

n-Butyl Acrylate Based Latex Interpenetrating Polymer Networks Used as Processing Modifiers and Impact Modifiers of Poly(vinyl chloride)

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ABSTRACT: A latex interpenetrating polymer network (LIPN), consisting of poly(*n*-butyl acrylate), poly(*n*-butyl acrylate-*co*-ethylhexyl acrylate), and poly(methyl methacrylate-*co*-ethyl acrylate) and labeled PBEM, with 1,4-butanediol diacrylate as a crosslinking agent was synthesized by three-stage emulsion polymerization. The initial poly(*n*-butyl acrylate) latex was agglomerated by a polymer latex containing an acrylic acid residue and then was encapsulated by poly(*n*-butyl acrylate-*co*-ethylhexyl acrylate) and poly(methyl methacrylate-*co*-ethyl acrylate). A polyblend of poly(vinyl chloride) (PVC) and PBEM was prepared

through the blending of PVC and PBEM. The morphology and properties of the polyblend were studied. The experimental results showed that the processability and impact resistance of PVC could be enhanced considerably by the blending of 6–10 phr PBEM. This three-stage LIPN PBEM is a promising modifier for manufacturing rigid PVC. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 1168–1173, 2004

Key words: core-shell polymers; emulsion polymerization; interpenetrating networks (IPN); impact resistance; poly(vinyl chloride)

INTRODUCTION

Latex interpenetrating polymer networks (LIPNs) constitute a unique type of polymer blend that is prepared by seeded emulsion polymerization (multistage emulsion polymerization).^{1,2} The preparation involves the creation of a seed latex of a crosslinked polymer (polymer 1), the subsequent introduction of a second monomer (monomer 2) along with its crosslinking agent into a reaction vessel, and polymerization. Because no fresh emulsifier is added during the second-stage polymerization, it is assumed that very little or almost no new nucleation takes place during the monomer 2 polymerization.³ Therefore, growth mainly occurs on the established latex particles. Previous research^{1–6} has shown that the particle morphology depends on the miscibility of monomer 2 in polymer 1, the compatibility of polymers 1 and 2, the hydrophilicity of the polymers, the addition method of the second monomer, the type and amount of the initiator and crosslinking agent, and the polymerization temperature.

Recently, three-layered LIPNs based on acrylic polymers have been reported in many patents.^{7–10} The apparent kinetics of the polymerization process for three-layered LIPNs and the morphology and dy-

namic properties were studied by Zhang and coworkers.^{11,12}

LIPNs are among the most active fields of applied techniques for IPNs. Some species have been used for industrial production. They have been widely used in plastic modification, coatings, adhesives, damping materials, and so forth.

As impact-resistant modifiers for thermoplastic polymers, such as polystyrene, poly(methyl methacrylate), and poly(vinyl chloride) (PVC), LIPNs, with respect to their properties, greatly depend on the particle diameter of the rubber core. It is well known that rubber with a larger particle diameter gives improved impact resistance and processability. However, the usual emulsion polymerization process generally gives smaller latex particles (0.04–0.14 μm). Thus, for particle applications, an effective method is required to increase the initial latex particle size to the desired size. The early agglomeration technique has significant disadvantages, such as high consumption energy, a rather low maximum size for agglomerated latex particles, difficulties in controlling and reproducing agglomerated latex particle diameters, and high quantities of coagulum. In recent years, it has been reported in the patent literature that one polymer latex A (agglomerated latex) can be agglomerated by the addition of another polymer latex B (agglomerating latex), so that the latex particle size is increased.^{13–17} These novel agglomeration methods are economical, reliable,

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and effective. The mechanism of agglomeration was studied by Zhang et al.¹⁸

A three-layered LIPN, consisting of poly(*n*-butyl acrylate), poly(*n*-butyl acrylate-*co*-ethylhexyl acrylate), and poly(methyl methacrylate-*co*-ethyl acrylate) and labeled PBEM, was prepared by three-stage emulsion polymerization and agglomeration, and it was used to make the PVC/PBEM polyblend. The morphology and properties of the polyblends were studied. The experimental results show that PBEM is a promising modifier for manufacturing rigid PVC.

