

***Joined and Sequential Interpenetrating Polymer
Networks Based on Poly(dimethylsiloxane)***

INTRODUCTION

A polymer blend may be broadly defined as an intimate mixture of two kinds of polymer molecules. Polymers I and II may be chemically joined together, as in the case of block and graft copolymers, or merely lie in juxtaposition, as in the case of the mechanical blends. The original sequential interpenetrating polymer networks (IPNs), a class of graft copolymers, were synthesized by forming a network of polymer I, swelling in monomer II plus crosslinker, and polymerizing in situ. Sequential IPNs have both polymers in network form, with the crosslink sites significantly more numerous than the grafted sites, so that for certain simple purposes the IPNs can be modeled by assuming grafting to be negligible. Another way of stating this is that virtually all crosslinks are intramolecular.

However, the case where all the crosslinks ideally occur through intermolecular joining also arouses interest. Two such cases already known include the castable polyesters^{1,2} and the graft copolymers of Bamford.³ Figure 1 compares the idealized structures of joined and sequential IPNs.⁴⁻⁶ The present note will cover synthesis and modulus-temperature studies on joined and sequential IPNs based on poly(dimethylsiloxane) (PDMS) and polystyrene (PS) or poly(methyl methacrylate) (PMMA). In the joined IPN portion of the study, the vinyl content of the PDMS will be treated as a variable, to control the extent of intermolecular crosslinking.

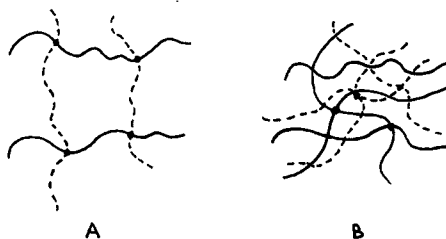


Fig. 1. Comparison of idealized joined and sequential IPN structures: (A) joined; (B) sequential; (—) polymer I; (---) polymer II; (●) crosslink site.

EXPERIMENTAL

Table I lists the compositions of the various PDMS elastomers that were used in the IPN syntheses. Throughout this paper, PDMS, suffixed by the manufacturer's number, will be used to designate these materials.

Sequential IPNs of PDMS 418-81, with both PMMA and PS, were prepared by swelling the plastic monomer divinyl benzene (0.5% by weight, based on monomer) and benzoyl peroxide (1% by weight) into crosslinked samples of the elastomer, which had

TABLE I
Commercial PDMS Elastomer used in IPN Preparation

| Supplier | Number | Diphenyl, mole-% | Vinyl, mole-% |
|----------|----------|------------------|---------------|
| GE | 418-88 | 5.3 | 0.0 |
| GE | 418-81 | 5.3 | 0.2 |
| GE | DSRE5701 | 0.0 | 0.6 |

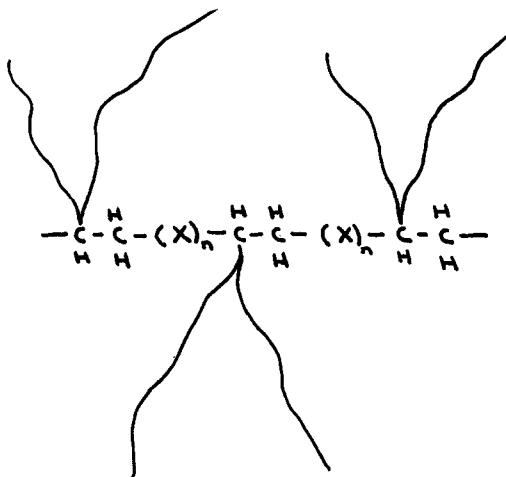


Fig. 2. Another way of visualizing the bonding mode of the present joined IPNs. $\text{CH}=\text{CH}_2$, poly(vinyl methylsiloxane) before crosslinking, emphasizing vinyl portion. Added acrylic group represented by X, where n has values in the range 10–100.

been previously press molded with dicumyl peroxide. The swollen systems were then stored overnight in a desiccator to attain equilibrium, and then charged to molds and pressed to 2500 psi at 100°C for 1 hr, simultaneously polymerizing and crosslinking monomer II.

Joined IPNs of the PDMS/PMMA system were prepared from PDMS of 0.0, 0.2, and 0.6% vinyl. For these reactions, uncrosslinked PDMS samples were swollen with methyl methacrylate monomer and initiator; the resulting solution was press molded as above. Compositions of all samples were calculated from elemental analyses provided by Dr. George Roberston, Florham Park, New Jersey.

