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by

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ABSTRACT

Novel acrylic/methacrylic interpenetrating polymer networks, IPN's, 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 IPN's, may exhibit high damping properties over temperature ranges as broad as approximately 100°C.

Two series of IPN's 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 IPN's to measure the change in the damping properties. For important IPN compositions, tangent 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 IPN's, as indicated by the tangent delta values.

In addition, a major part of this work was the process development of the thermal polymerization technique to produce relatively large (6.5 x 120 x 360 mm) sheets. The main problem associated with the large-scale synthesis was due to the high heat of polymerization and low thermal conductivity. This problem was alleviated through use of a partly polymerized monomer solution.

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 IPN's [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 Thomas [13] investigated a broad-temperature damping material using a latex IPN of poly(n-butyl acrylate) and poly(ethyl methacrylate). Material has been published relating IPN's 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 versus temperature. The Damping Function, D.F., the area under the E" versus temperature curve in the glass transition region, characterizes damping in a new way. The D.F. 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 versus temperature curve, L.A., and the tangent delta versus temperature curve, t.A., taking into account the machine background. In addition, a major point of both Fradkin et al.'s [15] and Chang et al.'s papers is additivity, the sum of the two homopolymers' D.F. or L.A. equalling the IPN's D.F. or L.A. value, D.F. and L.A. being defined slightly different. This paper will investigate the use of IPN technology to achieve high damping over a selected temperature range, namely Tan δ greater than 0.4 over a 75°C or wider temperature range and characterize these materials using L.A. More specifically, the variation in IPN composition, variation of glassy polymer component and the effect of graphite on damping properties of sequential acrylic/methacrylic IPN's will be examined.

EXPERIMENTAL

Synthesis

A series of sequential IPN's was bulk polymerized using thermal initiation. The monomers were cleaned by column chromatography technique using neutral alumina, followed by nitrogen purging for 15 minutes. 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, respectfully. Initiators included 2,2'-azobisisobutyronitrile (AIBN) and benzoyl peroxide (BPO). The mold, held together by large paper clamps, consisted of two 6.5 x 150 x 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 minutes. 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 throughly mixed under a nitrogen blanket. This partly polymerized n-butyl acrylate solution was poured into the mold and polymerized at 60°C for one day followed by 80°C for one day. The poly[cross-(n-butyl acrylate)] sheet was trimmed to approximately 6.5 x 120 x 360 mm, and placed into a vacuum oven at 70°C for 2 to 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 IPN's 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 a 80°C water bath for one day. Then the IPN sheet was vacuum dried at 70°C for 2 to 3 days.

The linear component of the semi II IPN's, 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 one day. After vacuum drying at 70°C for two 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 one day followed by 80°C for one day. The sample was then placed into a vacuum oven at 70°C for 2 days.

The filled IPN's 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 minutes 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 precedure then followed the same steps as for the unfilled full IPN's.

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 δ. 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 IPN's 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 δ. The 50/50 composition shows quite different behavior than the 65/35 and 75/25 compositions. 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 δ values between 0.4 and 0.5 over nearly a 100°C temperature range. When shown on the traditional logarithmic axis, Figure 2, the tan δ 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 IPN's was studied. These materials show quite different behavior from the full IPN's, Figure 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 IPN's. The 25/75 semi II IPN of PnBMA/PnBA shows tan δ values between 0.4 and 0.85 over nearly a 100°C temperature span encompassing 0°C. All three compositions of the semi II IPN's also fit the dual phase continuity models [20], suggesting supermolecular interpenetration. Table 1 shows the L.A. values corresponding to the two series of IPN's. Although the data are somewhat scattered, there is a fair correlation to the additivity finding of Chang et al.

Variation of Glassy Component

A series of 50/50 full IPN's based on PnBA as the "rubber" component was synthesized to investigate the effect of the second component's T_g on the damping properties. The second

component consisted of methacrylic homologs, each with decreasing T_g. Figure 4 shows that the height of the tan δ peak corresponding to the poly[cross-(n-butyl acrylate)] was constant with all IPN's. Of course the tan δ 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 δ at the methacrylate peak as polymer II was changed to higher methacrylates, suggesting greater molecular mixing.