EXPERIMENTAL

Materials

n-Butyl acrylate (*n*-BA), methyl methacrylate (MMA), ethyl acrylate (EA), and acrylic acid (AA), all chemically pure, were distilled *in vacuo* and stored at -10°C before being used. 1,4-Butanediol diacrylate (BDDA) was analytically pure. 2-Ethylhexyl acrylate (2-EHA), industrial-grade, was distilled *in vacuo* and stored at -10°C before being used. Potassium persulfate ($\text{K}_2\text{S}_2\text{O}_8$) and sodium tetraborate ($\text{Na}_2\text{B}_4\text{O}_7$) were chemically pure, and sodium dodecyl benzene sulfonate (SDBS) was more than 97% pure.

Synthesis of PBEM

Preparation of latex B (agglomerating latex)

Distilled water (80 mL), 0.35 g of SDBS, 0.1 g of $\text{K}_2\text{S}_2\text{O}_8$, and a specified amount of *n*-BA were charged into a 500-mL, four-necked flask and heated to 70°C under nitrogen; polymerization was carried out over 2 h. Then, in the second stage, the monomer mixture (*n*-BA and AA) and 0.1 g of $\text{K}_2\text{S}_2\text{O}_8$ were dropped in 30 min, and this was maintained for 3 h at 70°C .

Preparation of PBEM

In the first stage, monomer *n*-BA and crosslinking agent BDDA were mixed in a 1000-mL, four-necked bottle at 70°C . The change in the reaction temperature was no more than 0.2°C , and the agitation speed was 250 rpm. After deionized and deoxidized water was poured into the bottle, SDBS and a pH-modifying agent ($\text{Na}_2\text{B}_4\text{O}_7$) were added and dissolved with thorough stirring. The polymerization was carried out in a nitrogen atmosphere while a $\text{K}_2\text{S}_2\text{O}_8$ water solution was added. After the polymerization was completed, a definite quantity of latex B was added under agitation at room temperature (25°C) for 30 min; in the second stage, *n*-BA, 2-EHA, crosslinking agent BDDA, and $\text{K}_2\text{S}_2\text{O}_8$ were fed into the bottle, and the polymerization was carried out at 70°C for 2 h. During the third stage, MMA, EA, BDDA, and $\text{K}_2\text{S}_2\text{O}_8$ were dropped into the bottle and polymerized, and then

TABLE I
Recipe of PBEM

First Stage		Second stage		Third Stage	
<i>n</i> -BA	4.4 g	<i>n</i> -BA	14.0 g	MMA	12 g
BDDA	0.06 g	2-EHA	3.6 g	EA	3.0 g
$\text{K}_2\text{S}_2\text{O}_8$	0.05 g	BDDA	0.16 g	BDDA	0.10 g
SDBS	0.40 g	$\text{K}_2\text{S}_2\text{O}_8$	0.1 g	$\text{K}_2\text{S}_2\text{O}_8$	0.08 g
		SDBS	0.10 g		
		Latex B	1.5 wt %		

latex PBEM was produced. Because the crosslinking agent was added in every stage and the monomers penetrated, the synthesized PBEM latex was an LIPN. The emulsion was coagulated with aluminum sulfate, filtered, washed with deionized water to neutrality, and then dried at 80°C . A white powder was obtained. The PBEM recipe is shown in Table I.

Preparation of the PVC/PBEM polyblend

PVC (SG-5, Cangzhou Chemical Plant, Cangzhou, China) and PBEM were kneaded with additives (calcium stearate, organotin stabilizer, etc.) (Tianjin Chemical Co., Tianjin, China) in a GH-1000 kneader and mixed in a mixing roll to prepare a homogeneous mixture. The PVC/PBEM polyblend was made with a heat press.

Measurements

The latex particle diameter and its distribution were measured with an H-800 transmission electron microscope (Hitachi, Tokyo, Japan) and an IBAST/II image analyzer (Opton Co., Germany).

The morphology of the three-stage latex particles was observed through a transmission electron microscope (EM-H-800, Hitachi) after the specimen was stained with RuO_4 . RuO_4 is a good staining agent for copolymers containing polyethyl acrylate (PEA) or polystyrene (PS).

