

Effect of Crosslinking on Mechanical and Viscoelastic Properties of Semiinterpenetrating Polymer Networks Composed of Poly(Vinyl Chloride) and Isocyanate Crosslinked Networks

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ABSTRACT: Semiinterpenetrating polymer networks (SIPNs) of PVC/isocyanate/polytriol were prepared by premixing small (150 μm dia.) porous (30% voids) unplasticized PVC particles, 10% by weight of isocyanate, and a triol at different OH/NCO mol ratios. Three types of isocyanates (methylene bis-phenyl diisocyanate (MDI), oligomeric MDI isocyanates (PAPI), and toluene diisocyanate (TDI) prepolymer/polytriol) were used. Two-roll milling was followed by hot-press curing. The tensile, flexural, and impact strengths increased when small amounts of crosslinked isocyanate networks were created in PVC. The isocyanate/polyol hydroxyl stoichiometry was varied, and the effects of crosslinking on the tensile, impact, and flexural strengths of PVC/isocyanate/triol SIPNs were examined. The strength increments were greater when the OH/NCO mole ratio went from 0 to 0.25, than when it went from 0.25 to 1.0. In many cases, increasing OH/NCO mol ratio from 0.5 to 1.0 decreased tensile, impact, and flexural strengths. Both PAPI and MDI (30% NCO content) gave bigger improvements in the these mechanical strengths than the TDI (only 9.7% NCO). These SIPN blends exhibited lower $\tan \delta$ peak temperatures and a single distinct loss modulus, E'' , peak values at lower temperatures than those of PVC that had been exposed to the same processing temperatures. Substantial amounts of isocyanate networks exist in SIPN phases according to DMTA studies. The OH/NCO ratio did not generally correlate with the decreases in the glass transition temperatures in these three sets of blends. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 1402–1411, 2000

Key words: poly(vinyl chloride); isocyanates; polyol; semiinterpenetrating polymer networks; dynamic mechanical thermal analysis

INTRODUCTION

Semiinterpenetrating polymer networks (SIPNs) are increasingly being formed in polymer blends

comprised of high molecular-weight linear thermoplastics and reactive thermosetting resins.^{1–7} Barrett and Sperling^{1,2} reported SIPN blends made from poly(ethylene terephthalate) (PET), toluenediisocyanate-prepolymer, and castor oil. The resultant SIPNs exhibited enhanced impact resistance and crystallization rates. Danilov et al.⁸ studied a SIPN system composed of polyethylene (PE) and maleic anhydride-cured epoxy networks. Such blends exhibited improved mechanical strengths and adhesion to fibers and fillers.

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Dillon et al.⁹ developed a series of SIPNs from poly(tetrafluoroethylene) (PTFE) and silicones. SIPNs have been used as membranes for filtration, protective clothing, and for certain medical applications.^{10,11} Woo et al.¹² reported a polycarbonate/epoxy SIPN blend that exhibited improved processing performance and better mechanical properties.

SIPNs are composed of a thermoplastic polymer that is combined with thermoset monomer precursors that are then cured. These SIPNs resemble sequentially generated full IPNs that are prepared starting with polymer I, which is already crosslinked, and then another monomer, a crosslinker, and an activator are swollen into polymer network I and polymerized *in situ*. The crosslinking behavior and stoichiometry of the added monomer determine the morphology, miscibility and, therefore, the properties of both sequential IPNs and thermoplastic/thermoset SIPNs. However, there are some important differences. Usually, a high degree of crosslinking in sequential IPNs is important because it leads to small domains with large amounts of interphase. Thus, some phase-mixing occurs in many sequential IPN cases. The degree of conversion of IPN components at the onset of phase separation depends on the crosslinking level of each network. In many cases, the sequential IPN formation might have mainly been caused by the interphase mixing rather than by thermodynamic changes.^{13,14} In SIPNs made from performed thermoplastics and thermosetting precursors, the thermoset crosslinks may decrease the thermoplastic/thermoset miscibility.²⁻⁴ When crosslinking monomers cure within a swollen thermoplastic, phase separation is usually driven by the decrease in the entropy of mixing, which raises the free energy of the system. Thermoplastic chains can also lose conformational freedom as the thermoset network forms, creating another unfavorable entropy contribution. Thus, successful SIPN formation might be driven by a favorable mixing of the thermoplastic with the thermoset monomer precursors (enthalpy, entropy), the heat of crosslinking (enthalpy), and by crosslinking occurring faster than phase separation (kinetic). How can crosslinking of the blended prerresin components be controlled to occur before phase separation can occur? So far, a limited number of detailed studies on this topic have been published.¹⁵

Recently, we have been investigating the feasibility of introducing from 5 to 15% by weight of a single thermosetting liquid prerresin (chosen from epoxy, vinyl ester, and several isocyanate

classes) into unplasticized, linear high molecular-weight PVC at temperatures below the PVC melting point followed by curing to crosslink the thermoset resin matrix within the PVC.¹⁶⁻¹⁸ Improvements in the mechanical properties due to the SIPN formation occurred. The inclusion of a thermoset network containing functional polar groups within PVC could improve PVC adhesion to fibers or fillers.