Effect of Graphite

Table 2 shows the effect of incorporating graphite (Micro 750) into the PnBA homopolymer. The damping properties have increased as indicated by the higher tan δ and L.A. 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 IPN's show a 15 to 20 percent increase in tan δ values between the two peaks. Figure 5 shows this increase for the PnBA/PnBMA IPN. The tan δ height at the "rubber" peak was found to be the same, but the height of tan δ at the "plastic" peak decreased. The damping properties, as measured by L.A., for the 50/50 PnBA/PnBMA IPN also show a 20 percent increase, with the addition of graphite.

Platelet fillers, like graphite and mica, have been shown to increase tan δ and broaden the transition region [9,21,22]. Thurn [23] showed for an acrylic ester polymer there is a maximum in tan δ, with increasing platelet filler content, between 40 and 60 percent filler. Chen and Williams [7] 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 micro-constrained layer damping [22].

CONCLUSIONS

The full IPN of PnBA/PnBMA at 75/25 exhibits near constant tan δ values between 0.5 and 0.6, 50 to 60°C wide, and higher values at the upper extreme of the temperature range. The 25/75 PnBMA/PnBA semi II IPN exhibits tan δ 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 δ values in the intermediate temperature range, -20°C to 75°C.

Graphite added to poly[cross-(n-butyl acrylate)] increases the tan δ values and the area under the E" vs. temperature curve, L.A. It is concluded that graphite incorporated into IPN's offers additional mechanisms for damping, which increase the damping capability as indicated by the higher tan δ and L.A. values.

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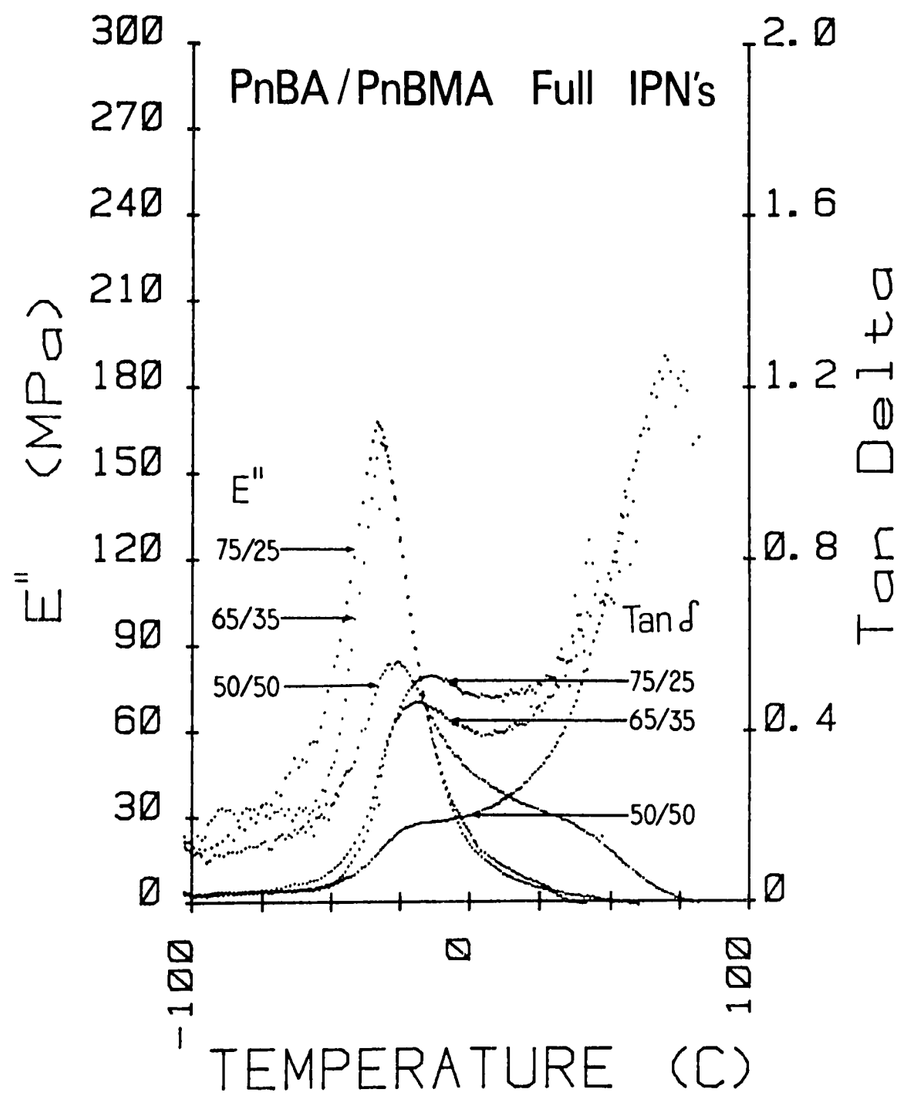
PnBA/PnBMA Full IPN's
E" (MPa)
Tan δ
300
270
240
210
180
150
120
90
60
30
0
2.0
1.6
1.2
0.8
0.4
0
E"
75/25
65/35
50/50
Tan δ
75/25
65/35
50/50
-100
0
100
TEMPERATURE (C)

