

The Application of Bulk Polymerized Acrylic and Methacrylic Interpenetrating Polymer Networks to Noise and Vibration Damping

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Synopsis

Novel acrylic/methacrylic interpenetrating polymer networks (IPNs) were examined by dynamic mechanical spectroscopy for their damping capabilities. While simple homopolymers exhibit high damping properties only over a 20–30°C range, multicomponent polymer systems with controlled degree of miscibility, such as IPNs, may exhibit high damping properties over temperature ranges as broad as approximately 100°C. Two series of IPNs based on poly(*n*-butyl acrylate) and poly(*n*-butyl methacrylate) were synthesized and the dynamic mechanical properties were investigated using a Rheovibron. Graphite was incorporated into the poly(*n*-butyl acrylate) homopolymer and a few IPNs to measure the change in the damping properties. For important IPN compositions, $\tan \delta$ values between 0.4 and 0.85 were observed over a 75°C plus temperature range. Graphite increased the damping properties of poly(*n*-butyl acrylate) and the IPNs, as indicated by the $\tan \delta$ values.

INTRODUCTION

Vibration damping in aircraft, automobiles, and machinery constitutes an important task for both the reduction of noise and the prevention of fatigue failure. When the object is to be used at a constant temperature, a simple homopolymer often suffices because vibrations over the audible range of 20–20,000 Hz can be damped effectively. This simple result can be calculated with aid of the WLF equation, which shows that a decade of frequency corresponds to 6–7°C, with most homopolymer transitions being 20–30°C wide. However, when temperature becomes a significant variable, the narrow temperature range of the glass transition causes most homopolymer damping materials to fail. One solution to the problem lies in selecting multicomponent polymer systems with controlled degrees of miscibility. With such systems, damping can be made to take place over the entire temperature range between the glass transitions of the two homopolymers.

Many techniques have been investigated to achieve damping over a wide temperature range. Multicomponent systems such as copolymers and mechanical blends^{1–9} have been used, although in many instances dynamic mechanical spectroscopy shows limited damping capability as indicated by two narrow

peaks. Another method to broaden the damping peaks is through the use of IPNs.¹⁰⁻¹² An IPN is defined as the combination of two polymers, which have been polymerized and/or crosslinked in the immediate presence of one another.¹² Crosslinks introduced into one or both polymers restricts the domain size and enhances the degree of molecular mixing.¹²

Sperling and Thomas¹³ investigated a broad-temperature damping material using a latex IPN of poly(*n*-butyl acrylate) and poly(ethyl methacrylate). Material has been published relating IPNs with damping capabilities over a wide temperature range.^{10,14,15} The IPN subject has been recently reviewed.^{9,12,16-18}

Most recently, work was done to determine quantitatively the relationship between molecular structure and damping.¹⁵ This led to plots of linear loss modulus vs. temperature. The damping function, DF, the area under the E'' vs. temperature curve in the glass transition region, characterizes damping in a new way. The DF value was found to be independent of decrosslinking or annealing, but dependent upon the individual polymers used in the IPN. In general, it was found to depend on chain structure alone. Chang et al.¹⁹ further investigated the area under the loss modulus vs. temperature curve, LA, and the $\tan \delta$ vs. temperature curve, tA, taking into account the machine background. In addition, a major point of both Fradkin et al.'s¹⁵ and Chang et al.'s papers is additivity on a weight fraction basis, the sum of the two homopolymers' DF or LA equalling the IPNs DF or LA value, DF and LA being defined slightly different. This paper will investigate the use of IPN technology to achieve high damping over a selected temperature range, namely $\tan \delta$ greater than 0.4 over 75°C or wider temperature range and characterize these materials using LA. More specifically, the variation in IPN composition, variation of glassy polymer component and the effect of graphite on damping properties of sequential acrylic/methacrylic IPNs will be examined.

EXPERIMENTAL

Synthesis

A series of sequential IPNs was bulk-polymerized using thermal initiation. The monomers were cleaned by column chromatography technique using neutral alumina, followed by nitrogen purging for 15 min. The first component, poly[*cross*-(*n*-butyl acrylate)], was prepared from a partly polymerized solution without crosslinks. The monomers used for the second component include methyl methacrylate, ethyl methacrylate, and *n*-butyl methacrylate. The crosslinker and chain transfer agents used were tetraethylene glycol dimethacrylate (TEGDM) and dodecanethiol, respectively. Initiators included 2,2'-azobisisobutyronitrile (AIBN) and benzoyl peroxide (BPO). The mold, held together by large paper clamps, consisted of two 6.5 × 150 × 500 mm glass plates separated by 6.5 mm I.D. PVC tubing as a gasket and 6.5 mm spacers.