The plasticizing behaviors of the PVC/PBEM polyblend were determined with a Brabender PLE-330 plasticorder (Duisberg, Germany). For the determination of the rheological properties, the polyblend was added to a mixing head at 160°C and 30 rpm, mixed thoroughly, and cut into a granulate. The rheological behavior was determined at 185°C with a 301 rheometer (Shimadzu Co., Tokyo, Japan) loaded with 70, 75, 90, 95, 110, 115, or 125 kg.

For the determination of the dynamic mechanical properties, a DDV-II-EA dynamic viscoelastometer (Toyo Baldwin Co. Ltd., Tokyo, Japan) was used at a

measuring frequency of 110 Hz and a heating rate of 2°C/min. A wafer 0.2–0.3 mm thick was made from PVC/PBEM with a hot press at 180°C.

A specimen (55 mm × 6 mm × 4 mm) was made for measuring the notched impact resistance. The tensile strength was determined with an RGT-10A electronic tensile tester with a computer controlling system (Shengzhen Sans Testing Machine Co. Ltd., Shengzhen, China).

The morphology of the PVC/PBEM polyblend was characterized with a gold-plated specimen with a Hitachi X-650 scanning electron microscope.

RESULTS AND DISCUSSION

Particle diameter and morphology of the PBEM latex particles

When the first-stage emulsion polymerization was completed, the average particle size was about 0.035 μm . After agglomeration, the particle diameter was increased to 0.150 μm . After the second- and third-stage polymerizations, the average particle diameter was about 0.185 μm . The particle size distribution is shown in Figure 1. The morphology of the end-use particles is shown in Figure 2. The darker shell portions of the particles represent the copolymer of MMA and EA stained by RuO_4 . The core parts of the particles are mainly the copolymer of *n*-BA and 2-EHA.

Plasticizing behavior

The plasticizing behavior and rheological properties of the PVC/PBEM polyblend are shown in Figures 3 and 4, respectively. Figure 3 shows that PBEM could

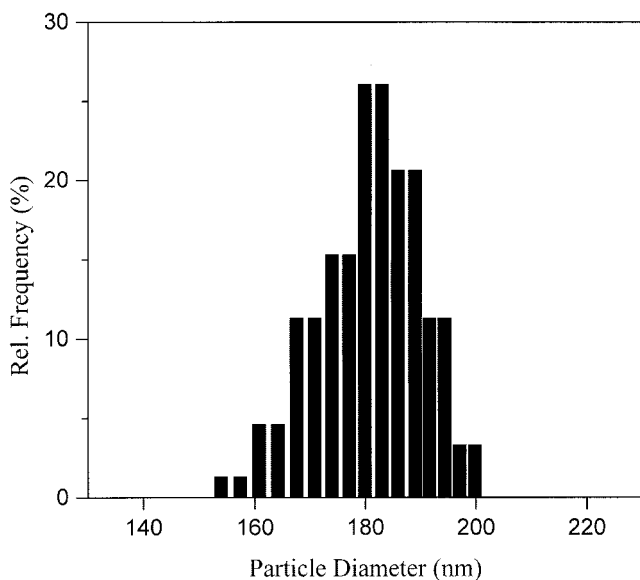


Figure 1 Particle diameter distribution of the PBEM latex.

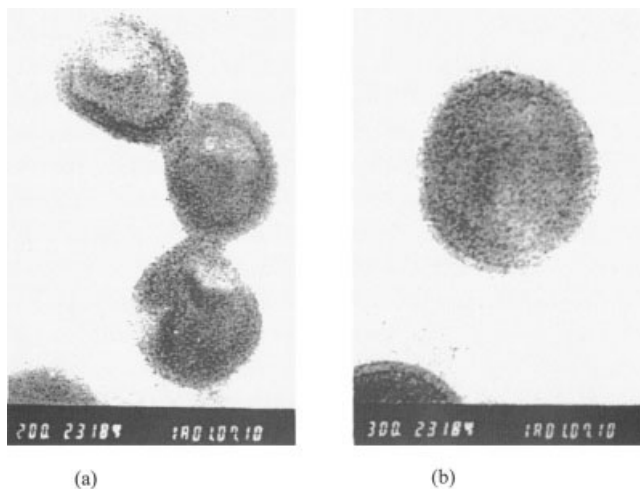


Figure 2 TEM graphs of the PBEM latex particles: (a) $K = 200 \times 10^3$ and (b) $K = 300 \times 10^3$.

shorten the gel time markedly: when the PBEM concentration was 8 phr, the gel time decreased to 2.0 min. The gel time was 15.3 min for the pure PVC resin.