FIGURE 1

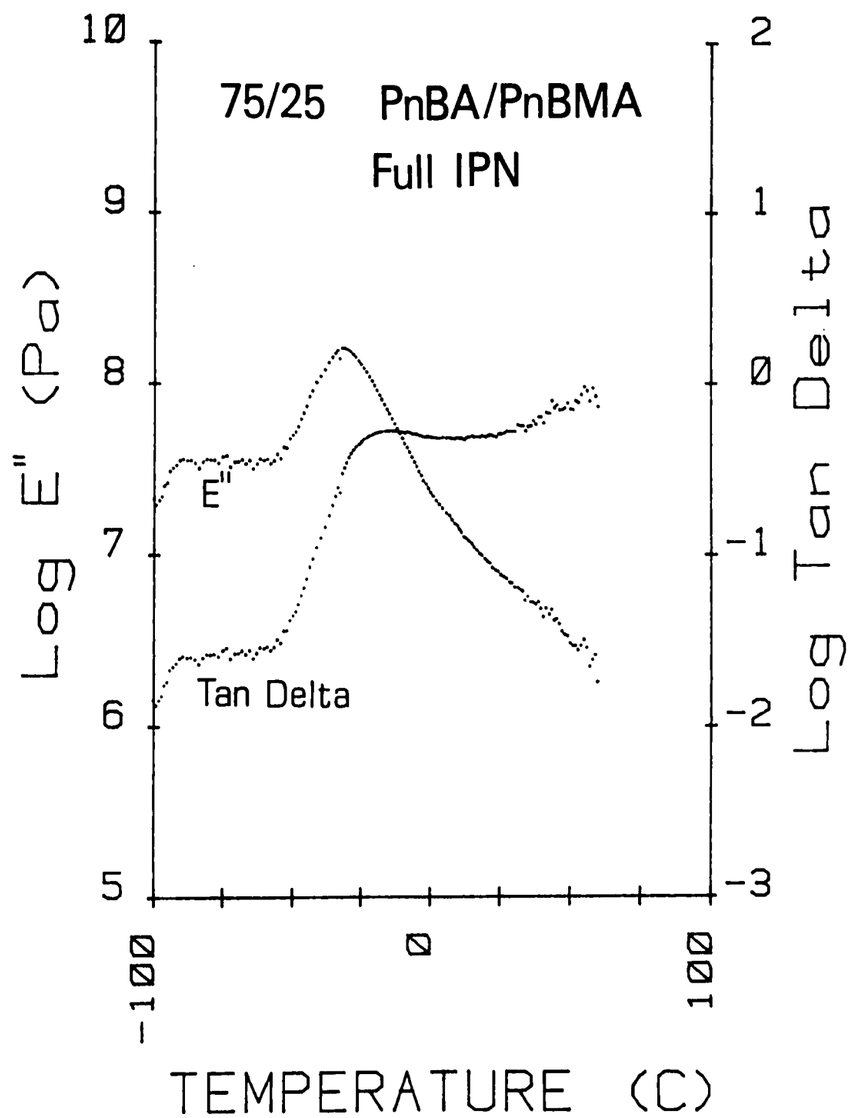
75/25 PnBA/PnBMA
Full IPN
Log E'' (Pa)
Log Tan Delta
E''
Tan Delta
10
9
8
7
6
5
2
1
0
-1
-2
-3
-100
0
100
TEMPERATURE (C)

