

Interpenetrating Polymer Networks of Castor oil Polyester and Poly(methyl methacrylate)

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SYNOPSIS

The physical and mechanical properties of interpenetrating polymer networks (IPNs) and semi-I IPNs of the castor oil polyester network and poly(methyl methacrylate) were investigated. In the semi-I IPNs, the second component was a copolymer of poly(methyl methacrylate) and polystyrene (PS) or poly(methyl methacrylate) and poly(*n*-butyl acrylate) (PnBA). The dynamic mechanical properties indicated the semi-I IPNs to be more compatible than the IPNs. The degree of molecular mixing was higher than that for IPNs. The impact strength showed a gradual increase with the increase in the percentage of PS or PnBA in the copolymer. The effect of the copolymerization of the second component on transparency was investigated. The transparency of the semi-I IPNs increased with the increasing composition of PnBA, but reduced with the increasing composition of PS. These results are discussed in light of existing theories.

INTRODUCTION

A necessary criterion for two polymers to be miscible is that the Gibbs energy change on mixing be negative. Attempts to calculate this Gibbs energy center on three contributions: (1) the normal (combinatorial) entropy change on mixing, (2) the interactional energy resulting from the change in distribution of interatomic contacts, and (3) contributions originating from changes in volume on mixing. All these contributions have been utilized to explain the lower critical solution temperature (LCST) behavior of polymer blends that forms the subject of various theories based on the equations of state. These theories attempt to describe the PVT properties of polymers and of their mixtures.¹⁻⁴ In the calculation of Gibbs energy change on mixing of two polymers, one assumes that the mixture obeys the same equation of state as do the pure components and that hard core volumes are additive.

A very extensively reported and documented phenomenon is the physical aging of glassy polymers like poly(methyl methacrylate) (PMMA) and polystyrene (PS). It is known that the loss of properties of these polymers is accompanied by the reduction of free volume.⁵ This problem of the reduction of free volume can be offset (a) by copolymerizing the glassy polymer with a second component and (b) by addition of filler or rubber particles that would give the additional property of impact modification. Both these methods can be combined in the synthetic procedure. Such a synthetic method results in interpenetrating polymer networks (IPNs) that exhibit an intimate mixture of two polymeric networks that are superimposed within each other, one being the elastomeric component and the other being the plastic component.

IPNs are prepared by swelling a cross-linked polymer (1) with a second monomer solution that contains an initiator and cross-linking agent. An IPN results upon polymerizing the second monomer *in situ*. A semi-I IPN results when polymer (1) is cross-linked and the second polymer (2) is linear. In our present study, with a view toward impact improvement of the glassy polymer PMMA, IPNs of

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castor oil polyester and of PMMA were investigated.

The use of renewable resources is of particular interest because of its potential to substitute for petrochemical derivatives. Castor oil is one such resource. Sebacic acid is made from castor oil and so is of much interest in exploring its usefulness as a petrochemical substitute. A number of workers have explored the use of castor oil as an elastomer for impact improvement of brittle plastics.^{6,7} The unique feature of PMMA is its transparency. However, PMMA is a highly brittle plastic. A number of authors⁸⁻¹⁰ have tried to improve the impact properties of PMMA, at the same time retaining its transparency. This investigation is an attempt in this direction. IPNs and semi-I IPNs of the castor oil polyester network (COPEN) and of PMMA were synthesized and characterized for their tensile and impact properties and the effect of the cross-linker type and density on the transparency of these materials.

EXPERIMENTAL

Materials

Interpenetrating polymer networks (IPNs) based on castor oil polyester and PMMA were synthesized. The description of the raw materials used is given in Table I. The monomers, MMA, styrene, and *n*-butyl acrylate (nBA) were washed prior to use with 10% NaOH aqueous solution to remove inhibitor, washed with distilled water, dried using CaCl₂, and finally distilled under vacuum. The distilled monomer was stored under molecular sieves. The cross-linkers tetraethylene glycol diacrylate (4-EGDA),

triethylene glycol diacrylate (3-EGDA), and diethylene glycol diacrylate (2-EGDA) for MMA were used without further purification.

Polyester Synthesis

Castor oil prepolymer was synthesized by taking the predetermined weight of castor oil and sebacic acid in a 500 mL flat flange reactor. Dibutyl tin oxide was used as catalyst. The reactor was equipped with argon inlet, condenser, and thermometer. The reaction was carried out under an argon blanket at 180°C and under constant stirring. The progress of the reaction was determined by the acid value of the contents that were removed (~ 1 g) at regular intervals. The reaction was stopped when the acid value dropped to 33.0, corresponding to a conversion of 0.79. Beyond this time, the contents of the reactor gelled to give a thick mass.