Into a 250 mL flask, 50 mL *n*-butyl acrylate, 0.09 g AIBN initiator, and 0.20 mL dodecanethiol were added. The contents of the flask were blanketed by nitrogen, and the flask was placed into a 80°C water bath for 10 min. The

flask with its partially polymerized contents was cooled to 0°C to stop the reaction. To this partly polymerized solution 75 mL *n*-butyl acrylate, 2.5 mL TEGDM, and 0.35 g BPO initiator were added and thoroughly mixed under a nitrogen blanket. This partly polymerized *n*-butyl acrylate solution was poured into the mold and polymerized at 60°C for 1 day followed by 80°C for 1 day. The poly[*cross*-(*n*-butyl acrylate)] sheet was trimmed to approximately 6.5 × 120 × 360 mm, and placed into a vacuum oven at 70°C for 2–3 days until constant weight was achieved.

The monomer II mixture consisted of methyl methacrylate, ethyl methacrylate, or *n*-butyl methacrylate monomer, 0.30 wt % AIBN, and 2 vol % TEGDM. The full IPNs were prepared by swelling the poly[*cross*-(*n*-butyl acrylate)] with monomer II, initiator and crosslinker and polymerizing *in situ* by placing the mold containing the swollen poly[*cross*-(*n*-butyl acrylate)] into an 80°C water bath for 1 day. Then the IPN sheet was vacuum dried at 70°C for 2–3 days.

The linear component of the semi II IPNs, poly(*n*-butyl methacrylate), was synthesized by bulk-polymerizing a mixture of *n*-butyl methacrylate, 0.03 wt % AIBN, and 1.4 vol % dodecanethiol at 80°C for 1 day. After vacuum drying at 70°C for 2 days, the poly(*n*-butyl methacrylate) was dissolved by *n*-butyl acrylate monomer containing 0.30 wt % BPO and 2 vol % TEGDM. This viscous solution was then poured into the mold and polymerized at 60°C for 1 day followed by 80°C for 1 day. The sample was then placed into a vacuum oven at 70°C for 2 days.

The filled IPNs were prepared by adding the filler to the partly polymerized *n*-butyl acrylate solution. The mixture was first manually stirred until the filler was dispersed into the viscous solution, and then mechanically stirred for 20 min under a blanket of nitrogen. The volume percent of graphite was kept low to minimize problems with dispersing the filler into the solution. The viscous solution was placed under a vacuum to aid in the removal of any trapped bubbles. The mixture was then poured into the mold and polymerized in the same manner as the unfilled homopolymer. The procedure then followed the same steps as for the unfilled full IPNs.

Dynamic Mechanical Spectroscopy

An Autovibron Dynamic Viscoelastomer (Rheovibron DDV-III-C Type; Toyo Baldwin Co., Ltd.) coupled with a HP 9825A computer and a HP 9872B plotter (assembled by Imass, Inc.) was used to obtain the storage modulus E' , loss modulus E'' , and the loss tangent, $\tan \delta$. The heating rate was approximately 1°C min, and the frequency was 110 Hz.

RESULTS AND DISCUSSION

Variation of Composition

Variation in composition of the PnBA/PnBMA full IPNs was achieved by swelling the poly[*cross*-*n*-butyl acrylate)] phase with various amounts of monomer II solution and polymerizing *in situ*. Figure 1 shows the effect of "rubber" content on the linear loss modulus and linear $\tan \delta$. The 50/50 composition shows quite different behavior than the 65/35 and 75/25 com-