The approach, described above, attempts to achieve some dissolution of thermoset precursor molecules into PVC followed by crosslinking before phase separation can occur. When a small thermoset precursor concentration is dissolved in PVC, the rate of gel formation is decreased by this dilution, becoming slower than in pure thermoset cures. This will delay phase separation while generating a less highly crosslinked thermoset network with longer average segment lengths between crosslinks. These more flexible networks should be more compatible with PVC and favor interpenetration. SIPN formation was evident in PVC/thermoset blends based on their mechanical and viscoelastic properties^{17,18} carried out in our laboratory and the thermoset dilution effect played a key role in SIPN formation.

The present article focuses on further characterizing the effect of crosslinking behavior on mechanical and viscoelastic properties of PVC/thermoset SIPNs made from (1) PVC/methylene bisphenyl diisocyanate (MDI)/polytriol, (2) PVC/oligomeric MDI isocyanates (PAPI)/polytriol, or (3) PVC/toluenediisocyanate (TDI)-prepolymer/polytriol components. It should be noted that Klempner et al. have described PVC/polyurethane SIPNs prepared from poly(ϵ -caprolactone diol) and poly(oxypropylene diol) mixtures. The former is miscible, and the latter is immiscible with PVC. The diols were cured MDI in the presence of PVC to give materials with microheterogeneous morphologies that were studied as sound absorbers.

EXPERIMENTAL

Materials

The PVC (PVC-5225, trade name) was supplied by Condea Vista Inc. as small particles (150- μ m average particle diameter). $\eta_{sp} = 1.56$ (cyclohexanone, 25°C), $M_n = 53,000$, $M_w = 98,000$. The calculated void volume was about 0.23 cm³/g, corresponding to a void percentage of about 30%.

ISONATE 1143L and PAPI 2027 (trade names) were supplied by Dow Chemical Co. ISONATE 1143L was methylene bis-phenyl diisocyanate (MDI) (isocyanate equiv. wt. 144.5, functionality 2.7, $\eta = 0.04$ (Pa-s) at 25°C) and PAPI 2027 was an oligomeric MDI isocyanate (isocyanate equiv. wt. 134, functionality 2.7, $\eta = 0.18$ (Pa-s) at 25°C). An isocyanate copolymer of toluene diisocyanate (TDI) and poly(tetramethylene ether) glycol (PTMEG) (PET-75D, trade name), with an NCO content of 9.15%, was supplied by Air Products and Chemicals, Inc. A polyether polyol (VORANOL 234-630, trade name) was supplied by Dow Chemical Co. VORANOL 234-630 was a trimethylol propane-based polyol structure with a molecular weight of 267 and an average functionality of 3.

Preparation of PVC/Isocyanate/Triol SIPN Blends

PVC/isocyanate/triol SIPNs were made from PVC 5225/PAPI 2027/VORANOL 234-630, PVC5225/PVC/ISONATE 1143L/VORANOL 234-630, and PVC5225/PET-75D/VORANOL 234-630. In each of these three series, the weight ratio of PVC/isocyanate was held constant at 90/10, but OH/NCO ratios of 0.25, 0.45, 0.65, 0.85, 1.0 were used for all three combinations, respectively, to give a total of 15 blends. The weight of the triol used to react with 100 g isocyanate at each given OH/NCO ratio was calculated according to the literature.²⁰

PAPI 2027 was heated at 65–75°C to reduce its viscosity and permit easy handling. PET-75D was heated at 80–90°C for about 1 h for the same reasons. The isocyanates and polytriol were degassed and dried at 55°C and 10 mmHg for 1 h to remove moisture before use. The weighed isocyanate and polytriol were thoroughly mixed at room temperature and then poured into a preweighed quantity of the PVC powder. This combination was premixed at room temperature in a solid mixer using high-speed stirring (1000 rpm) for 1–2 min, followed by continuous blending on a two-roll mill at 50°C until it mixed completely. Then the blend was pressed into an aluminum mold and cured at 155°C on a hydraulic press machine under 250–320 atm for 1 h.

A pure PVC-5225 sample was also hot pressed at 155°C and at about 320 atm for about 1 h to compare its properties with those of the SIPNs.

Mechanical Property Tests

Tensile tests were performed using a Zwick 1435 Universal test machine according to ASTM

D638M. Tensile strengths and elongations at break were measured at room temperature. The loadcell was set at 5000 kN, the crosshead speed at 10 mm/min, and the gauge at 25 mm. Three to five separate specimens were measured and the values were averaged.

Three-point bending tests were conducted at room temperature on a Zwick 1435 Universal test machine, according to ASTM D790M-I. The loadcell was set at 500 N, the span at 30 mm, and the test speed at 5 mm/min. Flexural properties of each composition were determined from the average value of five to seven test specimens.

Izod impact strengths were measured at room temperature on a TMI 45-02 impact tester according to ASTM D256 using a 1-lb pendulum weight. Five to seven SIPN specimens were tested and the average value was used.