IPN Synthesis

All IPNs were synthesized by the thermal polymerization technique. Initially, the required weight percent of the castor oil prepolymer was taken in a clean dry 500 mL reactor. The monomer mixture was prepared separately by taking MMA monomer, initiator benzoyl peroxide, and the cross-linker or comonomer and chain transfer agent 1-dodecanethiol and mixed thoroughly. This monomer mixture was added to the reactor and stirred until the prepolymer dissolved. Simultaneously, argon gas was bubbled through the contents to remove any dissolved oxygen. The temperature of the reactor was then raised and the polymerization continued at 70°C. Initially, the polyester, which is viscous, was the continuous

Table I Description of Raw Materials and Technical Data

Material	Abbreviation	Source	Technical Data
Castor oil	CO	Local market	OH value = 169 M.W. = 925.8 Acid value = 2 Purity = 97%
Sebacic acid	SA	Aldrich	M.W. = 202.7
Methyl methacrylate	MMA	Local market	Purified
Styrene	S	Local market	Purified
<i>n</i> -Butyl acrylate	nBA	Local market	Purified
Dibutyl tin oxide	DBTO	Fluka	Catalyst
Benzoyl peroxide	BPO	Fluka	Catalyst
Diethylene glycol diacrylate	2-EGDA	Aldrich	Cross-linker
Triethylene glycol diacrylate	3-EGDA	Aldrich	Cross-linker
Tetraethylene glycol diacrylate	4-EGDA	Aldrich	Cross-linker

phase. As polymerization proceeded, the second component molecular weight increased. This led to phase separation, which was observed by the appearance of turbidity. As polymerization continued further, after a particular conversion, under the conditions of vigorous stirring, PMMA became the continuous phase. Beyond this, gelation occurred. The contents of the reactor were poured into the mold after phase inversion and before gelation depending on the composition of the contents. After specific time periods, depending on the composition of the two networks, the contents of the reactor were poured into a glass mold of size 20×20 cm separated by an elastomeric gasket of 0.3 cm thickness. The mold was kept in an air-circulating oven maintained at 70°C for curing and further at 180°C for 12 h. The various compositions synthesized are given in Table II.

MATERIALS AND METHODS

Free Volume

The free volumes of the cross-linked and copolymerized PMMA and of castor oil polyester were calculated from their specific volumes. The specific volumes of these polymers were measured by the dilatometric method, the details of which are discussed elsewhere.¹¹ The specific volumes and the free volumes are given in Table III.

Dynamic Mechanical Spectroscopy

The dynamic mechanical properties of these IPNs and semi-I IPNs were measured on a Rheovibron

direct reading viscoelastometer model DDV-IIC (manufactured by Toyo Measuring Instruments Co., Japan). The measurements were carried out over a range from -120 to $+120^\circ\text{C}$ using a frequency of 3.5 Hz and a heating rate of about $1^\circ\text{C}/\text{min}$. Sample dimensions were about $0.03 \times 0.15 \times 2.0$ cm.

Tensile Strength

The tensile strengths were measured on a Instron tensile tester according to the ASTM method 1708. Micro tensile samples in a dumbbell shape were cut from the cast IPN sheets, and the cut sides were polished to remove any visual flaws. Three test pieces of each sample were taken and the average reported.

Impact Strength

Izod notched impact strength was measured according to ASTM method D 256. The notch depth was 0.25 cm of a "V" shape and the angle was 22.5° . Five samples were tested and the average of five values are reported.

Light Scattering (Transparency)

Transparency measurements were carried out on a digital haze computer manufactured by Suga Test Instruments Co., Japan, at wavelength of 400–800 nm. The samples of about 0.3 cm thickness were polished on both sides. No correction was made for the light reflected from each surface. The mean

Table II Composition of the IPNs and Semi-I IPNs

Code	Composition	Cross-linker	Copolymer
Full IPNs			
IPN 1	10/90	2-EGDA (3%)	—
IPN 2	10/90	3-EGDA (3%)	—
IPN 3	10/90	3-EGDA (9%)	—
IPN 4	10/90	4-EGDA (3%)	—
Semi-I IPNs			
IPN 5	10/85-5	—	PS
IPN 6	10/80-10	—	PS
IPN 7	10/60-30	—	PS
IPN 8	10/85-5	—	PnBA
IPN 9	10/80-10	—	PnBA
IPN 10	10/50-40	—	PnBA

Table III Specific Volumes of Cross-linked PMMA and Copolymer of PMMA with PS and PnBA

Polymer	Cross-linker (wt %)		v_{sp}	$\alpha \times 10^4$	v_f
	4-EGDA				
PMMA	3		0.800	4.012	0.081
PMMA	9		0.837	3.285	0.071
P(MMA-co-S)	70-30		0.962	2.484	0.174
COPEN	—		1.058	5.549	0.139

chord intercept length, L_i , was calculated at a wavelength of 500 nm. The PMMA refractive index was taken as 1.4770 at 25°C. The refractive index for COPE was determined at 25°C and was found to be 1.4647.