FIGURE 2

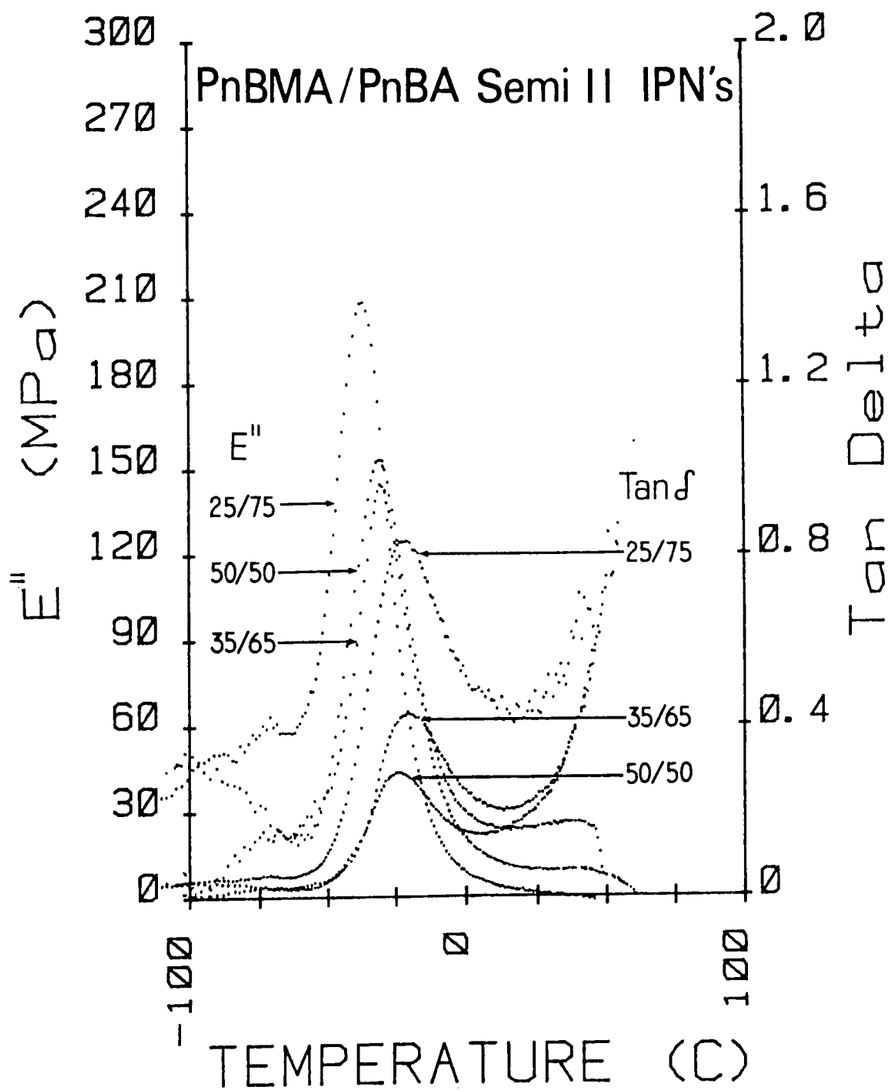
PnBMA/PnBA Semi II IPN's
E" (MPa)
Tan Delta
E"
Tanδ
25/75
50/50
35/65
25/75
35/65
50/50
300
270
240
210
180
150
120
90
60
30
0
2.0
1.6
1.2
0.8
0.4
0
-100
0
100
TEMPERATURE (C)