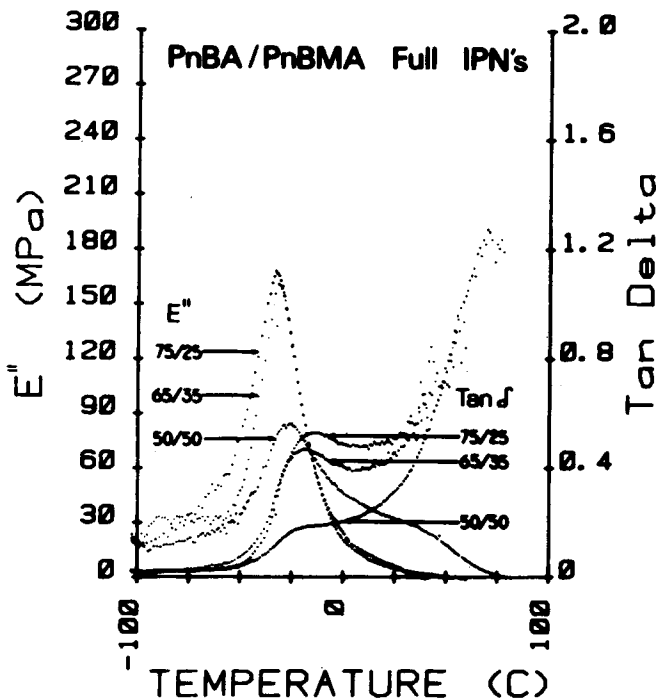


Fig. 1. DMS showing the effect of variation of composition for PnBA/PnBMA full IPNs.

positions. The decided reduction in the E'' peak height for the 50/50 composition may indicate dual phase continuity. Dynamic mechanical spectroscopy for the 75/25 full IPN shows $\tan \delta$ values between 0.4 and 0.5 over nearly a 100°C temperature range. When shown on the traditional logarithmic axis (Fig. 2) the $\tan \delta$ curve for the 75/25 full IPN exhibits a 100°C plateau. In all three cases the data fit the Davies and Budiansky models for dual phase continuity,²⁰ data not shown.

The variation in composition of a series of PnBMA/PnBA Semi II IPNs was studied. These materials show quite different behavior from the full IPNs (Fig. 3). The valley between the two peaks is more pronounced, indicating a lesser degree of miscibility. The difference in the synthesis, reflected in having one polymer without crosslinks is the most probable reason for the reduced miscibility in the semi II IPNs. The 25/75 semi II IPN of PnBMA/PnBA shows $\tan \delta$ values between 0.4 and 0.85 over nearly a 100°C temperature span encompassing 0°C . All three compositions of the semi II IPNs also fit the dual phase continuity models,²⁰ suggesting supermolecular interpenetration. Table I shows the LA values corresponding to the two series of IPNs. Although the data are somewhat scattered, there is a fair correlation to the additivity finding of Chang et al.¹⁹

Variation of Glassy Component

A series of 50/50 full IPNs based on PnBA as the "rubber" component was synthesized to investigate the effect of the second component's T_g on the

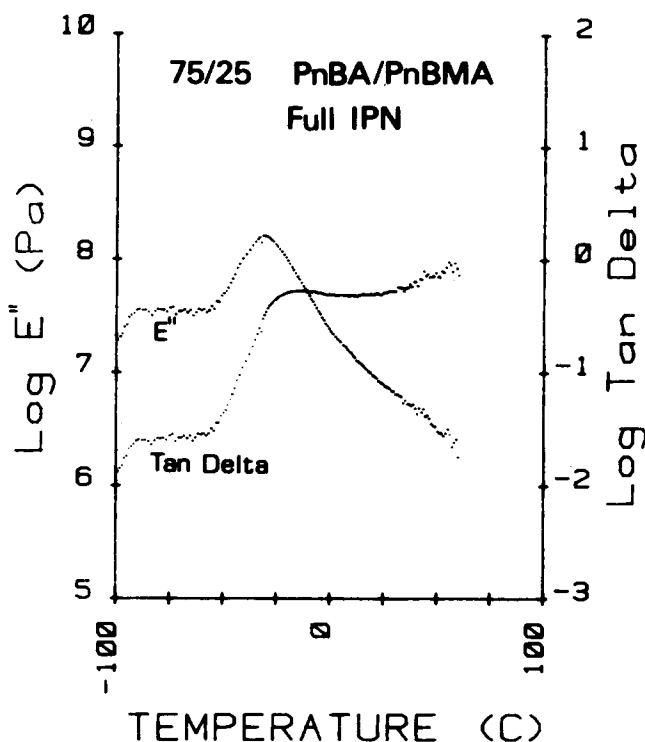


Fig. 2. DMS of 75/25 PnBA/PnBMA full IPN on logarithmic axis.

damping properties. The second component consisted of methacrylic homologs, each with decreasing T_g . Figure 4 shows that the height of the $\tan \delta$ peak corresponding to the poly[*cross*-(*n*-butyl acrylate)] was constant with all IPNs. Of course, the $\tan \delta$ peak for the methacrylate polymer moved to lower temperatures as the polymer II was changed to higher methacrylates. Not so obvious was the increase in $\tan \delta$ at the methacrylate peak as polymer II was changed to higher methacrylates, suggesting greater molecular mixing.