RESULTS AND DISCUSSION

Free Volume

The free volumes calculated from the specific volumes, v_{sp} , are given in Table III. For PMMA, as the cross-link density increases, the free volume decreases. As can be seen, the v_f for COPEN is higher than for cross-linked PMMA, whereas it is less than that for P(MMA-co-S). This explains the higher extent of mixing in IPN 7. The effect of the free volume variation on the miscibility can be seen from the other tests carried out.

The dynamic mechanical results of the samples taken are shown in Figures 1 and 2. These give the $\log E''$ versus temperature curves. Figure 1 gives the modulus curves for the full IPNs. The T_g 's were taken as the maximum in the $\log E''$ versus temperature curves. The T_g values are compiled in Table IV. There is an inward shift in the T_g 's of both the polyester network and PMMA. The maximum shift has been observed for IPN-4, where 4-EGDA is the cross-linker at a 3% level. No shift is observed for IPN-1 where 2-EGDA is the cross-linker. All these IPNs are two-phase materials, with the plastic phase of PMMA being the continuous phase and the polyester being the dispersed phase. At the same percentage of cross-linker, a longer cross-linker results in a more open network size, leading to better mixing. The extent of mixing can be quantified from the Fox equation [eq. (1)], which is used for random copolymers to estimate the composition within each phase⁹:

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \quad (1)$$

where $w_1 + w_2 = 1$. The quantity T_g represents the glass transition temperature of the phase being considered, and w_1 and w_2 are the weight fractions of the elastomeric and plastic components, respectively. The quantities T_{g1} and T_{g2} are the homopolymer T_g 's.

Using the T_g values in Table IV, the compositions within each phase were calculated using eq. (1) and are shown in Table V. The results show about 0–15% mixing between the two components. The modulus curves for the semi-I IPNs with PS and PnBA are given in Figure 2. The T_g values for these semi-I IPN are given in Table VI. Using the values in Table VI, the compositions within each phase as calculated from eq. (1) are given in Table VII. At the same percentage of the comonomer, the shift in the T_g 's is more for PnBA than for PS. For semi-IPN 10 with 40% PnBA in the copolymer, only a single T_g was observed. This shows that there is extensive mixing at the molecular level.

Transmittance

For two incompatible polymers, with different refractive indices, the transmittance or turbidity would give a measure of molecular mixing and phase sizes. The effect of the cross-linker type and cross-link

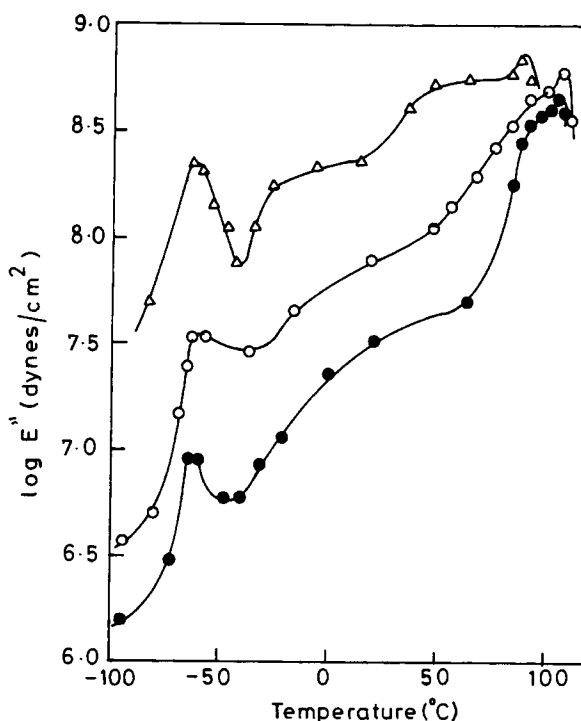


Figure 1 Loss modulus versus temperature curves for IPN 1 (●), IPN 2 (○) and IPN 4 (Δ).