Dynamic Mechanical Thermal Analysis

Storage moduli, E' , the loss moduli, E'' , and loss factor ($\tan \delta$) were determined in the bending mode using a Polymer Laboratories DMA MK3 instrument. A dual-level bending mode was employed. Small amplitude bending oscillations (both 1 and 10 Hz) were used at a gap setting of 14.00 mm. A heating rate of 2°C/min. was employed from –50 to +170°C. Test specimens were approximately about 1–2 mm thick, 6-mm wide, and 45 mm long.

RESULTS AND DISCUSSION

Mechanical Properties of PVC/Isocyanate/Triol SIPNs

Tensile and impact strengths and elongations at break for the three classes of PVC/isocyanate/triol blends are summarized in Table I. Flexural strengths and flexural moduli, and deflections at maximum loading (three-point bending) for these same samples are summarized in Table II.

The tensile and flexural strengths and the flexural moduli of the blends were greater than those of PVC in all cases. In most cases, the elongations at break, maximum bending deflections, and impact strengths also increased. In some cases the properties improved dramatically when small amounts of isocyanate crosslinked networks were created in PVC. The following examples illustrate this point. Blending PAPI/triol (10% PAPI by wt. and a OH/NCO ratio of 0.75) into PVC increased the cured blend's tensile strength to 40.1 vs. 15

Table I Tensile Properties and Izod Impact Strength of PVC/Isocyanate/Triol SIPNs

Blend Sample	PVC/Isocyanate/Triol Composition (Weight Ratio)	OH/NCO Equivalent Ratio	Tensile Strength ^a (MPa)	Elongation at Break (%)	Izod Impact Strength ^b (J/m)
PVC ^c	100/0	0	15.9 ± 3.7	0.1	21.9 ± 4.4
PVC/PAPI/triol	90/10/1.1	0.25	23.2 ± 4.3	0.7 ± 0.1	27.8 ± 6.5
	90/10/2.2	0.5	31.3 ± 4.1	0.4 ± 0.1	36.9 ± 5.4
	90/10/3.3	0.75	40.1 ± 3.6	0.2	26.2 ± 2.3
	90/10/4.4	1	33.9 ± 4.9	0.2	24.9 ± 1.9
PVC/MDI/triol	90/10/1.1	0.25	26.5 ± 4.6	0.6 ± 0.3	27.3 ± 7.7
	90/10/1.98	0.45	28.4 ± 1.7	0.2	35.8 ± 4.8
	90/10/2.86	0.65	29.7 ± 5.7	0.2	26.9 ± 2.4
	90/10/3.7	0.85	29.1 ± 1.1	0.2	26.1 ± 4.3
PVC/TDI/triol	90/10/4.4	1	29.1 ± 3.6	0.2	25.3 ± 3.5
	90/10/0.33	0.25	22.8 ± 5.8	0.2	23.0 ± 4.2
	90/10/0.65	0.5	20.1 ± 2.2	0.6 ± 0.1	25.6 ± 3.3
	90/10/0.98	0.75	19.3 ± 1.8	0.9 ± 0.1	21.3 ± 1.6
	90/10/1.3	1	16.8 ± 4.5	1.1 ± 0.2	20.5 ± 2.4

^a Tensile test (ASTM D638M). Loadcell: 5 kN, Test speed: 10 mm/min, gauge: 25 mm.

^b Izod impact test (ASTM D256). Hammer: 1 lb Izod.

^c Pure PVC samples were molded at 155°C.

MPa for PVC. Blending MDI/triol (10% MDI and a OH/NCO ratio of 0.45) into PVC and curing increased the impact strength from 21.9 J/m for PVC to 35.8 J/m for the resulting SIPN. The PVC/PAPI/triol SIPN (10% PAPI and a OH/NCO ratio of 0.5) exhibited a flexural strength of 49.7 vs.

26.5 MPa for PVC. Thus, SIPN formation enhanced the mechanical strengths.

Crosslinking Effect on Mechanical Properties

The effects of crosslinking on the tensile, impact, and flexural strengths of PVC/isocyanate/polyt-