FIGURE 3

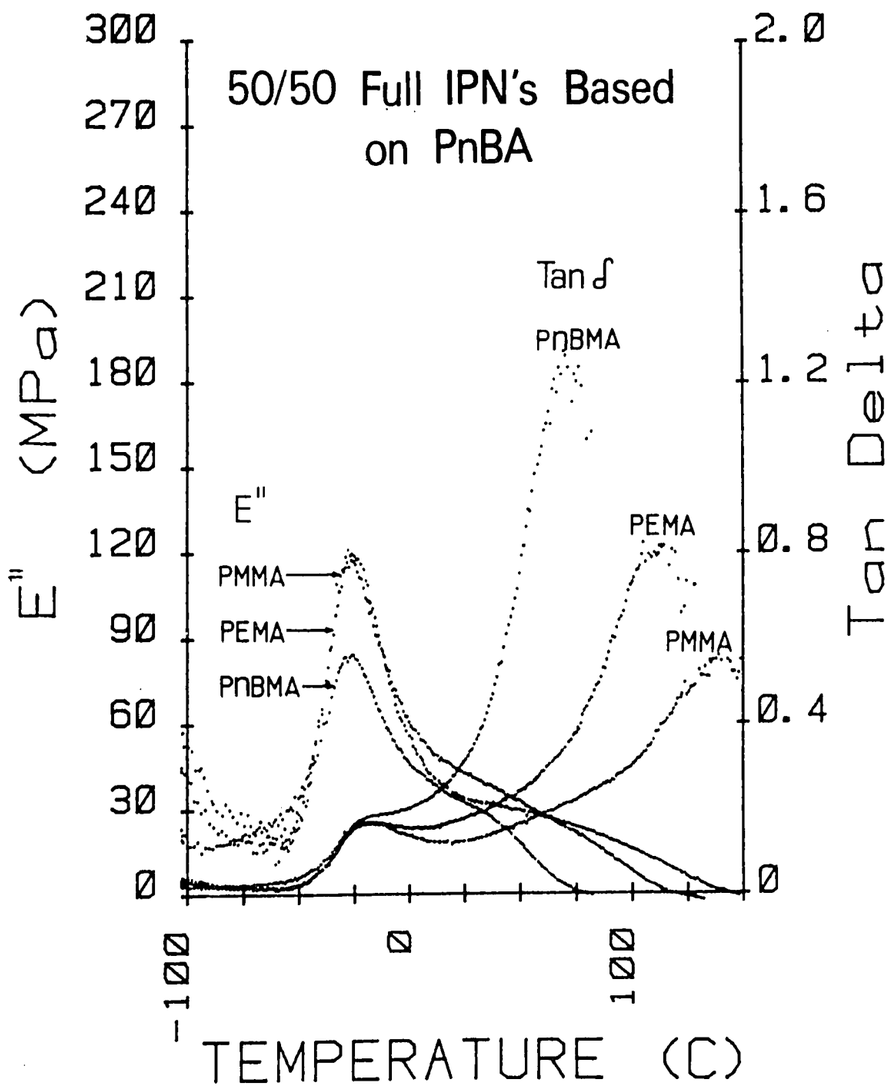
50/50 Full IPN's Based on PnBA
E" (MPa)
Tan δ Delta
300
270
240
210
180
150
120
90
60
30
0
2.0
1.6
1.2
0.8
0.4
0
E"
Tan δ
PnBMA
PEMA
PMMA
PMMA
PEMA
PnBMA
-100
0
100
TEMPERATURE (C)