Effect of Graphite

Table II shows the effect of incorporating graphite (Micro 750) into the PnBA homopolymer. The damping properties have increased as indicated by the higher $\tan \delta$ and LA values. These small differences were attributed to low volume percent filler. Graphite filled poly[*cross*-(*n*-butyl acrylate)] was used to make the filled 50/50 PnBA/PnBMA and PnBA/PEMA IPN formulations. In both cases the graphite filled IPNs show a 15–20% increase in $\tan \delta$ values between the two peaks. Figure 5 shows this increase for the PnBA/PnBMA IPN. The $\tan \delta$ height at the “rubber” peak was found to be the same, but the height of $\tan \delta$ at the “plastic” peak decreased. The damping properties, as measured by LA, for the 50/50 PnBA/PnBMA IPN also show a 20% increase, with the addition of graphite.

Platelet fillers, like graphite and mica, have been shown to increase $\tan \delta$ and broaden the transition region.^{9,21,22} Thurn²³ showed that, for an acrylic

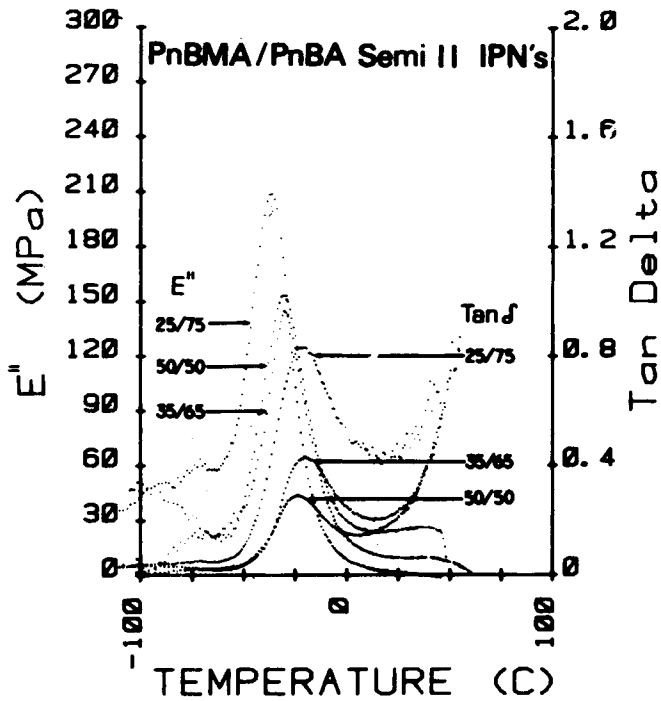


Fig. 3. DMS showing the effect of variation of composition for PnBMA/PnBA semi II IPNs.

TABLE I
LA Values for Various IPNs

Type of IPN	LA (GJ K/m ³)
PnBA/PnBMA full	
50/50	9.8
65/35	11.8
75/25	8.8
PnBMA/PnBA semi II	
50/50	11.8
35/65	9.0
25/75	9.8
PnBA/PMMA	
50/50	14.0
PnBA/PEMA	
50/50	13.2
50/50 with 6 vol % graphite	13.4
PnBA/PnBMA	
50/50	9.8
50/50 with 6 vol % graphite	11.8
PnBA	8.0
PMMA	31.8 ¹⁹
PEMA	23.0 ¹⁹
PnBMA	15.0

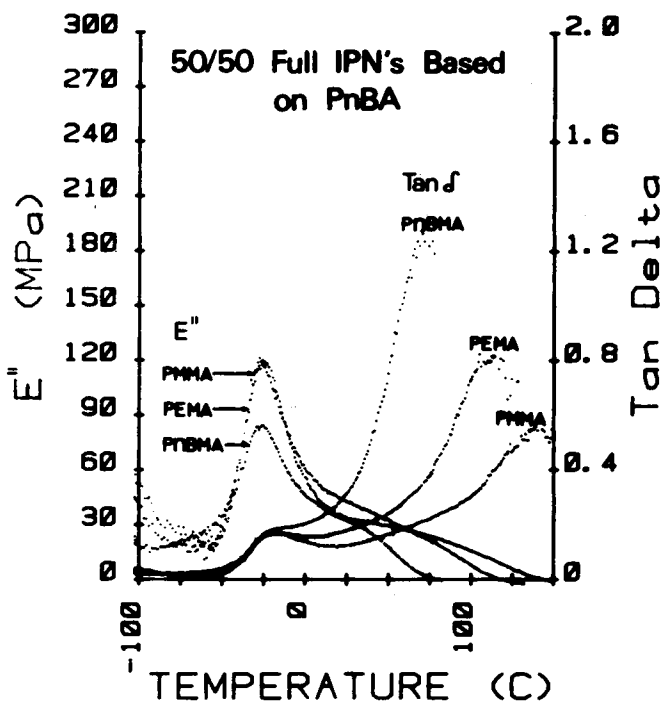


Fig. 4. LMS showing the effect of variation of glassy component from PMMA to higher methacrylics.