Table II Flexural Properties of PVC/Isocyanate/Triol SIPNs

Blend Sample	PVC/Isocyanate/Triol Composition (Weight Ratio)	OH/NCO Equivalent Ratio	Flexural Strength ^a (MPa)	Flexural Modulus (GPa)	Deflection at Maximum Load ^b (mm)
PVC ^c	100/0	0	26.5 ± 5	1.8 ± 0	0.5 ± 0.1
PVC/PAPI/triol	90/10/1.1	0.25	45.8 ± 1.7	2.2 ± .002	0.8 ± 0.1
	90/10/2.2	0.5	49.7 ± 1.8	2.9 ± 0.05	0.6
	90/10/3.3	0.75	49.2 ± 6.7	2.4 ± 0.4	0.8 ± 0.1
	90/10/4.4	1	42.6 ± 0.4	2.1 ± 0.2	0.7 ± 0.1
PVC/MDI/triol	90/10/1.1	0.25	45.3 ± 4.3	2.4 ± 0.2	0.8 ± 0.1
	90/10/1.98	0.45	46.3 ± 1.8	2.4 ± 0.7	0.8 ± 0.1
	90/10/2.86	0.65	43.8 ± 1.4	2.4 ± 0.1	0.8 ± 0.1
	90/10/3.7	0.85	42.1 ± 3.5	2.4 ± 0.3	0.7
PVC/TDI/triol	90/10/4.4	1	37.2 ± 2.1	2.3 ± 0.05	0.6
	90/10/0.33	0.25	44.4 ± 6.5	1.8 ± 0.2	1.0 ± 0.1
	90/10/0.65	0.5	45.8 ± 5.3	2.1 ± 0.5	1.1 ± 0.2
	90/10/0.98	0.75	38.6 ± 2.1	1.8 ± 0.4	1.1 ± 0.2
	90/10/1.3	1	31.2 ± 1.7	1.7 ± 0.1	0.7

^a Three-point flexural test (ASTM D790). Loadcell: 500 N, test speed: 5 mm/min, span: 30 mm.

^b Midspan deflection at maximum loading.

^c Pure PVC samples were molded at 145°C.

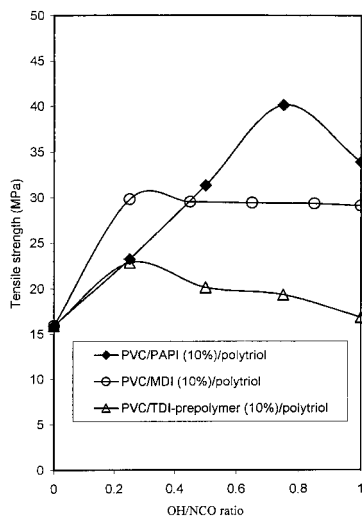


Figure 1 Effect of the OH/NCO ratio on the tensile strength of PVC/isocyanate/polytriol SIPNs.

riol SIPNs were examined by varying isocyanate/polytriol hydroxyl stoichiometry in a way that increased the OH/NCO ratio from 0 to 1. This change would produce increasingly crosslinked polyurethanes. Three different types of isocyanates (PAPI, MDI, and TDI) were reacted with a triol, and the OH/NCO ratio was varied within each system while holding the weight of isocyanate constant at a 10%. The crosslink density, unfortunately, is not the only variable. As the OH/NCO ratio rises increasingly, more triol is added so that the weight fraction of PVC decreases a small amount. The tensile, impact, and flexural strengths of these three classes of blends are shown in Figures 1, 2, and 3, respectively.

Figure 1 shows the tensile strengths of the three PVC/isocyanate/polytriol systems upon varying the OH/NCO ratio. The tensile strengths of PVC/PAPI/triol system increased from 15.9 to 40.1 MPa as OH/NCO ratio increased from 0 to 0.75, but then dropped off. The tensile strengths of the PVC/MDI/triol system changed very little as the OH/NCO ratio changed from 0.25 to 1. However, a large initial increase from 15.9 to 29 MPa took place when the OH/NCO ratio increased from 0 to 0.25. In contrast, the PVC/TDI/polytriol system gave the smallest tensile strength enhancements among the three isocyanate/polytriol systems when compared over the same OH/NCO ratio range. The PVC/TDI/polytriol blends gave a maximum increase in tensile strength to 22.8 MPa at a 0.25 OH/NCO ratio, but the tensile strengths decreased thereafter as the OH/NCO ratio increased from 0.25 to 1.0.

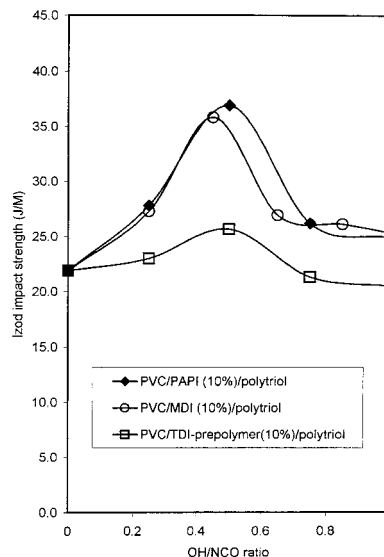


Figure 2 Effect of the OH/NCO ratio on the impact strength of PVC/isocyanate/polytriol SIPNs.

The maximum increase in impact strength for all classes of PVC/isocyanate/triol blends occurred at an OH/NCO ratio of 0.45–0.5. This is observed in Figure 2. Both PVC/PAPI/triol and PVC/MDI/triol systems gave much larger impact strength enhancements than were observed in the PVC/TDI/triol system when compared at the same OH/NCO ratios. A decrease in impact strength was observed for all three of these SIPN classes when OH/NCO ratio increased above 0.5.