Figure 2 illustrates another, more pragmatic way of visualizing the proposed joined IPN structure. Addition of an acrylic or other double bond-containing monomer, II, before crosslinking tends to space the polymer-I chains with polymer-II chains. For the present midrange preparations, polymer-II chains are estimated to contain 10 to 100 mers, based on PDMS vinyl content and overall composition. The structures in Figure 2 suggest an interesting nomenclature. If $n = 0$, the polymer might be considered as poly[vinyl poly(dimethylsiloxane)], which emphasizes the mode of crosslinking. With $n > 0$, the material might be considered as a random copolymer of the added monomer and vinyl poly(dimethylsiloxane).

A Gehman torsion apparatus⁷ was used to measure three times the shear modulus at 10 sec, $3G(10)$, as a function of temperature from -150°C to $+150^\circ\text{C}$. A liquid-nitrogen cooled-air bath was used for work below 0°C . A heat-up rate of $1^\circ\text{C}/\text{min}$ was used in all runs. Modulus work was done on both the sequential and joined IPNs.

RESULTS

All of the IPNs synthesized exhibited a greater or lesser extent of opacity at room temperature. The sequential materials had a translucent blue-white color, and the joined IPNs were opaque white. This occurrence of opacity is evidence of a multiphase structure,⁸ and the difference in appearance indicates that the joined phase domains are probably larger than the corresponding sequential phase domains.

Log $3G(10)$ versus temperature is plotted in Figures 3–5 for the several samples investigated. These graphs all exhibit two glass transitions, one for the plastic phase and one for the rubber phase. This behavior emphasizes the phase separation characteristics

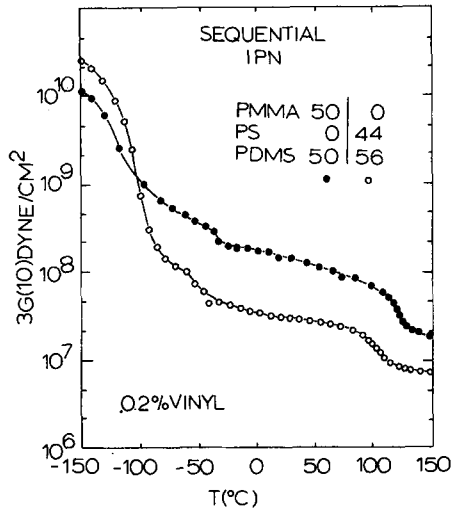


Fig. 3. Modulus-temperature curves for PDMS/PS and PDMS/PMMA sequential IPNs prepared from PDMS 418-81. Note presence of two glass transitions near -120°C and $+100^{\circ}\text{C}$ for PDMS and PS, respectively. Although crystallinity is suppressed by the addition of phenyl groups to the PDMS, a slight melting transition is observed near -50°C . As with all true sequential IPNs, a normal rubber plateau is observed above the higher glass transition.

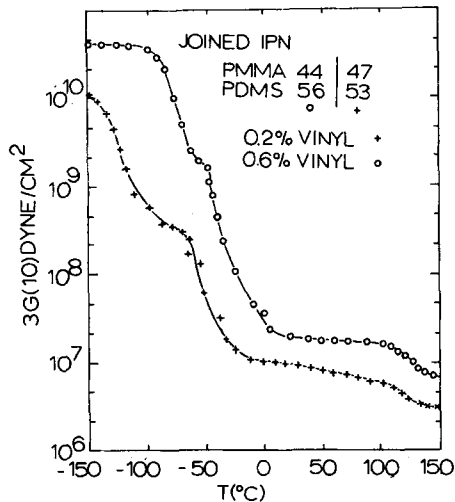


Fig. 4. Modulus-temperature curves for joined IPNs of PDMS/PMMA, containing differing vinyl contents. Again, two T_g values and a T_m are observed. The joined IPNs are significantly softer and more elastic than the counterpart sequential IPNs, 500% extension being easily attained.

TABLE II
Properties of Homopolymers and Sequential IPNs

| | $T_M, ^\circ\text{C}$ | $T_g, ^\circ\text{C}$ | $\delta, (\text{cal/cc})^{1/2}$ | $I.N.^a$ |
|--|-----------------------|-----------------------|---------------------------------|----------|
| Poly(dimethyl siloxane) 0% vinyl, 0% diphenyl | -54 | -123 | 7.3 | — |
| Poly(methyl methacrylate) | — | 105 | 9.5 | 0.786 |
| Polystyrene | — | 100 | 9.1 | 0.919 |

^a For PDMS 418-81.

