

Studies on Semiinterpenetrating Polymer Networks Based on Poly(vinyl chloride-co-vinyl acetate) and Poly(alkyl methacrylates)

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SYNOPSIS

A number of semi-interpenetrating polymer networks (IPNs) based on linear poly(vinyl chloride-co-vinyl acetate) and poly(alkyl methacrylates) were synthesized. The semi-IPNs were found to be transparent, high strength materials. The IPNs show only one glass-transition temperature and it is dependent on the composition as studied by differential scanning calorimetry and dynamic mechanical analysis. These IPNs are also characterized by high $\tan \delta$ values. The tensile strength of the IPNs were found to be higher compared to the starting polymers. In order to compare the properties of these IPNs with the corresponding homopolymers and blends, the latter were synthesized and the properties were studied. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Interpenetrating polymer networks (IPNs) are gaining importance in recent years due to their applications as broad range vibration dampers,¹⁻⁵ impact resistant modifiers,^{6,7} and engineering plastics.^{8,9} Synthesis of IPN offers an excellent method of combining a plastic and an elastomer at use temperature, to give rise to polymers of interesting characteristics not obtained by polymer blending or grafting.¹⁻⁵ Recently, we have reported the studies on a number of semi-IPNs based on poly(vinyl chloride-co-vinyl acetate) (PVC-VA), a brittle thermoplastic, and poly(butyl acrylate) (PBA), a low strength elastomer, having the properties of a reinforced rubber.¹⁰

The present study deals with the properties of semi-IPNs based on PVC-VA and various alkyl methacrylates. Also a comparative study of the properties of these IPNs with the corresponding blends are discussed.

EXPERIMENTAL

Materials

PVC-VA, 85/15 w/w, (Union Carbide, USA) was used without further purification. Butyl methacrylate (BMA), ethyl methacrylate (EMA), and methyl methacrylate (MMA) monomers (Fluka) were freed from inhibitor and distilled under reduced pressure before use. Tetraethylene glycol dimethacrylate (TEGDM, Fluka) was used as received. Azobisisobutyronitrile (AIBN) was recrystallized from ethanol. Methyl isobutyl ketone (MIBK), benzene, and methanol were of AR grade from Qualigens, India.

Synthesis

Semi-IPNs of PVC-VA/BMA were prepared as follows: 10 g PVC-VA resin powder was thoroughly mixed with 18 mL BMA monomer containing 0.03 g AIBN and 0.4 mL TEGDM. The mixture was allowed to stand at room temperature for 4 h and the viscous mass obtained was poured into a stainless steel mold ($15 \times 100 \times 150 \text{ mm}^3$) held between two stainless steel plates. It was then polymerized at

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80°C under a pressure of 150 kg/cm² for 1 h. The IPN sheet was then kept under reduced pressure at 80°C for 24 h to remove unreacted monomer. This ensured complete polymerization of methacrylate monomer and no further weight loss. Composition of the above IPN was found to be 50% PVC-VA and 50% PBMA by weight. Some monomer was lost during the polymerization and also during the complete removal of residual free monomer. Because the weight of PVC-VA remains constant during all these stages, the actual composition has been calculated from the total weight of IPN.

IPNs of EMA and MMA were also prepared by the same method. Because the volatility of EMA and MMA are more than that of BMA, a slight excess of monomers were used to get a 50/50 composition. IPNs of different compositions were made by changing the PVC-VA/MA monomer ratio. Samples of different dimensions were made by changing the mold dimensions.

The homopolymers of various MAs were prepared by solution polymerization using benzene as solvent and AIBN as initiator. The polymers were purified by reprecipitation from methanol. The films of homopolymers were prepared by solution casting using MIBK as solvent. The blends of MAs with PVC-VA of 50/50 composition were also prepared by solution casting using MIBK as solvent. The films were dried under reduced pressure at 50°C for a prolonged time until the samples showed no further weight loss.

Thermal Analysis

Differential scanning calorimetric (DSC) studies were carried out on a Dupont DSC (910) from 25

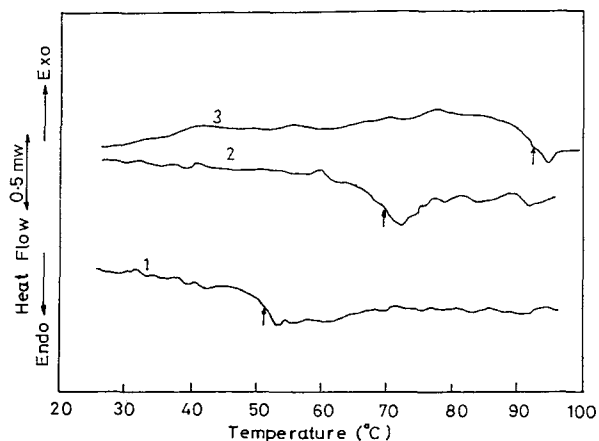


Figure 1 DSC thermogram of semi-IPNs: (1) PVC-VA/PBMA 50/50; (2) PVC-VA/PEMA 50/50; (3) PVC-VA/PMMA 50/50.