The flexural strengths increased from 26.5 MPa for PVC to 45.8, 45.3, and 44.4 MPa at a 0.25

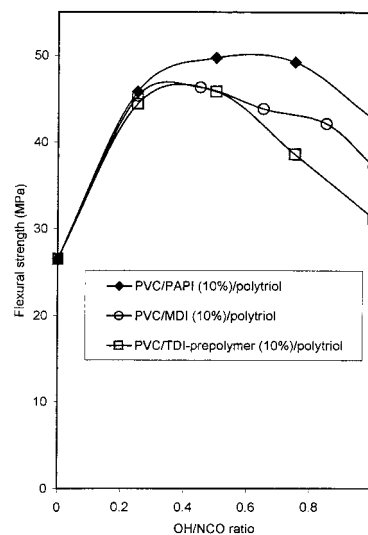


Figure 3 Effect of the OH/NCO ratio on the flexural strength of PVC/isocyanate/polytriol SIPNs.

OH/NCO ratio for the PVC/PAPI/triol, PVC/MDI/triol, and PVC/TDI/triol blends, respectively (see Fig. 3). The flexural strengths of the PVC/PAPI/triol blends only slightly increased as the OH/NCO ratio increased from 0.25 to 0.75, and then decreased when the OH/NCO ratio was further raised from 0.75 to 1.0. A modest flexural strength decrease for the PVC/MDI/triol blends and a big decrease for the PVC/TDI/triol were observed upon increasing the OH/NCO ratio from 0.25 to 1.0.

Crosslink density can contribute to the formation and development of properties in SIPNs. Attempts were made to observe this contribution by examining properties as a function of the OH/NCO ratio when holding the amount of isocyanate constant. As more triol is added, the crosslink density should go up as more urethane functions form. For all three isocyanate/triol systems, a greater increase in tensile strength occurred as the OH/NCO ratio went from 0 to 0.5 than when it increased 0.5 to 1.0 (see Fig. 1).

Increases in impact strength were only observed when the OH/NCO ratio went from 0 to 0.5 for all three systems (see Fig. 2). Again, the enhancement of flexural strength vs. the change in OH/NCO ratio was most pronounced as this ratio increased from 0 to 0.25 (see Fig. 3). Several effects are operating including crosslink density changes, a decrease in PVC weight fraction, an increase in the triol weight fraction as OH/NCO goes up, and the different solubilities and compatibilities that are present among the blend precursors as the OH/NCO ratio varies. Another important factor is that more flexible thermoset segments exist between crosslinks that are more distant. These segments are more compatible with PVC.^{16–18}

The isocyanate functional group content of the thermoset precursor also appears to be an important factor in the SIPN formation. Both PAPI and MDI used in this study contained 30% by weight NCO content, and these two isocyanates gave much bigger improvements in the three mechanical strengths than TDI produced. However, TDI contained only a 9.7% by weight NCO content. Both PAPI/triol and MDI/triol systems exhibited mechanical strength (e.g., tensile and flexural) enhancements over a wider OH/NCO range. Greater isocyanate group content should increase solubility in PVC, a favorable factor for generating PVC/polyurethane SIPNs. Furthermore, higher isocyanate content should enhance the probability of reaction with the polytriol to generate urethane links after these components have

been diluted in PVC. Therefore, the physical structure of the SIPNs and their resulting mechanical properties varied when changing both the NCO content (e.g., weight fraction of isocyanate functional groups in the blend) and the crosslink density. Low overall weight fractions of an isocyanate component, which has a high isocyanate functional group content, appear favorable for generating the SIPN structure within PVC. However, the details of structure vs. composition and effects on mechanical properties are complex, and remain largely unknown.

Dissipation Factor ($\tan \delta$) of PVC/Isocyanate/Triol SIPNs

Plots of the bending dissipation factor ($\tan \delta$) vs. temperature at 10 Hz for all three of the groups of SIPN blends (PVC/PAPI/triol, PVC/MDI/triol, and PVC/TDI/triol) are shown in Figures 4 through 6, along with that of pure PVC that had been heated to 155°C. The $\tan \delta$ peak temperatures (at both 1 and 10 Hz) for all three groups of SIPN blend classes are listed in Table III. The effect of varying the OH/NCO mol ratios ratio (from 0.25 to 1.0) for each type of PVC/isocyanate/polytriol blends is illustrated in these figures and in Table III.

PVC exhibits low $\tan \delta$ values in the glass region (-50 to $\sim 70^\circ\text{C}$). Then a sharp rise in $\tan \delta$ occurs as major segmental motions are activated between 70 to 95°C . At 10 Hz, the $\tan \delta$ peak occurred at 93°C . This is higher than the

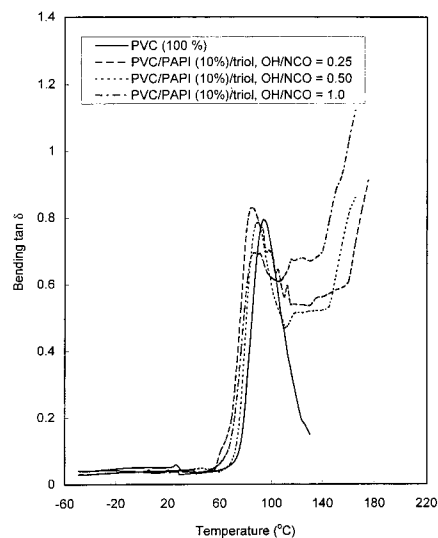


Figure 4 Dissipation factor ($\tan \delta$) vs. temperature in PVC/PAPI(10%)/polytriol SIPN blends at 10.0 Hz at a heating rate of $2^\circ\text{C}/\text{min}$.

