

Semi- and Fully Interpenetrating Polymer Networks Based on Polyurethane–Polyacrylate Systems. VI. Polyurethane–Poly(methyl Acrylate-co-Ethyl Acrylate) Semi-1-Interpenetrating Polymer Networks

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Synopsis

Dynamic mechanical and longitudinal sonic velocity measurements have been made on a series of semi-1-IPNs in which the network component is a polyurethane and the linear constituent a copolymer of methyl acrylate and ethyl acrylate. Dynamic mechanical analysis reveals phase separation. The shifting of the polyurethane glass transition in both the $\tan \delta$ - and the E'' -temperature plots indicates that some mixing occurs. The longitudinal sonic velocity results indicate that the polyurethane is present as a continuous phase in all the materials investigated.

INTRODUCTION

An interpenetrating polymer network (IPN) may be defined as a material consisting of a pair of networks at least one of which has been synthesized and/or crosslinked in the presence of the other. The subject has been reviewed¹⁻⁴ several times recently.

If only one of the polymers is crosslinked, the product is referred to as a semi-IPN. For a given system, two different semi-IPNs exist. When the first formed material, polymer 1, is crosslinked, a semi-1-IPN results. When polymer 1 is linear and polymer 2 is a network, then the material is a semi-2-IPN.

Studies of semi-IPNs have been reported by several groups of authors. Both Allen et al.⁵⁻⁹ and Kim et al.¹⁰ have reported studies of polyurethane-polymethyl methacrylate semi-IPNs. Klempner et al.¹¹ have also investigated the morphologies and the properties of both semi-1 and semi-2-IPNs of a polyurethane–polyacrylate system. The earlier papers in this series have all been concerned¹²⁻¹⁶ with polyurethane–polyacrylate semi-IPNs.

The properties of semi-1-IPNs based on a polyurethane (PU) network¹² and a linear copolymer prepared from a feed containing equal parts by weight of methyl acrylate (MA) and ethyl acrylate (EA) are discussed in this paper.

EXPERIMENTAL

The preparation of the polyurethane networks has been described¹² in an earlier paper. In outline, they were synthesized from Adiprene L-100,¹⁷

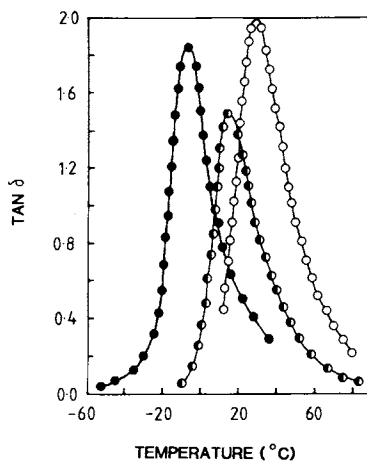


Fig. 1. $\text{Tan } \delta$ -temperature plots (11 Hz) of PMA (○), PEA (●), and the copolymer (◐).

butane-1,4-diol, and trimethylol propane. The butane-1,4-diol was added to provide chain extension so that the molecular weight between crosslinks of the networks was maintained approximately constant⁵ at approximately 6400 g/mol as the overall composition was changed. The NCO/OH ratio for the polyurethane was 1.1.

The semi-1-IPNs were prepared by dissolving all the reactants in the required amount of a destabilized mixture (equal parts by weight) of MA and EA. Dibutyl tin dilaurate (2 wt %) was added to promote the polyurethane synthesis. These mixtures were then degassed and poured into molds¹² and held at 20°C for 24 h to allow the polyurethane synthesis to occur. The temperature was then raised to 60°C for 18 h and then to 90°C for a further 6 h to polymerize the copolymer. This latter polymerization was initiated with AIBN (0.1% w/w).

The polyurethane homopolymer networks were prepared in an inhibited mixture of the comonomers of the linear component. These monomers were removed slowly, under vacuum, once the network had formed. The linear copolymer was synthesized in the same mold¹² and under identical conditions used for its synthesis in the semi-1-IPNs.

All materials were placed under vacuum, at 20°C, for at least 10 days prior to use.