ester polymer, there is a maximum in $\tan \delta$, with increasing platelet filler content, between 40 and 60% filler. Chen and Williams⁷ concluded that the increase in damping in their lead-powder-filled polyester system, at intermediate temperatures where segmental motions are not hindered, was due to the heavier mass absorbing the vibrational energy. Platelet fillers have been shown to offer other damping mechanisms, such as particle-particle friction and particle-polymer friction, or microconstrained layer damping.^{21,22}

DISCUSSION

A number of acrylic/methacrylic latex IPN formulations similar in overall composition to the present materials were characterized by both noise and vibration damping equipment in the 1970s.^{12-15,24-28} Both constrained layer damping and extensional damping modes were employed. In general, these

TABLE II
Effect of Graphite on the Dynamic Mechanical Properties of Poly(*n*-Butyl Acrylate)^a

	Tan δ peak height	E'' peak height	LA LA (GJ K/m ³)
Unfilled	2.2	200 MPa	8.0
Graphite	2.1	230 MPa	8.6

^a Filler concentration was 6 vol %.

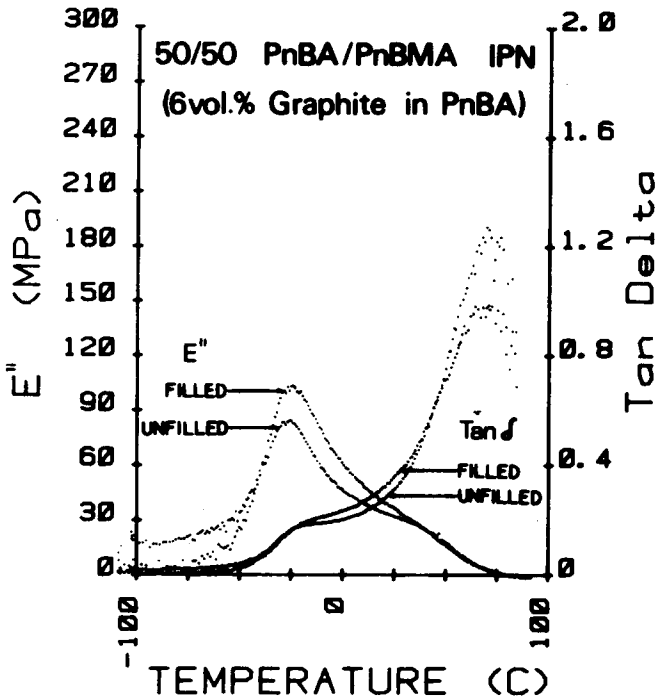


Fig. 5. DMS showing the effect of 6 vol % graphite on the dynamic mechanical properties of a 50/50 PnBA/PnBMA full IPN.

materials damped over the entire glass transition range, which sometimes spanned 100°C or more. The damping at any one temperature was less than that obtained with homopolymers at their much sharper T_g 's.

The development of the LA function is useful in characterizing the exact meaning of a good damper vs. a poor damper. If one restricts measurements to a single temperature and a single frequency, the polymer with the highest E'' or $\tan \delta$ peak will be best. However, most engineering applications span a range of temperatures and/or frequencies, and the areas under the curves provide a measure of the overall effectiveness.

CONCLUSIONS

The full IPN of PnBA/PnBMA at 75/25 exhibits near constant $\tan \delta$ values between 0.5 and 0.6, 50–60°C wide, and higher values at the upper extreme of the temperature range. The 25/75 PnBMA/PnBA semi II IPN exhibits $\tan \delta$ values between 0.4 and 0.85 over the same temperature range.

The change of polymer II from PMMA to PEMA to PnBMA decreased the upper temperature limit at which the IPN was effective in damping. This change had the effect of raising the $\tan \delta$ values in the intermediate temperature range, –20–75°C.

Graphite added to poly[*cross*-(*n*-butyl acrylate)] increases the $\tan \delta$ values and the area under the E'' vs. temperature curve, LA. It is concluded that graphite incorporated into IPNs offers additional mechanisms for damping,

which increase the damping capability as indicated by the higher $\tan \delta$ and LA values.

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