These plasticizing behaviors stemmed from PBEM being filled to the intervals and gaps among the PVC particles and were due to the compatibility between PVC and PBEM. Thus, the total touched area among the PVC particles increased, and the frictional force between the particles was enhanced.

The rheological curves of PVC/PBEM and PVC are shown in Figure 4. The fluidity of the PVC melt increased because of blending with PBEM.

Effect of the amount of PBEM on the impact resistance of the PVC/PBEM polyblend

As shown in Figure 5, the impact resistance was enhanced as the PBEM concentration increased.

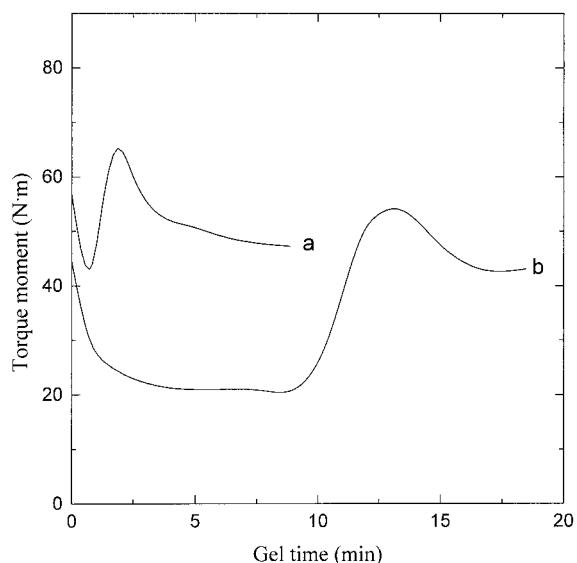


Figure 3 Curves of the plasticizing behaviors stemming from PBEM: (a) PVC/PBEM (8 phr) and (b) PVC.

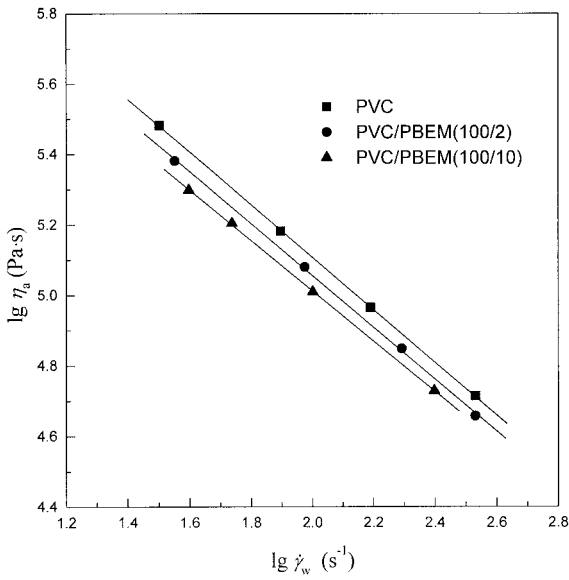


Figure 4 Viscosity/shear-rate curves of the PVC/PBEM polyblends.

The technological process conditions had a distinct influence on the impact resistance of PVC/PBEM. As shown in Figures 6 and 7, the optimal conditions were a mixing temperature of 175°C and a time of 3–5 min.