FIGURE 4

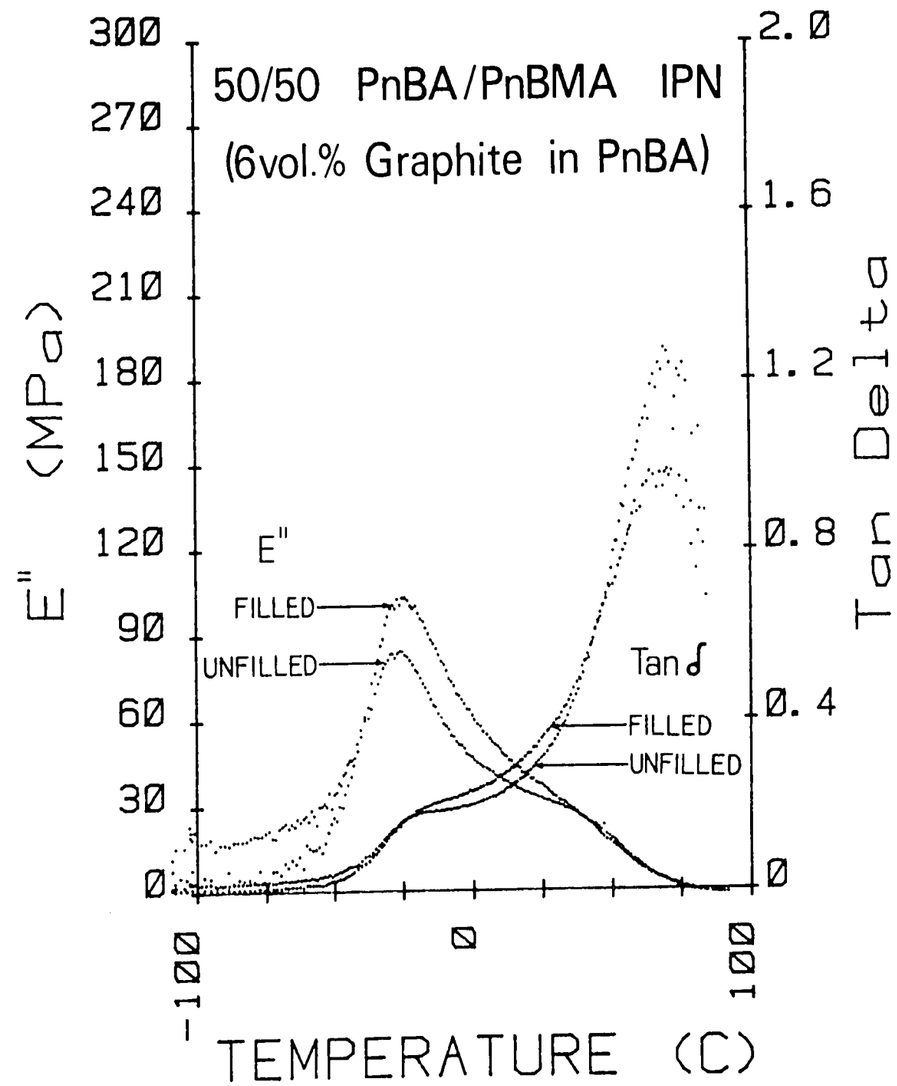
50/50 PnBA/PnBMA IPN
(6vol.% Graphite in PnBA)
E" (MPa)
300
270
240
210
180
150
120
90
60
30
0
E"
FILLED
UNFILLED
Tan δ
FILLED
UNFILLED
2.0
1.6
1.2
0.8
0.4
0
Tan Delta
-100
0
100
TEMPERATURE (C)

FIGURE 5

TABLE 1- L.A. values for various IPN's

TYPE OF IPN	L.A. ($GJ \bullet K/m^3$)
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

TABLE 2- Effect of Graphite on the Dynamic Mechanical Properties of Poly(n-butyl acrylate)

	Tan δ Peak Height	E" Peak Height	L.A. $\frac{GJ \cdot K}{m^3}$
Unfilled	2.2	200 MPa	8.0
Graphite	2.1	230 MPa	8.6

Filler Concentration was 6 vol.%

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APPENDICES

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The second part of the research was to develop a large scale synthesis technique to provide 6.5 x 6.5 x 300 mm samples for the Navy's independent testing. The development goal of the polymeric damping materials was to achieve high damping properties over an approximate 100°C temperature range, with particular interest to the tan δ values in the -5 to 20°C temperature range. The types and quanities of monomers and initiators, along with the mold's construction, were important factors in the process development of the large scale, thermally initiated IPN's.

