % in the graft copolymer product is illustrated in Figure 5. At lower contents of graft copolymer product (5 and 10%), the T_g of the blends was observed to shift slightly to higher temperatures, while a higher content of graft copolymer product (15%) T_g moved to a lower temperature. The glass transition of PVC becomes broad with the addition of the graft copolymer product. The increase in T_g and modulus of the blends at a lower graft copolymer product content may be attributed to the grafting of poly(St-co-MMA) formed on the NR chain, which is miscible with PVC. Higher contents of graft copolymer product (15 wt %) provide high elastomer concentration and induce more entanglements. As a consequence, the elastomer segments lose flexibility and the plateau region is more prominent. The inflection or plateau region of the modulus curve was due to chain entanglements. The results from dynamic mechanical analysis are given in Figure 6 in terms of $\tan \delta$. With the addition of the graft copolymer content, the T_g values shifted to higher temperatures and the damping values slightly decreased with a reduction in peak height (Fig. 6). There is good interaction between the phases of NR and PVC due to the miscibility produced in the NR segment by the incorporation of poly(St-co-MMA). The widening of the peak at T_g and the reduction of the peak height indicate that a partial compatibility was produced in these blends.

In graft copolymers, NR constitutes the main polymeric chain to which two polymeric segments [viz.,

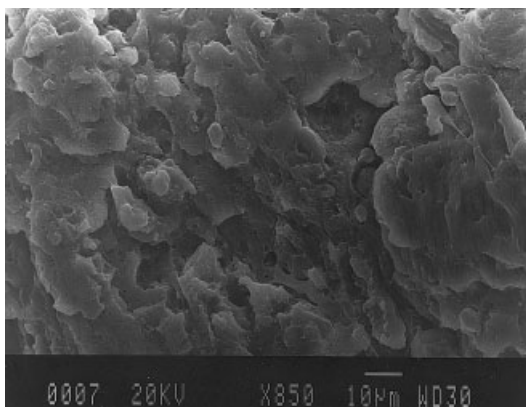


Figure 10 Scanning electron micrograph of fractured surface of PVC/NR-g-(St-co-MMA) (15% graft copolymer product).

polystyrene and poly(methyl methacrylate)] are attached. The former contributes to the toughness of the material, whereas the grafting of polystyrene and poly(methyl methacrylate) on NR imparts good compatibility. The increase of impact strength can be visualized by Figure 7-10. A brittle and scaly surface was observed for PVC with the microcharacteristics typical of a rigid and glassy surface. The PVC matrix is relatively large and smooth without NR-g-(St-co-MMA), suggesting brittle failure (Fig. 7). However, the fractured surfaces become relatively rough when an amount of NR-g-(St-co-MMA) is added into PVC/graft copolymers blend (Fig. 8-10). For 5% graft copolymer product content (Fig. 8), the coarse distribution of grafted NR in PVC matrix could be observed in that the PVC/graft copolymer binary blends clearly exhibit a two-phase structure. With 10% graft copolymer product content (Fig. 9), the matrix was not continuous; the graft copolymers were evenly distributed in the PVC matrix, and the two phases were separated. For 15% graft copolymer product content (Fig. 10), large domains of NR-g-(St-co-MMA) were clearly observed where agglomeration of NR-g-(St-co-MMA) started because of the incompatibility between the phases, which led to cavity formation. The cavities represented a two-phase behavior. The extent of stress whitening that is enhanced by the holes enlarging increases with the rubber content in the PVC/graft copolymer blends. The rubber particles in the blends dissipate impact energy mainly by the voids in the matrix caused by the cavitated rubber particles. It can be observed that the domain size and coarseness related to the ductility of the blend increased with the increase in the percentage of graft copolymers in the blends. It seems probable that the increase in the im-

pact strength is related to the NR content in graft copolymers. As a result, the impact strength of PVC/graft copolymer blend increases with an increase in the amount of graft copolymer product from 5 to 15% (Fig. 3).

CONCLUSION

The preparation and characterization of polymer blends with structured NR-based latex particles are carried out by a batch emulsion polymerization process; a NR latex was coated with a shell of poly(St-co-MMA). These core-shell structured particles were incorporated as impact modifiers into a brittle polymer matrix by using a screw extruder. A copolymer shell made the NR compatible with the PVC matrix. Dynamic mechanical properties showed that the PVC homopolymer is miscible with the poly(St-co-MMA) chains in NR-g-(St-co-MMA). The improved impact strength was observed in blends of PVC on incorporation of the graft copolymer content. SEM reveals that the increases in rubber content with an increase in the amount of graft copolymers result in greater ductility of these blends. It indicates that grafted NR core-shell particles toughened PVC effectively.

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