This was probably because the blending of PVC and PBEM was a cooperative process of PVC particle breakage and dispersion, the deformation of PBEM particles, and the adhesion of the interphase surface. The process reached a synergetic state only at specified temperature and time, just as for the PVC/acrylonitrile–butadiene–styrene (ABS) system.¹⁹

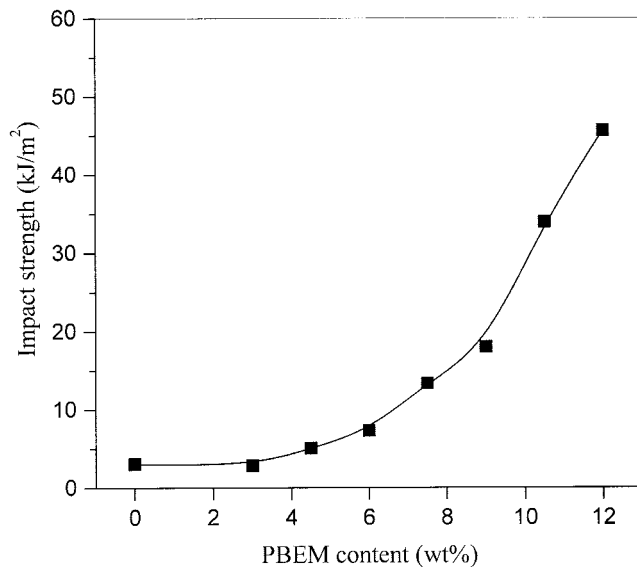


Figure 5 Relationship between the PBEM content in the polyblends and the notched impact strength.

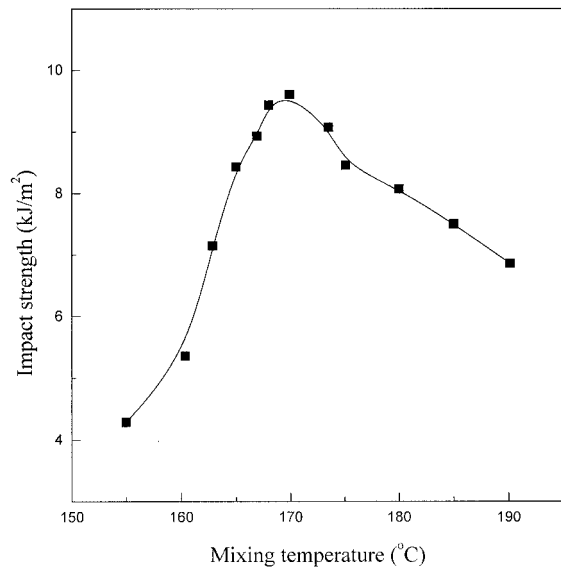


Figure 6 Effect of the mixing temperature on the impact strength of the PVC/PBEM polyblend.

These cases are related to the morphology of the PVC/PBEM polyblend. Figure 8 shows a marked network morphology in the polyblend. This morphology corresponded to the higher impact resistance of PVC/PBEM. When the mixing temperature and mixing time were not fit, a network morphology was not obtained, as shown in Figures 9 and 10, and the impact resistance was lower.

Effect of the PBEM concentration on the mechanical properties and dynamic mechanical spectra

The effects of the PBEM concentration on the breaking strength (σ_B), yield strength (σ_Y), and elongation at

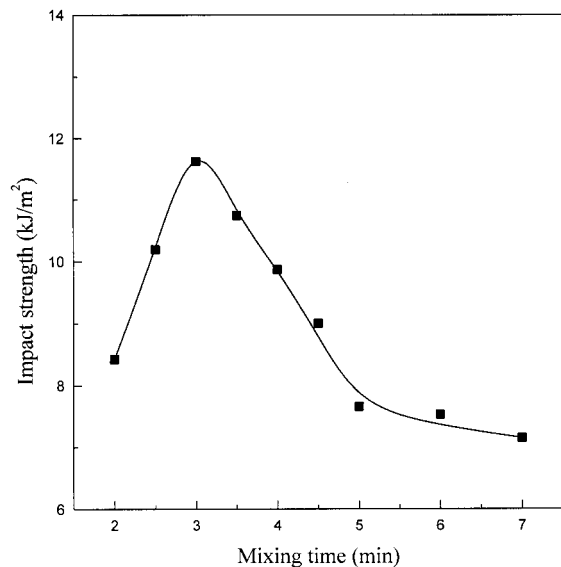


Figure 7 Effect of the mixing time on the notched impact strength of the PVC/PBEM polyblend.

