

**LOSS MODULUS AND DAMPING BEHAVIOR OF
POLY(VINYL METHYL ETHER)-POLYSTYRENE BLENDS AND IPN'S**

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Abstract

Sequential full interpenetrating polymer networks, IPN's, were synthesized by crosslinking poly(vinyl methyl ether), PVME, with dicumyl peroxide, swelling in styrene, divinylbenzene and initiator and polymerizing in situ. The miscibility of PVME and polystyrene (PS) IPNs was examined by dynamic mechanical spectroscopy (DMS) and differential scanning calorimetry (DSC). DSC indicates an increase in the breadth of the glass transition region for midrange compositions in linear blends and IPNs. Similarly, DMS data shows a narrow glass transition region for a 70/30 weight composition PVME/PS IPN and increasingly broader regions for 50/50 and 30/70 PVME/PS IPNs. The broad transitions probably indicate a degree of microheterogeneous phase separation that may be dependent upon composition and degree of crosslinking. Various degrees of haziness or turbidity of a series of 50/50 PVME/PS samples indicates that the chemical blend is clear and miscible, while the semi-II, the semi-I and the full-IPN are phase separated. A cloud point curve was determined from PVME/PS physical blends by optical microscopy, confirming earlier studies and serving as a miscibility guideline.

Introduction

Polymers constitute useful noise and vibration damping materials near their glass transition temperature, T_g .^{1,2} The onset of coordinated chain molecular motion in the T_g region can be used to convert vibrational energy into heat. Whereas homopolymers may be efficient dampers over a range of 30°C around T_g , interpenetrating polymer networks, IPN's, have been shown to exhibit damping over a broader range of temperatures.³ An IPN may be defined as a combination of two polymers in network form.⁴ Similar to other multicomponent polymer materials, the vast majority of IPN's are phase separated⁵ and the introduction of crosslinks into each polymer limits the domain size.

The only single phase, miscible IPNs reported are the poly(2,6-dimethylphenylene oxide) (PPO) and polystyrene (PS) IPNs.⁶ The corresponding blend of this system is miscible and does not undergo thermally induced phase separation before degradation.⁷

The phase separation behavior of the linear blend of poly(vinyl methyl ether) (PVME) and polystyrene (PS) has been characterized by small angle neutron scattering⁸ and by other methods.^{9,10} The phase diagram for this system has been developed indicating a lower critical solution temperature (LCST) which is dependent upon composition and molecular weight. Electron irradiation of the blends, which introduces random crosslinking, has been shown to increase the size of the single phase region of the phase diagram.¹⁰ In this paper, PVME/PS IPNs and blends are synthesized and preliminary miscibility and damping behavior of the IPNs are examined by dynamic mechanical spectroscopy (DMS) and differential scanning calorimetry (DSC).

Previous Work

Research on sound and vibration damping began at Lehigh University in the early 1970's, under a contract from Aberdeen Proving Grounds. The objective was to prepare a two-layer constrained layer damping system in the form of a latex paint, based on interpenetrating polymer network technology.¹¹ The main advantage of the new material was its capability of damping over very broad temperature ranges, from -30 to 100°C.^{2,12} The constraining layer was a filled epoxy composite material.

More recently, research at Lehigh centered about understanding the basic nature of the damping phenomenon itself. How were the polymer molecules actually absorbing the

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energy? The result was a group contribution analysis, wherein each moiety in the polymer contributes to the loss modulus integral in the vicinity of the glass transition temperature.¹³ By examining the area under the loss modulus-temperature curves, a quantitative analysis was developed based on the assumption of a weight fraction additive contribution of the structural units within the repeat unit to the total loss area. The basic equation for the LA group contribution analysis is¹³

$$LA = \sum_{i=1}^n \frac{(LA)_i M_i}{M} = \sum_{i=1}^n \frac{G_i}{M} \quad (1)$$

where M_i is the molecular weight of the i^{th} group in the repeating unit, M is the molecular weight of the whole mer, G_i is the molar loss constant for the i^{th} group, $(LA)_i$ is the loss area contributed by the i^{th} group, and n represents the number of moieties in the mer. As a corollary to eq. (1), an additive mixing rule can be written for use with copolymers and multicomponent polymer materials,¹³

$$LA = w_I(LA)_I + w_{II}(LA)_{II} + \dots = \sum_{i=1}^n w_i(LA)_i \quad (2)$$

where w_I , w_{II} , ... represent the weight fractions of the components in the material.

Table I summarizes loss areas, $(LA)_i$, and molar loss constants, G_i , for a number of moieties derived from group contribution analysis.¹⁴ The group contribution analysis provides a predictive method for LA values via the structure of the polymer.