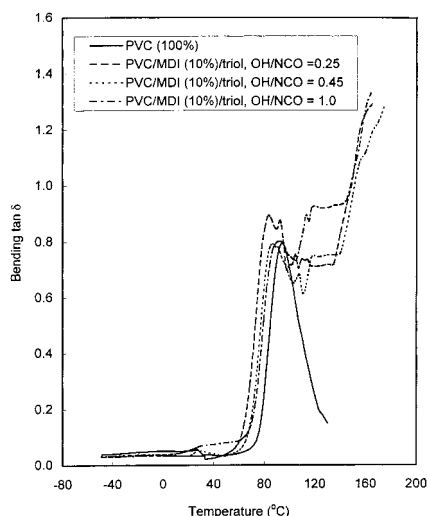


Figure 5 Dissipation factor ($\tan \delta$) vs. temperature in PVC/MDI(10%)/polytriol SIPN blends at 10 Hz at a heating rate of $2^\circ\text{C}/\text{min}$.

literature value for the PVC glass transition temperature of 71°C .²¹ This might be expected, because (1) the PVC had been heated for 1 h at 145°C to mimic the PVC exposure in the SIPN samples, (2) $\tan \delta$ curves give poorer estimates of T_g than those given by the point of maximum slope in E' vs. temperature plots, and (3) the high frequency used in the DMTA measurements. At higher temperatures, $\tan \delta$ values drop with increasing molecular motion.

The $\tan \delta$ curves of these three classes of SIPNs exhibited maxima at temperatures lower than that for PVC (e.g., $<93^\circ\text{C}$) at all of the OH/NCO ratios. This suggests that PVC is plasticized by the isocyanate crosslinked networks in all three blend classes. Perhaps greater disorder or more free volume occurs in these blends, which lowers the T_g . In addition, all three of PVC/polyurethane blends exhibit a complex plateau region at higher temperature. Then the $\tan \delta$ values exhibit a sharp rise that continues between 150 – 170°C until the limiting temperature of the experiments. PVC/polyurethane regions bound tightly enough within a network could give this behavior. Also, viscous flow/flow energy dissipation cannot operate to lower the value of $\tan \delta$. Thus, to various degrees, PVC is both plasticized (which lowers the temperature of the $\tan \delta$ maxima) and entangled (partially locked) in place, which results in the higher temperature $\tan \delta$ plateau curves. However, phase separation into fairly large PVC and predominantly crosslinked polyurethane domains does not explain the $\tan \delta$ curves or many of the mechanical property observations. Thus, substan-

tial SIPN type phases seem to be present in these blends.

The $\tan \delta$ peak temperatures at both 1 and 10 Hz for all three groups of SIPN blends are lower than those for PVC at all of the OH/NCO ratios. Lowering of the damping peak temperature and increasing the damping peak height are both indicative of molecular mixing taking place in the polymer blends.^{22,23} A crosslinked isocyanate structure, which is both swollen and entangled with PVC chains, would be generated if a molecular level mixing takes place in the precured PVC/isocyanate/polytriol blend and is maintained after the crosslinking is completed. Enthalpic interactions between the thermoset segments and PVC segments (hetero-contact) of the final SIPN could be less favorable (less exothermic) than pure PVC–PVC or thermoset–thermoset segmental (homo-contact) interactions. Therefore, free volume should increase, and the segments are less tightly held together. In other words, the dilute isocyanate matrix plasticizes the PVC while also entangling it. Therefore, large segmental motions are activated in the SIPN blends at a lower temperature than in pure PVC, despite the fact that the crosslinked thermoset, when formed as pure phase, would have a higher T_g . A single T_g value for each blend that is lower than the T_g for PVC is important evidence that the SIPNs were formed. In conclusion, it appears that substantial amounts of SIPN type phases must be present in the three classes of blends.

There was no general correlation between the OH/NCO ratio and the $\tan \delta$ peak temperature in

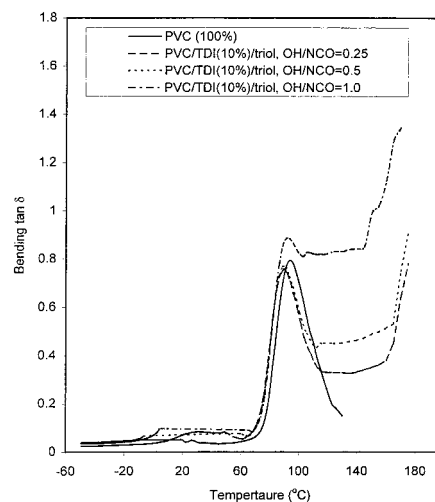


Figure 6 Dissipation factor ($\tan \delta$) vs. temperature in PVC/TDI-prepolymer(10%)/polytriol SIPN blends at 10 Hz at a heating rate of $2^\circ\text{C}/\text{min}$.