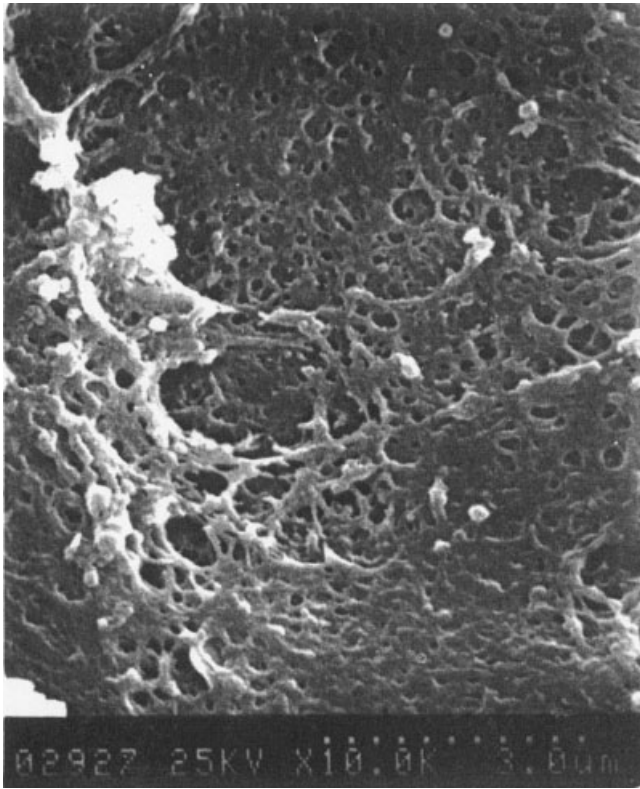


Figure 8 Scanning electron micrograph of a PVC/PBEM (100/8) polyblend. The magnification ratio was 10,000, the mixing temperature was 175°C, and the mixing time was 5 min.

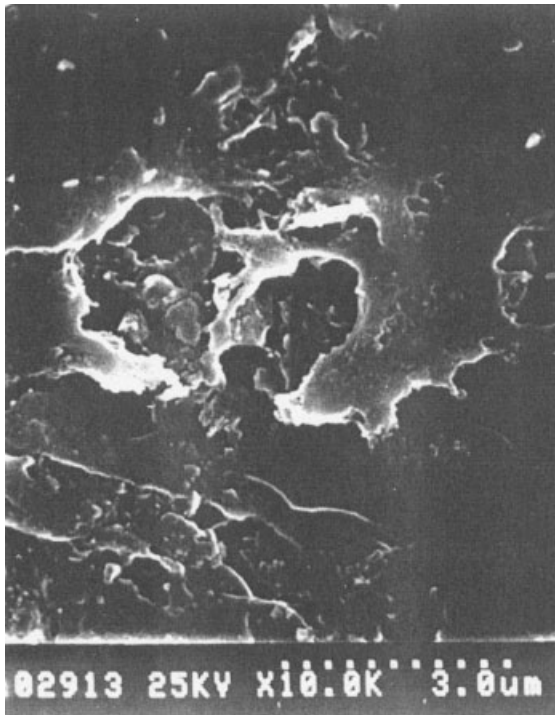


Figure 9 Scanning electron micrograph of a PVC/PBEM (100/8) polyblend. The magnification ratio was 10,000, the mixing temperature was 175°C, the mixing time was 7 min.

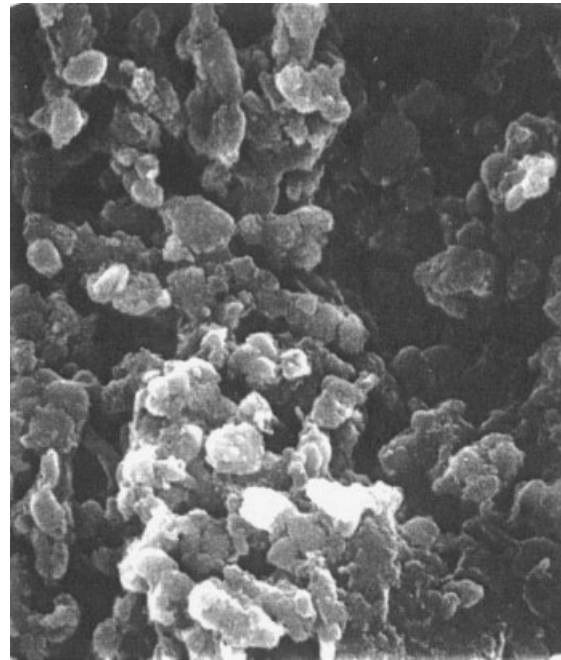


Figure 10 Scanning electron micrograph of a PVC/PBEM (100/8) polyblend. The magnification ratio was 10,000, the mixing temperature was 150°C, and the mixing time was 5 min.