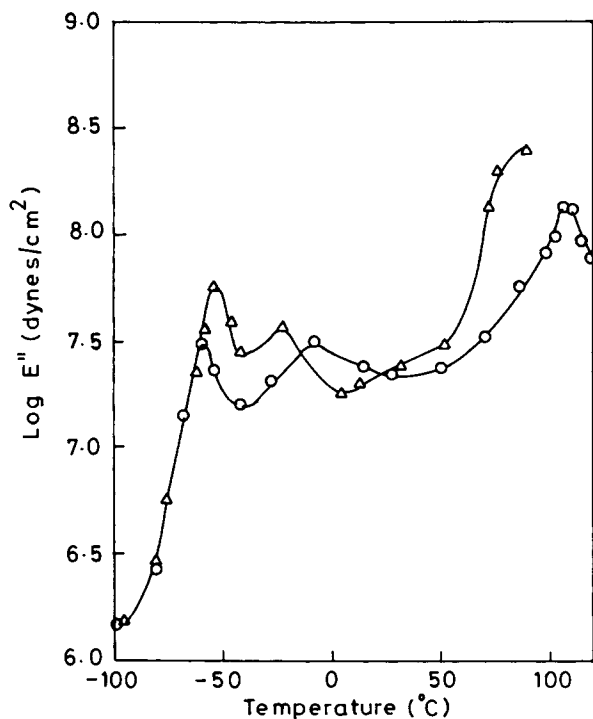


Figure 2 Loss modulus versus temperature curves for IPN 6 (O) and IPN 9 (Δ).

density and also of the composition of the copolymer in the semi-IPNs would give different turbidity. The effect of changes in synthetic parameters are given in Table VIII. The fraction of light transmitted by a sample, T , was determined, and turbidity, τ , was calculated through the Beer-Lambert extinction law [eq. (2)]:

$$\tau = -\frac{1}{x} \ln T \quad (2)$$

where x is the sample thickness. The amount of light scattered by the micro heterogeneities has been described by the theory of Debye et al.¹² It is possible

Table IV Glass Transition Temperatures of the Full IPNs

Code	Composition	T_{g1} (°C)	T_{g2} (°C)
COPEN		-68.0	—
IPN 1	10/90 (2-EGDA)	-68.0	106.0
IPN 2	10/90 (3-EGDA)	-62.0	106.0
IPN 3	10/90 (3-EGDA)	-57.0	107.0
IPN 4	10/90 (4-EGDA)	-58.0	101.0
PMMA	—	—	107.0

Table V Estimate of Molecular Composition within Each Phase for IPNs

Code	Elastomeric		Plastic	
	w_1	w_2	w_1	w_2
IPN 1	1	0	0.01	0.99
IPN 2	0.94	0.06	0.01	0.99
IPN 3	0.89	0.11	0	1.0
IPN 4	0.87	0.13	0.02	0.98

to measure the average domain size of a two-phase system from the refractive index difference of the scattering particles and the volume fraction of the dispersed phase. A semiempirical approach has been suggested by Blundell et al.¹³ At a given wavelength λ , the mean chord intercept length, L_i , of the heterogeneities is deduced from the relationship

$$L_i = \frac{\lambda y}{4\pi(1-\phi)} \quad (3)$$

From the following set of equations, y is determined through the experimental value of turbidity:

$$\tau = \frac{2\pi\phi(1-\phi)}{\lambda} \cdot \frac{(\Delta n)}{n} \cdot B(y) \quad (4)$$

where

$$B(y) = \frac{y^2 + 2}{y} \cdot \left(\frac{y^2 + 2}{y^2 + 1} - \frac{2}{y^2} \cdot \ln(y^2 + 1) \right) \quad (5)$$

and ϕ , n , and Δn are the volume fraction, the refractive index of the dispersed phase, and the difference in the refractive indices between the two phases, respectively. This approach has been applied

Table VI Glass Transition Temperatures of Semi-I IPNs

Code	T_{g1} (°C)	T_{g2} (°C)
Semi-I IPNs (PS)		
IPN 5	-60.0	98.0
IPN 6	-62.0	104.0
IPN 7	-53.0	78.0
Semi-I IPNs (PnBA)		
IPN 8	-60.0	93.0
IPN 9	-58.0	84.0
IPN 10	—	25.0

Table VII Estimate of Composition in Each Phase for Semi-IPNs

Code	Elastomeric		Plastic	
	w_1	w_2	w_1	w_2
Semi-I IPNs (PS)				
IPN 5	0.92	0.08	0.02	0.98
IPN 6	0.94	0.06	1	0
IPN 7	0.85	0.15	0.09	0.91
Semi-I IPNs (PnBA)				
IPN 8	0.92	0.08	0.02	0.98
IPN 9	0.89	0.11	0.12	0.88

by previous workers,¹⁴ and it is used in this investigation to calculate the intercept length, L_1 , from the transmittance of the full IPNs and the semi-IPNs. At the same cross-linker percentage, IPN-1 with 2-EGDA gives the best transparency. A tighter network tends to reduce the domain sizes. This is similar to increasing the cross-link density. When the cross-link density is increased from 3% to 9% for 3-EGDA, the transmittance increases as seen in Table VIII.