Table III Tan δ Peak Temperatures for PVC/Isocyanate/Triol SIPNs at 1 and 10 Hz

Blend Sample ^a	OH/NCO Ratio (Mol Ratio)	Tan δ Peak Temp. at 1 Hz (°C)	Tan δ Peak ΔT^b at 1 Hz (°C)	Tan δ Peak Temp. at 10 Hz (°C)	Tan δ Peak ΔT^b at 10 Hz (°C)
PVC	0	87.4	0	93.4	0
PVC/PAPI/triol	0.25	79.9	-7.5	83.6	-9.8
	0.5	83.4	-4	89.3	-4.1
	0.75	83.1	-4.3	86.9	-6.5
	1	73.6	-13.8	79.9	-13.5
PVC/MDI/triol	0.25	76.6	-10.8	82.8	-10.6
	0.45	80.7	-6.7	86.4	-7
	0.65	82.1	-5.3	88.3	-5.1
	0.85	83.2	-4.2	89.4	-4
PVC/TDI/triol	1	84.4	-3	89.9	-3.5
	0.25	83.6	-3.8	89.7	-3.7
	0.5	82.6	-4.8	88.7	-4.7
	0.75	84.4	-3	90.3	-3.1
	1	85.2	-2.2	91.1	-2.3

^a Weight ratio of PVC/Isocyanate is 90/10 for each PVC/isocyanate/triol blend.

^b $\Delta T_{\tan \delta \text{ peak}}$ is the difference in temperature between the tan δ peak temperature of pure PVC and that of the SIPN blend at the frequency given.

these three sets of blends. This suggests that the lowering in the blends' glass transition temperature (e.g., one measure of tan δ peak temperature) might have been caused by both the interphase mixing and thermodynamic changes. The crosslinking "locks in" some degree of the original, preure compatibility between the thermoset monomers and PVC when crosslinking is faster than phase separation. Therefore, the SIPNs can be considered to be in a state of quasi-equilibrium with a molecular level of mixing. The cured SIPN blends have a higher degree of intermixing than would exist at equilibrium because of kinetic control. PVC becomes trapped in the dilute matrix during curing before phase separation could reach its equilibrium position.

Storage Moduli, E' , and Loss Moduli, E'' , of PVC/Isocyanate/Triol SIPNs

Plots of the bending storage moduli (E') and bending loss moduli (E'') vs. temperature at 10 Hz for the PVC/PAPI/triol blends are shown in Figure 7, together with those of pure PVC. Similar plots were obtained for the PVC/MDI/triol and PVC/TDI/triol blends. The temperatures at which the maximum slope of the E' vs. temperature plot occurs (one measure of T_g) are given in Table IV, along with the E'' peak temperatures, for all three SIPN groups.

PVC exhibited high storage moduli (E') values (>750 MPa) at low temperatures, followed by a decrease in modulus of several decades in the vicinity of 65–85°C. Defining T_g at the point of the maximum slope on the E' versus temperature curves leads to a T_g of about 81.2°C at 10 Hz for PVC. Defining T_g as the peak temperature in the loss modulus (E'') vs. temperature curve gives a

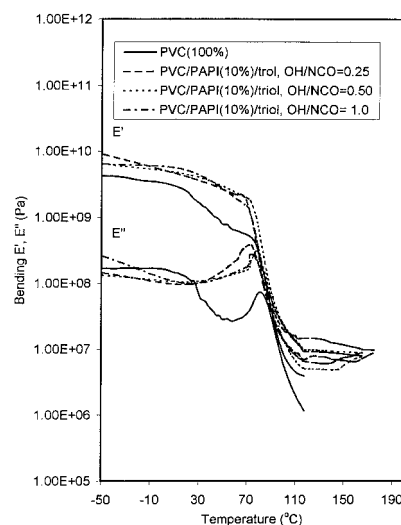


Figure 7 Temperature dependence of the dynamic storage moduli, E' , and the dynamic loss moduli, E'' , for PVC/PAPI(10%)/polytriol SIPN blends at 10 Hz and at a heating rate of 2°C/min.

Table IV The Temperatures at the Onset of the Maximum Slope of the Storage Moduli, E' , vs. Temperature Plots and the Peak Temperatures in the Loss Moduli, E'' , vs. Temperature Plots