break (ϵ_B) are shown in Figure 11. σ_Y and σ_B decreased as the PBEM concentration increased; in contrast, ϵ_B increased as the PBEM concentration increased.

The dynamic mechanical spectra of PBEM, PVC, and the PVC/PBEM polyblend are shown in Figure 12. For PBEM, there are two distinct spectrum peaks corresponding to -38.2 and 138°C ; for the PVC/

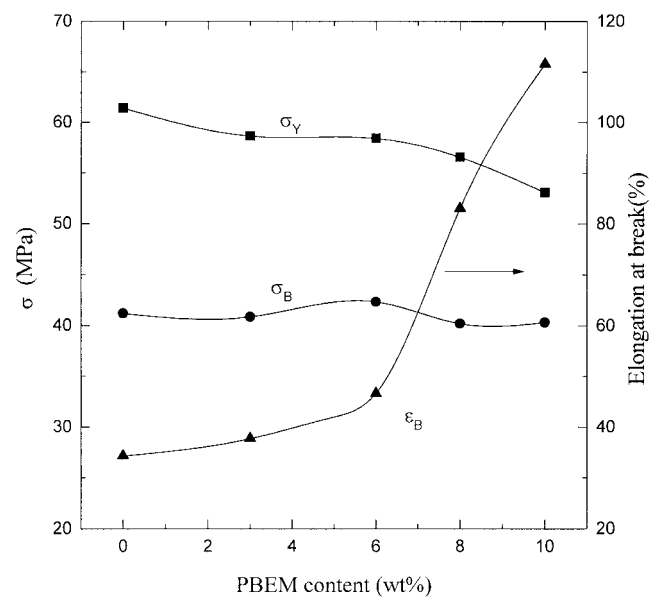


Figure 11 Effect of the amount of PBEM on σ_Y , σ_B , and ϵ_B .

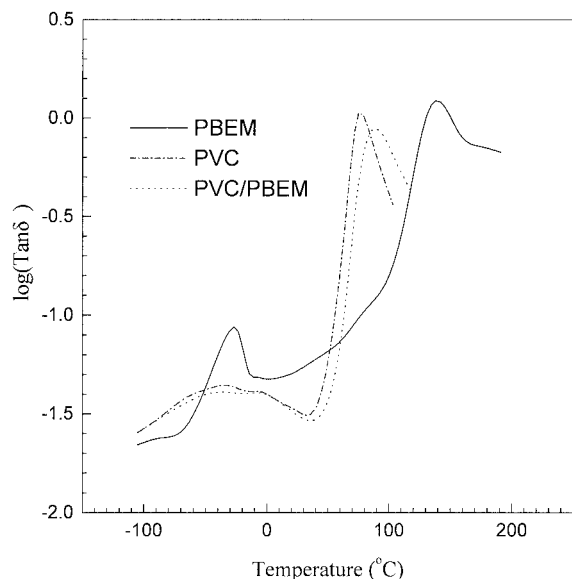


Figure 12 Dynamic mechanical spectra.

PBEM polyblend, two glass-transition temperatures (T_g 's) are shown: -33°C and 97.2°C . The higher T_g (97.2°C) is close to T_g of pure PVC. Experimental data indicated that PVC/PBEM had a dual-phase structure and that PBEM had good compatibility with PVC.

CONCLUSIONS

PBEM can considerably improve the processability and impact resistance of rigid PVC. According to the experimental data, the notched impact strength can be

increased by 4–12 times through blending with 6–12 phr PBEM. The blending conditions have an obvious influence on the impact strength of the PVC/PBEM polyblend. The optimal mixing temperature and time are $170\text{--}180^\circ\text{C}$ and 3–4 min, respectively.

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