In the semi-IPNs where there is no second network, the transparency and, hence, the intercept length, L_i , seems to depend on the extent of molecular mixing. In the case of IPN 5, at a 85-5 composition of PS, the transparency is the highest, though the extent of molecular mixing is higher in IPN 7, at the 60-30 composition of PS. This is because at the higher PS concentration the PS size itself starts scattering because of its higher bulky nature.

In the semi-IPNs where PnBA is the copolymer, with castor oil polyester and PnBA compatible in all proportions, the transparency increases with increasing PnBA content. This is also shown by the DMA measurements. In IPN-10, at the 50-40 composition of PnBA, the DMA shows no individual component transition but a broad transition. This is shown by the better transparency of all the semi-I IPNs and also from the mechanical properties of these particular compositions.

Mechanical Properties

The mechanical properties reflect the observations in the previous section. A higher degree of molecular mixing should give better impact properties. This is evident in semi-IPN 7 and semi-IPN 10 (Table IX). The improvement in impact properties results in a reduction in tensile strength. Within an error of 10% in the measurement of impact properties, there is a definite trend in the series of IPNs under discussion. The increase in cross-link density and increasing percentage of PS and PnBA all contribute to the increasing impact strength. The transparency values and the impact properties seem to be complimentary. Except in the semi-IPN-7, improved transparency has been achieved with a corresponding improvement in impact strength. The reasons for this is twofold. First, a better molecular mixing leads to better interfacial adhesion between the elastomeric and plastic components. Second, the size of the dispersed phase reduces with the increased degree of mixing, thus giving better transparency. However, it is necessary to mention here that none of these materials are transparent in the true sense (which

Table VIII Light Transmittance Values of the IPNs and Semi-IPNs

Code	% Transmittance	Intercept Length, L_1 (nm)
IPN 1	67.9	28.3
IPN 2	45.6	38.9
IPN 3	51.0	36.2
IPN 4	51.5	35.9
Semi-I IPNs (PS)		
IPN 5	63.5	30.4
IPN 6	58.4	32.7
IPN 7	Opaque	—
Semi-I IPNs (PnBA)		
IPN 8	—	—
IPN 9	64.7	29.8
IPN 10	73.5	25.7

Table IX Tensile and Impact Strength of the IPNs and Semi-IPNs

Code	Tensile Strength (kg/cm ²)	Impact Strength (kg cm/cm)
Full IPNs		
IPN 1	216	1.49
IPN 2	166	0.91
IPN 3	346	1.65
IPN 4	203	1.08
Semi-IPNs		
IPN 5	290	1.58
IPN 6	269	1.60
IPN 7	162	1.74
IPN 8	260	1.08
IPN 9	280	1.40
IPN 10	26	16.4

require transmittance of 80% and above). At best, these materials are translucent. But it is seen that an improved molecular mixing does improve transparency of these IPNs. The transmittance values are given in Table VIII.

CONCLUSIONS

The premise that 'free volume' contributes to the extent of molecular mixing is justified from the results obtained in this investigation. In the case of the type of the cross-linker, at the same level of cross-linking, the bigger the size of the cross-linker, the better is the extent of molecular mixing. When divinyl benzene was used as the cross-linker (not reported in this paper), the IPNs were opaque and there was also no impact strength improvement. 4-EGDA gives a better degree of mixing and, therefore, better impact strength. When PS is the copolymer, there are two effects that are contributing to the observed results. COPEN and PMMA are incompatible in all proportions. This is due to the unfavorable interactions between them. The introduction of a third component that is relatively nonpolar dilutes these unfavorable interactions, thus leading to

better mixing. The other is the entropic contribution, i.e., the effect of the 'free volume' increase of the second component. As the PS percentage increased, the compatibility improved. A similar explanation is justified for PnBA, though grafting between the two phases is not ruled out. The transparency results vindicate this argument for both semi-IPN systems.

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