Table I Glass-Transition Temperatures (T_g) of Polymers, Blends, and IPNs

Name Predicted	Experimental T_g (°C)	T_g Predicted (°C)	
		Eq. (1) ^a	Eq. (2) ^b
Homopolymers			
PVC-VA	69	—	—
PBMA	20	—	—
PEMA	58	—	—
PMMA	100	—	—
Blends			
PVC-VA/PBMA 50/50	42	43	45
PVC-VA/PEMA 50/50	52	63	64
PVC-VA/PMMA 50/50	90	84	85
Semi-IPNs			
PVC-VA/PBMA 50/50	50	43	45
PVC-VA/PBMA 30/70	40	33	35
PVC-VA/PEMA 50/50	70	63	64
PVC-VA/PEMA 30/70	70	61	61
PVC-VA/PMMA 50/50	93	84	85
PVC-VA/PMMA 30/70	97	90	91

^a Calculated from Eq. (1).

^b Calculated from Eq. (2).

to 100°C at a heating rate of 5°C/min. A sample weight of 5 mg was used.

Dynamic mechanical spectra were recorded using a dynamic mechanical analyzer (Dupont DMA Model 983) at a temperature between 25 and 125°C. The measurements were carried out at a heating rate of 5°C/min and at the resonance mode.

Mechanical Properties

The tensile strength and elongation at break of the IPNs were determined on an Instron Testing Machine (Model 1123) at a crosshead speed of 20 mm/min using parallel strips of 1.5 × 10 × 100 mm dimensions.

RESULTS AND DISCUSSION

The semi-IPNs and the blends based on PVC-VA and MAs were transparent and homogeneous. The glass-transition temperatures (T_g s) of polymethacrylates, PVC-VA, and various blends and IPNs were measured using a DSC. A few representative spectra are produced in Figure 1 and the values are summarized in Table I. The midpoint of the deflection in the DSC thermogram is taken as the T_g . All the semi-IPNs and blends gave only one T_g between

the T_g s of the two starting polymers. The T_g s were also found to be composition dependent. This clearly indicates that there is no phase separation. Studies on blends based on PVC-VA and MAs were reported to be conditionally compatible.¹¹⁻¹³

The theoretical T_g was calculated from the two well-known equations

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

$$T_g = w_1 T_{g1} + w_2 T_{g2} \quad (2)$$

where T_{g1} and T_{g2} represents the T_g s of PVC-VA and MAs, w_1 and w_2 are their weight fractions, and T_g is of the blends/IPNs. The experimental values of the semi-IPNs are slightly higher than that of the blends. This is expected because unlike blends, in the semi-IPNs one phase is cross-linked and therefore account has to be taken for the increase in T_g due to the cross-linking.¹ Apart from this, the experimental and theoretical values are in good agreement showing that these semi-IPNs are fully homogeneous systems.

Dynamic Mechanical Analysis

Dynamic mechanical analysis is very helpful in understanding the homogeneity as well as the damping effectiveness of IPNs. Sperling et al.^{1,2} characterized the $\tan \delta$ values as a measure of the damping characteristics of IPNs. $\tan \delta$ is given by the ratio E''/E' where E'' is the loss modulus representing the amount of mechanical energy dissipated as heat during the DMA experiment and E' is the storage modulus. Because damping is nothing but the mechanical energy dissipation, the higher the $\tan \delta$ value, the higher the damping. Polymers having high

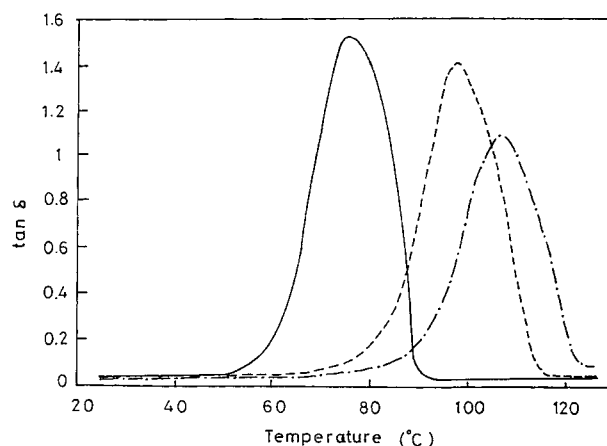


Figure 2 $\tan \delta$ vs. temperature plots of semi-IPNs: (—) PVC-VA/PBMA 50/50; (---) PVC-VA/PEMA 50/50; (-·-·-) PVC-VA/PMMA.

damping generally have $\tan \delta$ values greater than 0.5 whereas low damping polymers such as polystyrene, polyethylene, etc., have low $\tan \delta$ values.^{2,14}