Experimental

Synthesis

Styrene monomer, Polysciences Inc., and divinyl benzene, Scientific Polymer Products, were cleaned by a column chromatographic technique using neutral alumina. Poly(vinyl methyl ether), Scientific Polymer Products, $M_w = 1.3 \times 10^5$ g/mole, was supplied as a 50 wt% toluene solution. Dicumyl peroxide, Phaltz and Bauer, benzoin, Adrich Chemical, and toluene, Fisher Chemical, were used as received.

Crosslinked PVME sheets were prepared in the following manner. Dicumyl peroxide was added to the PVME by a solution blending technique. After mixing the solution was placed in a teflon mold and the toluene was removed under vacuum at 100°C.

Table I. Summary of Group Contributions to LA¹⁴

Group	Group Location ^a	(LA) _i (GPa·K)	G _i (GPa·K)(g/mol)
$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ -\text{C}-\text{C}- \\ \quad \\ \text{H} \end{array}$	1	3.4	91.8
-O-	1	19.1	305.8*
$\begin{array}{c} \text{O} \\ \\ -\text{C}-\text{O}-() - \text{H} \end{array}$	2	20.8	936
$\begin{array}{c} \text{O} \\ \\ -\text{O}-\text{C}-() - \text{H} \end{array}$	2	20.1	905
$\begin{array}{c} \text{O} \\ \\ -\text{C}-\text{OH} \end{array}$	2	20.8	936
	2	11.9	916
-CH ₃	2	11.0	165
-OCH ₃	2	21.7	674
-C≡N	2	23.2	603
-O-H	2	4.7	80
-Cl	2	9.2	327
	3	3.5	287
	3	2.2	166
$\begin{array}{c} \text{CH}_3 \\ \\ -\text{CH}_2-\text{CH}-\text{CH}_3 \\ \\ -\text{CH}- \end{array}$	3	-1.7	-98
	3,4	0.5	7
-CH ₂ -	3	-3.0	-42
-C≡N	3	14.5	377
-Cl	3	15.7	556

^a1: backbone; 2: side group attached to backbone directly; 3: side group not attached to backbone; 4: value derived from isobutyl side group.

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The resulting 2 mm thick sheet was then cured at 160°C for 60 mins. in a nitrogen atmosphere.

IPN's were prepared from the crosslinked PVME sheets by swelling in a mixture of styrene, divinyl benzene and benzoin. After equilibrium was achieved, swollen mass was then placed between Mylar sheets and glass plates. The mold was then sealed and placed in a UV box and photopolymerized for 72 hours. Semi-I IPN's, in which only the first component, PVME, is crosslinked, were synthesized by swelling in styrene and initiator, without crosslinker. Semi-II IPN's, in which the second component, PS, is crosslinked, were prepared by dissolving linear PVME in the styrene, divinyl benzene and benzoin solution. Synthesis of linear PS in the presence of linear PVME results in the formation of a chemical blend. UV photopolymerization was used in each case, similar to that for the full IPN case. Physical blends were prepared by synthesizing PS separately and solution blending to achieve the desired composition. Chemical blends differ from physical blends in that during the polymerization of the second component grafting may occur as the result of chain transfer to polymer.

Instrumental

A Mettler TA3000 system DSC30 (Mettler Instrument Co.) was used to obtain heat capacity thermograms. Ten mg samples were evaluated from -100 to 150°C at a heating rate of 10°C and a N₂ flow rate of 100 cc/min.

An Autovibron Dynamic Viscoelastometer (Rheovibron DDV-III-C; Toyo Baldwin Co., Ltd.) coupled with a computer and 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. The classical plots of the logarithmic loss modulus, E'', were converted to the corresponding linear plots by a computer program.

The cloud point curve was determined using a Zeiss microscope (Opto-Systems Inc.) equipped with a microprocessor controlled hot stage at a heating rate of 2°C/min. Films were cast from toluene onto glass slides from 10 wt% polymer solutions. The films were then dried under vacuum at 100°C.

Results and Discussion

A series of 50/50 PVME/PS samples were synthesized and the miscibility of the components was evaluated. The chemical and physical blends were found to be clear while the semi-I, semi-II and the full-IPN were observed to be hazy. Such

haziness indicates a degree of heterogeneity, usually phase separation.

The cloud point diagram determined for the PVME/PS blends at varying compositions is shown in Fig. 1. The results are in accord with previously determined phase diagrams for the PVME/PS system excepting molecular weight differences.¹⁰ Microscopic phase separation was observed with generally coarser morphology at increased PVME content. With annealing at lower temperatures, the phase separation was observed to be reversible, and clear films were obtained again.