Monomers

The temperature range of interest for high damping was -5 to 20°C at 110 Hz, thus the Tg of the "rubber" component was limited to less than -5°C and the Tg of the "plastic" component was limited to greater than 20°C. Table 1 shows the monomer boiling point and Tg of the acrylic and methacrylic polymer series. Along with the Tg requirement, the boiling point of the monomer was an important factor.

The temperature of polymerization was limited between 60 and 80°C due to the initiators used, AIBN and BPO. This limitation restricted the use of monomers with boiling points greater than 100°C. To satisfy these requirements, n-butyl acrylate was chosen as the "rubber" component and n-butyl methacrylate and lower methacrylates were chosen as the "plastic" component.

Initiator

AIBN produces nitrogen gas upon decomposition, this caused bubbles to form in initial experiments[†]. Therefore, BPO was used for the polymerization of Monomer I.

[†]Later experiments indicated bubbles might be caused by over-heating of the monomer.

The lower temperature initiator was needed at this stage to prevent too high of a temperature change due to the low thermal conductivity of the Polymer I and the heat of polymerization. AIBN was used in the polymerization of Polymer II, where at least to the naked eye it did not produce bubbles. BPO was the initiator used to produce Polymer I in the full IPN's and Polymer II in the semi II IPN's.

Construction of Mold

The mold consisted of two 1/4 x 6 x 18 inch glass plates, separated by two 1/4 inch I.D. PVC tubing and 1/4 inch spacers, and held together by large paper clamps. See Figure 1 for the schematic. The tubing ends were plugged with high temperature vacuum grease. PVC was chosen as the material for the gasket. The EPDM rubber cord used in the low temperature U.V. light process was unsatisfactory. The cord caused the monomer solution to discolor and inhibited the polymerization. The best method to contain the monomer solution was to use two gaskets, as shown in the Figure 2.

Synthesis Technique

Due to the Trommsdorff effect, high rate of heat generation, and low heat transfer of the polymer, a partly polymerized solution without crosslinks was used. The heat transfer was impeded by high viscosity and low thermal conductivity (approximately 0.12 Btu $f^{-1}h^{-1}\cdot F^{-1}$) of the polymerizing solution. The first polymer network was produced using a partly polymerized solution consisting of poly(n-butyl acrylate) and n-butyl acrylate monomer, and was produced by the following manner.

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

covered flask was placed into a 80°C water bath for 10 minutes. The flask with its partly 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 throughly mixed under a nitrogen blanket. This partly polymerized n-butyl acrylate solution was poured into the mold and polymerized at 60°C for one day followed by 80°C for one day. The poly[cross-(n-butyl acrylate)] sheet was trimmed, to approximately 6.5 x 120 x 360 mm, and placed into a vacuum oven at 70°C for 2-3 days until constant weight was achieved.

A satisfactory temperature was chosen such that the gelation time was quick enough to prevent (1) evaporation of monomer and (2) leakage of monomer solution via degradation of the mold's PVC gasket. The temperature, of course, could not be too high so that the temperature rise due to the heat of polymerization was significant to boil the monomer. The partly polymerized solution, as discussed previously, was also used to control the temperature rise.

TABLE I - Boiling Points of monomer and Tg of Polmer

	Acrylic		Methacrylic	
	b.p.(°C)	Tg(°C)	b.p.(°C)	Tg(°C)
methyl	80	+3	100	+105
ethyl	99	-22	118	+65
n-propyl	-	-44	-	+35
n-butyl	147	-56	163	+21
n-hexyl	-	-	184	-5

b.p.'s from "Polymer Technology Encyclopedia",Vol. 12, 249(1970).
Tg's from L.E. Nielsen,"Mechanical Properties of Polymers", Reinhold, 1962.