Dynamic mechanical analysis of PVC-VA and various semi-IPNs was carried out from 25 to 125°C and the results are summarized in Table II. A few representative $\tan \delta$ vs. temperature plot and E' vs. temperature plots are given in Figures 2 and 3, respectively. All the IPNs showed only one $\tan \delta$ peak and are in conformity to the single T_g obtained using DSC. PVC-VA/PBMA IPNs showed the highest $\tan \delta$ value (1.55) followed by EMA and MMA based IPNs (Table II). In almost all cases, T_{\max} was found to be -30°C higher than the T_g obtained from DSC, a fact observed by other workers also.^{10,15,16} By increasing the MA content, the $\tan \delta$ value shows a slight decrease in all IPN systems and might be due to the low $\tan \delta$ of MAs compared to PVC-VA (Table

Table II DMA Studies of Semi-IPNs

Polymer/IPN	Tan δ_{\max}	T_{\max} (°C)	E' at 30°C (GPa)
PVC-VA	1.60	102	2.50
PBMA ^a	1.40	60	—
PVC-VA/PBMA 50/50	1.55	77	1.60
PVC-VA/PBMA 30/70	1.50	73	1.58
PEMA ^a	1.19	92	—
PVC-VA/PEMA 30/70	1.42	97	2.45
PVC-VA/PEMA 50/50	1.15	80	2.50
PMMA ^a	1.27	127	—
PVC-VA/PMMA 30/70	1.15	106	2.65
PVC-VA/PMMA 30/70	1.10	115	3.00

^a From Chang et al.³

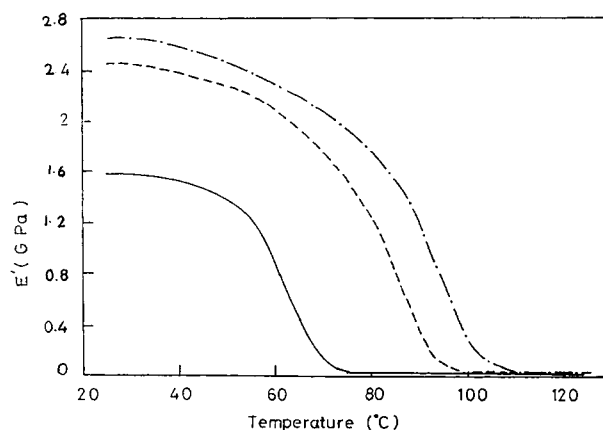


Figure 3 E' vs. temperature plots for semi-IPNs: (—) PVC-VA/PBMA 50/50; (---) PVC-VA/PEMA 50/50; (-·-·-) PVC-VA/PMMA 50/50.

II). The DMA study thus shows that all the semi-IPNs are characterized by having high $\tan \delta$ value or high damping characteristics.

The storage modulus value (Table II) of PVC-VA/PMMA is the highest, showing that this IPN has the highest modulus. Because PBMA is a soft material, IPN based on BMA shows low E' value or low modulus value, which is confirmed by tensile studies as well.

Tensile Properties

The tensile properties of PVC-VA, PMAs, blends, and semi-IPNs were studied and the data are given in Table III. PBMA is elastomeric having high elongation. PMMA has high strength and low elongation. Thus the tensile strength of the MAs depends on the nature of the alkyl group. All IPNs have high strength compared to the corresponding blends (Table III). PVC-VA/PMMA-based IPNs showed the highest strength (615 kg/cm^2) and the strength increased by increasing the MMA content. This is due to the fact that PMMA has much higher tensile strength compared to PVC-VA, PBMA, and PEMA (Table III). Also PVC-VA/PMMA IPNs have more strength compared to the two starting polymers and their blends that is due to the presence of cross-linking.¹⁷

In PVC-VA/PBMA, the tensile strength decreased with increased MA content because the PBMA has a lower strength compared to the PVC-VA copolymer.

Table III Tensile Properties of Polymers, Blends, and IPNs

Name	Tensile Strength (kg/cm ²)	Elongation (%)
Homopolymers		
PVC-VA	475	35
PBMA	214	472
PEMA	350	125
PMMA	500	2
Blends		
PVC-VA/PBMA 50/50	303	5
PVC-VA/PEMA 50/50	338	4
PVC-VA/PMMA 50/50	403	3
Semi-IPNs		
PVC-VA/PBMA 50/50	380	8
PVC-VA/PBMA 70/30	325	8
PVC-VA/PEMA 50/50	470	7
PVC-VA/PEMA 30/70	500	6
PVC-VA/PMMA 50/50	550	11
PVC-VA/PMMA 70/30	615	10

CONCLUSION

Semi-IPNs derived from PVC-VA and various alkyl MAs give transparent, high strength materials which may find applications as engineering plastics. Synthesis of these semi-IPNs are by a simple one-step procedure. The IPNs show only one glass transition unlike PVC-VA/acrylate IPNs.¹⁰ DSC and DMA studies show that there is no phase separation. DMA studies also show that they have high damping characteristics. Thus the present study shows that by varying the MA structure and the percentage composition in the PVC-VA-MA systems, IPNs of desirable strength and damping can be obtained.

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