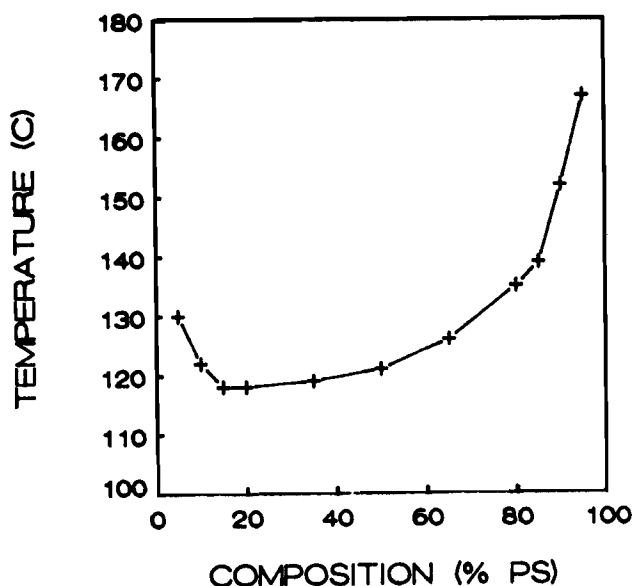


Fig. 1. The cloud point phase diagram for physical blends of PVME and PS, showing lower critical solution temperature, LCST, behavior.

Thermal analysis of PVME/PS IPN's indicates only one glass transition temperature located between the homopolymer Tg's. The position of the Tg is dependent upon composition but it does not follow the prediction of the Fox equation,¹⁵ Table II.

Table II. Characterization of PVME/PS IPN's and Homopolymers.

% PVME	Loss Area		Loss Peak °C	Tg (DSC) °C	Fox Eqn. °C
	(exper.)†	(calc.)			
	GPa*°K				
100	8.9	13.2	-15	-24	-15
70	10.8	12.1	-4	-16	14
50	12.4	11.5	16	-8	38
30	11.6	10.7	(20) 67	20	65
0	9.4	9.7	117	93	117

Network	Crosslinker level	Mc (g/mol)
x-PVME	7.5 wt % dicumyl perox.	18,000
x-PS	1 mol % DVB	7,700

† based on $E' = 2.85 \times 10^{10}$ dynes/cm²

The breadth of the transition also increases dramatically with increased PS content. The broad glass transition, resulting from the clustering of molecules near the lower critical solution temperature, is similar to broad transitions associated with microheterogeneous multicomponent polymer materials. Figure 2 compares the glass transition region of a physical blend, cast from toluene, and an IPN of the same composition. Both exhibit broad transitions, however, the IPN is significantly broader than the blend.

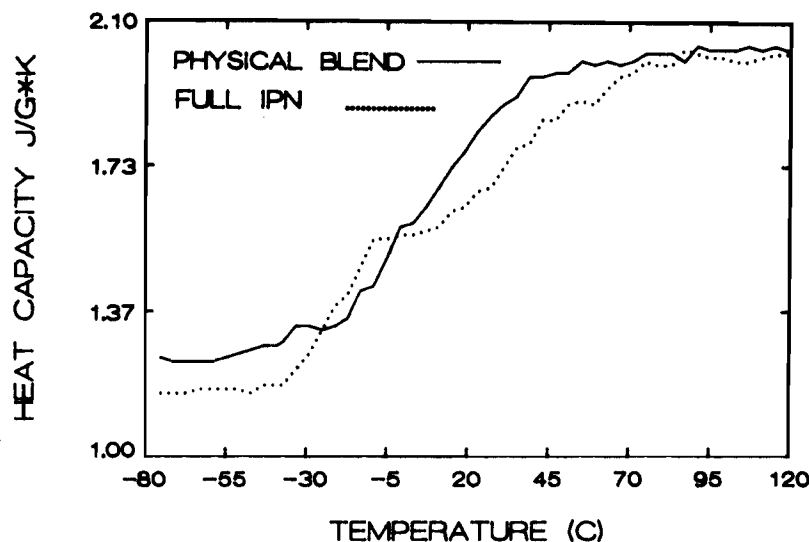


Figure 2. Differential Scanning Calorimetry of a PVME/PS physical blend and full-IPN. 50 wt % PS in each sample. Heating rate 10°C/min.

The dynamic mechanical spectra of a series of PVME/PS IPNs is shown in Fig. 3, illustrating the linear loss modulus plots. The homopolymers both show narrow, well defined loss peaks. The 70/30 PVME/PS IPN loss modulus curve is slightly broader than the PVME homopolymer peak. There is a dramatic change in the shape of the loss curve with increasing PS weight fraction as shown for the 50/50 and 30/70 IPNs. The loss modulus peak extends over a range of 100°C and in the 30/70 sample there is an observable shoulder on the low temperature end of the peak. The broad transitions indicate a degree of microheterogeneous phase separation that may be dependent on composition and the degree of crosslinking. Recently, Bauer et al. found that phase separation occurred as the crosslink density of polystyrene was increased for semi-II IPNs, where only PS is crosslinked.¹⁶ The IPNs synthesized in this lab have PS crosslinking levels corresponding to the crosslink level which resulted in phase separation of the semi-II IPNs in the work of Bauer et al.