Blend Sample ^a	OH/NCO Ratio (Mol Ratio)	$T_{\text{at } E' \text{ max.slope}}$ ^b at 10 Hz (°C)	$\Delta T_{\text{at } E' \text{ max.slope}}$ ^c at 10 Hz (°C)	$T_{E'' \text{ peak}}$ ^d at 10 Hz (°C)	$\Delta T_{E'' \text{ peak}}$ ^e at 10 Hz (°C)
PVC	0	81.2	0	82.5	0
PVC/PAPI/triol	0.25	70.1	-11.1	71.1	-11.4
	0.5	75.3	5.9	80.7	-1.8
	0.75	77.5	-3.7	81.4	-1.1
	1	74.1	-7.1	79.1	-3.4
PVC/MDI/triol	0.25	65.2	-16	67.3	-15.2
	0.45	69.8	-11.4	72.6	-9.9
	0.65	70.2	-11	73.9	-8.6
	0.85	71.8	-9.4	74.7	-7.8
	1	72.5	-8.7	76.1	-6.4
PVC/TDI/triol	0.25	60.5	-20.7	75.7	-6.8
	0.5	62.7	-18.5	77.4	-5.1
	0.75	63.9	-17.3	78.1	-4.4
	1	69.7	-12.4	79.8	-2.7

^a Weight ratio of PVC/Isocyanate is 90/10 for each PVC/isocyanate/triol blend.

^b $T_{\text{at } E' \text{ max.slope}}$ is the temperature at the onset of the maximum slope in the E' vs. temperature plots of the samples.

^c $\Delta T_{\text{at } E' \text{ max.slope}}$ is the difference in this onset of maximum slope temperature between the SIPN blend and PVC.

^d $T_{E'' \text{ peak}}$ is the peak temperature of the E'' vs. temperature plots.

^e $\Delta T_{E'' \text{ peak}}$ is the difference between the E'' peak temperatures of the SIPN blend and PVC.

PVC T_g value of 82.5°C at 10 Hz. At higher temperatures (above 100°C), both moduli are low as PVC becomes viscous. All the PVC samples also showed a decrease in both storage and loss moduli values well before the T_g region (~ 20 to 40°C).

Almost all of the blends exhibited the major sharp drop in their storage modulus, E' , at a temperature lower than the 81°C value for PVC (Fig. 7 and Table IV summarizes data for all the classes of blends). These results are accord with the $\tan \delta$ peak temperature measurements (at either 1 or 10 Hz), which were lower for the blends than for PVC (Table III). Both measurements provide evidence that isocyanate permeation within PVC introduces free volume. A similar conclusion is reached by examining the loss modulus, E'' , curves. Every blend exhibited a single distinct peak in the E'' vs. temperature curves at all of the OH/NCO ratios (Fig. 7, Table IV). Furthermore, all the blends exhibited peak values of E'' at lower temperatures than were given by PVC samples that had been exposed to the same processing temperatures. These E'' peak temperature values at 10 Hz for all three classes of blends are presented in Table IV. The E'' peak temperatures (at 10 Hz) can be used to define the T_g values for the respective PVC/thermoset blends. It is clear by examining Figure 7 and Tables III–IV that isocyanate–PVC interactions have lowered the T_g of substantial weight frac-

tions (if heterogeneous) of each of these blends. Thus, the E'' plots are consistent with the $\tan \delta$ and E' vs. temperature behavior.

The Question of Grafting. Does It Effect Morphology and Properties?

Grafting is known to have a major effect on both the morphology and properties of IPNs.²⁴ Thus, the question of whether or not the polyurethane network becomes grafted or not to PVC in these SIPNs is important. Only a portion of the PVC can be extracted in refluxing THF, and this fraction increased with time up to 48 h. However, tight entanglement of the PVC might prevent such extraction over long periods. Therefore, a low molecular weight fraction of PVC (2000–4000 mol. Wt., ~ 50 DP) was used to make model samples of the PAPI, MDI, and TDI SIPNs of PVC by the same method described in the experimental section. If grafting had occurred, then not all the PVC would be extracted. However, this low molecular weight PVC could not become as tightly entangled as would the higher molecular weight PVC. Extraction of these samples appeared to almost completely remove the original PVC. A tiny amount remained. The thermal treatment at 145°C causes some HCl elimination and traces of residue. Thus, no strong evidence for grafting exists in these low molecular weight PVC SIPNs.

While this does not definitively rule out the presence of any grafting in the SIPNs made from the commercial PVC, it suggests that grafting is not a significant contributor in these materials.

CONCLUSIONS

Semiinterpenetrating polymer networks (SIPNs) composed of PVC and diluted crosslinked isocyanate networks were made by introducing small quantities of the isocyanate/polytriol components (10% isocyanate by weight and different OH/NCO mol ratios) into small-sized, solid, porous PVC particles followed by low-temperature roll milling (50°C) and hot-press molding at 155°C. The mechanical properties improved when isocyanate crosslinked networks were created within PVC. The strength increments were usually greater when going from 0 to 0.25 OH/NCO mol ratios than when going from 0.25 to 1.0 OH/NCO mol ratios. One possible interpretation is that more flexible and dilute crosslinked polyurethane networks seem to be more compatible with PVC, and this promotes SIPN formation. The mechanical tests indicated that functional group content of the isocyanate is also an important factor in the SIPN formation. A low weight fraction of the isocyanate component that contains a higher content of NCO functional groups appears to be favorable for generating the SIPN structure within PVC. A substantial amount of an SIPN-like phase must be present in the PVC/isocyanate blends according to DMTA studies. These SIPN blends can be considered as the kinetic product of crosslinking reactions that occur before phase separation can proceed.

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