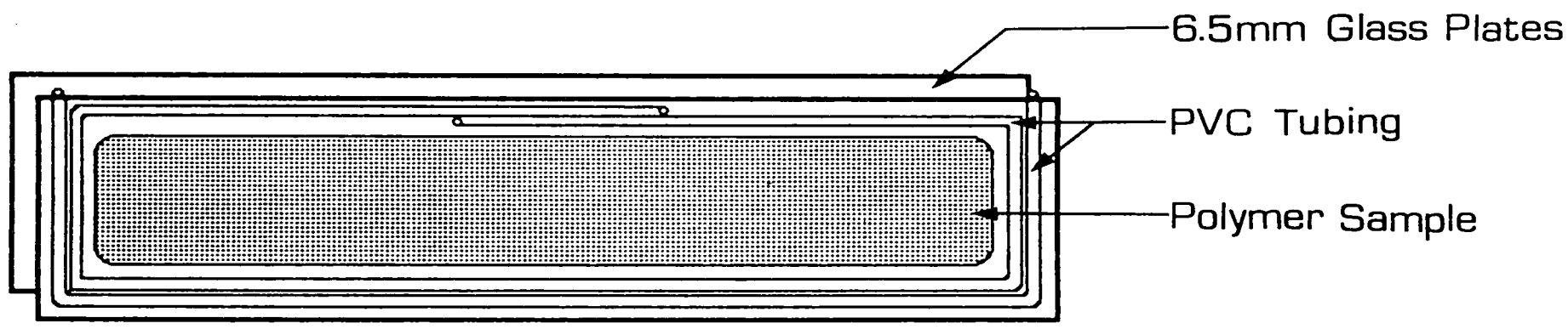
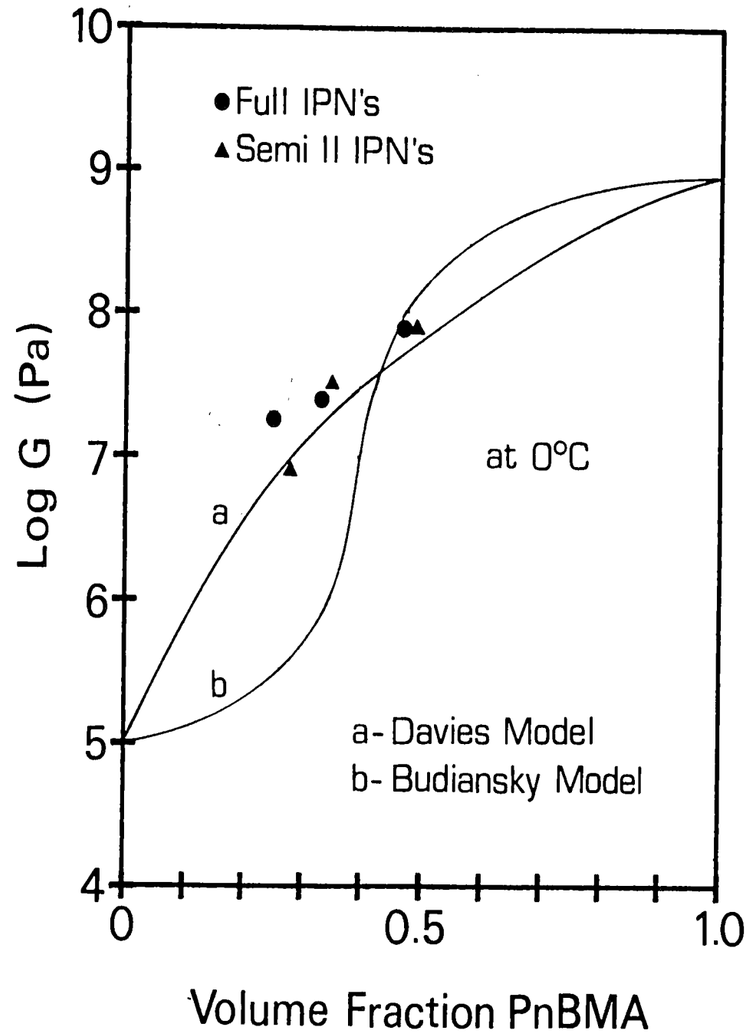


FIGURE 1


10
9
8
7
6
5
4
Log G (Pa)
● Full IPN's
▲ Semi II IPN's
at 0°C
a
b
a- Davies Model
b- Budiansky Model
0
0.5
1.0
Volume Fraction PnBMA