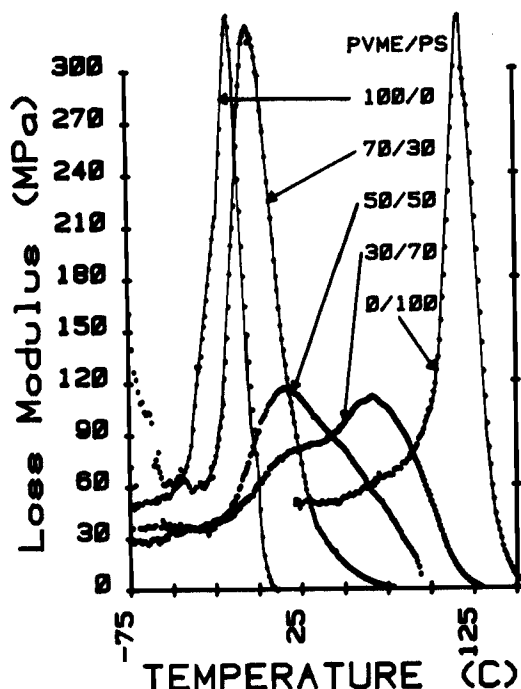


Fig. 3. Linear loss modulus versus temperature curves for PVME/PS full-IPN's and homopolymers. Rheovibron DDV-III dynamic mechanical spectroscopy at 110 Hz, heating rate 1°C/min.

The loss areas, LA's, obtained for the IPN's and homopolymers are compared with the values predicted from equation (2) and Table II. Except for the crosslinked PVME homopolymer, the LA values obtained by DMS are within 10% of the values predicted by the group contribution analysis. The large deviation in the LA value obtained for the crosslinked PVME homopolymer may be attributed to oxidation during sample preparation, as evidenced by sample discoloration, which was not observed in the IPN samples.

To examine the effect of phase separation on the loss modulus, a sample of a 50/50 chemical blend was phase separated at 130°C and then evaluated by DMS, Fig. 4. Note that the 50/50 PVME/PS blend shows a broad transition indicative of clustering. This result is in accord with previous dynamic mechanical spectra of PVME/PS blends.⁹ Comparatively, PPO/PS blends exhibit narrow loss moduli peaks that vary predictably over the entire range of composition.⁶ Since the LCST for PPO/PS is significantly higher than the experimental temperatures employed, clustering does not occur, and narrow transitions are obtained. As compared to the untreated blend, the thermally treated PVME/PS blend shows a broader transition and also a larger loss area which may be attributed to a change in morphology. Similarly, the IPN shows a broader transition, however, the area is the same as the untreated blend, within experimental error. It should be noted that the phase separated blend has a milky white appearance whereas the IPN is slightly hazy. The degree of phase separation in the two cases is significantly different.

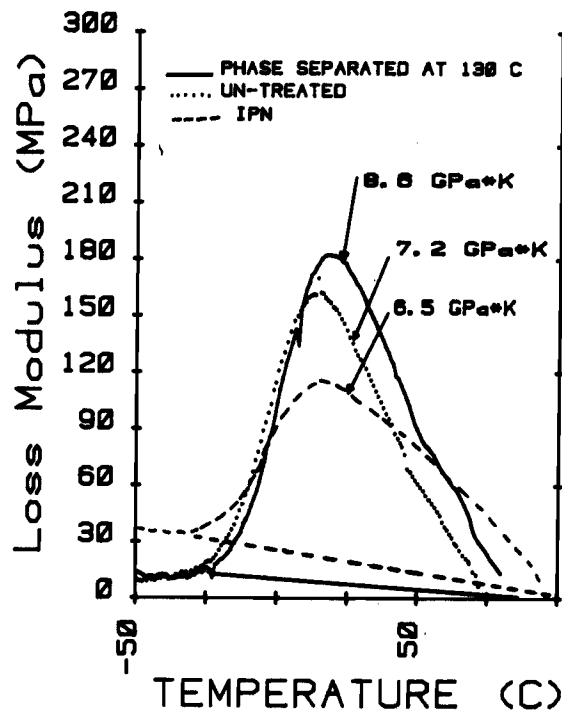


Fig. 4. Linear loss modulus curves for 50/50 PVME/PS chemical blends, under two different conditions, and a full-IPN. Baseline corrections are also shown.

Conclusions

The IPNs synthesized appear to be less miscible than the corresponding chemical and physical blends. The phase separated IPNs, having broader glass transition regions than the corresponding linear blends, enable damping over a broader temperature region.

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