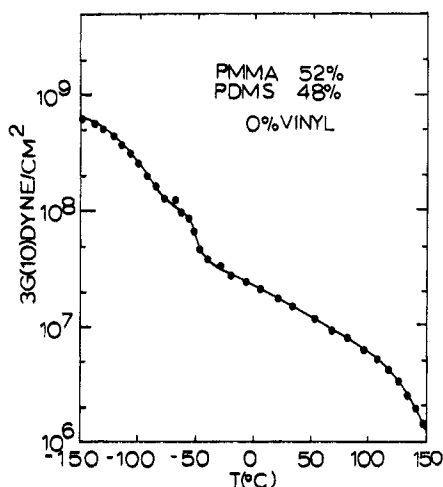


Fig. 5. Modulus-temperature curve for PDMS/PMMA solution-type graft copolymer with PDMS containing no vinyls. The lack of a rubbery plateau indicates no organized network formation. Extrapolating the sequence from Figure 4 to the case of no vinyls, this composition may be viewed as a joined IPN with essentially no intermolecular crosslink sites.

of IPNs. As expected, a silicone-rubber melting transition was observed in each of the modulus-temperature runs. Table II lists the literature values of the glass transition temperature, T_g , and melting temperature, T_m , values for the homopolymer species.⁹

The sequential materials were tough and leathery at room temperature, showing more phase continuity for the plastic component than the more elastomeric joined IPNs. Surprisingly, the joined IPNs all exhibited long-range rubber elasticity, with high strengths attained at ca. 500% elongation. In this context, the joined IPNs behaved similarly to the thermoplastic elastomer block copolymers.⁹

DISCUSSION

The theory of rubber elasticity was applied to the joined IPNs to test the effect of vinyl content on crosslink density. The equation $G = \phi nRT$, with the ideal rubber assumption of $\phi = 1$, was applied.⁹ In this equation n represents the number of network chains per unit volume, and R and T represent the gas constant and the absolute temperature, respectively. Values of n increased with vinyl content, showing that increasing the quantity of potential crosslink sites increased the crosslink density. Table III lists values of n calculated for the PMMA-joined IPN series. The values of n for the 0.2% and 0.6% vinyl PMDS IPNs were corrected by subtraction of the value of n ob-

TABLE III
 Crosslink Density

| Vinyl, % | PMMA, % | n , (moles/cc) $\times 10^6$ (150°C data) | Corrected n , (moles/cc) $\times 10^6$ |
|----------|---------|--|---|
| 0.0 | 52 | 1.2 | — |
| 0.2 | 47 | 3.4 | 2.2 |
| 0.6 | 44 | 7.4 | 6.2 |

tained from the zero vinyl-containing material, the crosslink density of the zero vinyl-containing material being assumed to be due to physical crosslinks. The ratio of these corrected n values was then taken. It showed approximately a threefold increase in crosslink density, with a tripling of vinyl content (0.6% as compared to 0.2% vinyl), a valuable confirmation of the suggested structures.

The incompatibility number ($I.N.$),⁸ based on a semiempirical approach to slope variations in polymer blend modulus-temperature curves, was applied as a measure of incompatibility to the present materials. The $I.N.$ equation may be written

$$I.N. = 1 - \left[\frac{X_1^{-1} + X_3^{-1}}{2X_2^{-1}} \right] \quad (1)$$

where $X = d \log 3G(10)/dT$, the subscripts 1 and 3 corresponding to the two glass transitions, and the subscript 2 corresponding to the plateau between the transitions. The values of $I.N.$ obtained for the two plastic-rubber systems are listed in Table II; they show PS to be less compatible with PDMS than is PMMA, which is the opposite of the result predicted from the solubility parameter values δ (see Table II).

At temperatures of about -100°C , it was noted that the PMMA containing joined IPNs became transparent. One explanation for this is presented by Rosen.¹⁰ He notes that indexes of refraction of polymers increase, but at differing rates, as temperature decreases. The transparency of the PDMS/PMMA system may therefore be caused by a convergence of indexes of refraction of the rubber and plastic components at low temperature. Unfortunately, no temperature-dependent refractive index data were available for the silicone rubbers, so an actual comparison could not be made.

Saam and co-workers^{11,12} have examined the corresponding PS-PDMS block copolymer system. Their modulus-temperature studies and electron micrographs support the notion of two distinct phases. The present study results are in general agreement with those of Saam.

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