All dynamic mechanical measurements were made using a Model DDV-II-B Rheovibron Dynamic Viscoelastometer. The heating rate was ap-

TABLE I
Dynamic Mechanical Data (11Hz) and Densities for PMA, PEA, and the Copolymer

Material	Density at 23°C (kg/m ³)	$\text{Tan } \delta_{\text{max}}$	Half-peak width (°C)	T_g (°C)
PMA	1210	≈2	31	+30
PEA	1110	≈1.85	27	- 6
PEA/PMA	1150	1.50	28	+15

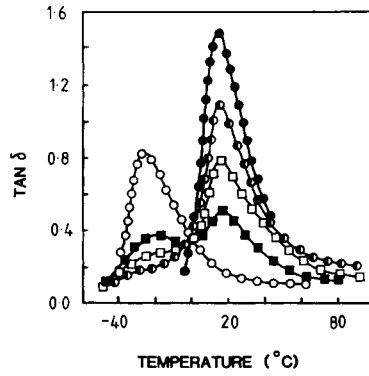


Fig. 2. $\text{Tan } \delta$ -temperature plots (11 Hz) of PU (○), the copolymer (●), and the semi-1-IPNs containing 20 (◐), 40 (◑), and 60 (■) wt % polyurethane.

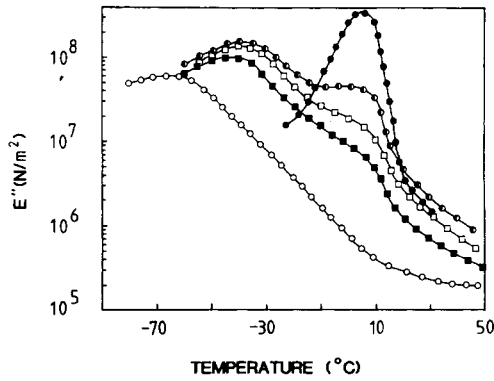


Fig. 3. E'' -temperature plots (11 Hz) of PU (○), the copolymer (●), and the semi-1-IPNs containing 20 (◐), 40 (◑), and 60 (■) wt % polyurethane.

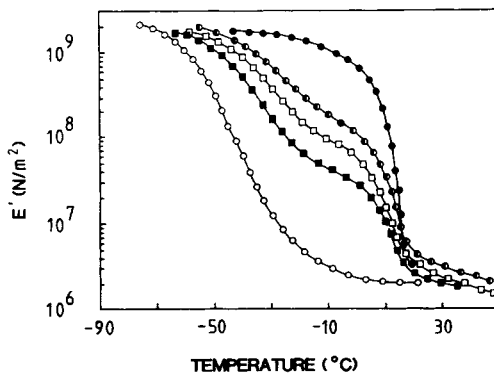


Fig. 4. E' -temperature plots (11 Hz) of PU (○), the copolymer (●), and the semi-1-IPNs containing 20 (◐), 40 (◑), and 60 (■) wt % polyurethane.

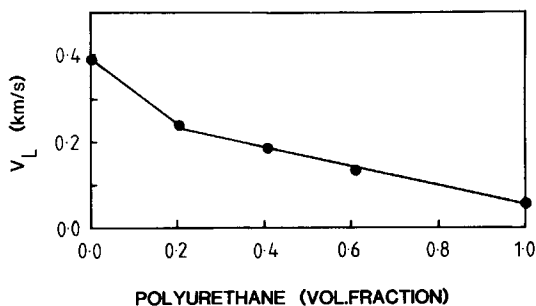


Fig. 5. V_L -composition plot at 20°C.

proximately 1°C/min. A Morgan Pulse Propagation Meter (Model PPM-5R) was used to measure the longitudinal sonic velocities V_L .

RESULTS AND DISCUSSION

Three semi-1-IPNs were prepared containing 20, 40, and 60 wt %, respectively, of the polyurethane network. For ease of reference the material containing, for example, 20 wt % of polyurethane will be referred to as the 20PU-80PMA/PEA semi-1-IPN.

Figure 1 shows $\tan \delta$ vs. temperature plots for PMA, PEA, and the copolymer. The copolymer exhibits only one glass transition. The glass transition temperature, T_g , was 15°C, which is close to being midway between the T_g of PMA (30°C) and that of PEA (-6°C).

Table I shows some dynamic mechanical data and also density values for the copolymer and the homopolymers.

The half-peak width of the copolymer is not significantly different from its components, indicating that there is no strong interaction between the two types of repeat units. $\tan \delta$ -temperature plots for the semi-1-IPNs and for the constituents are shown in Figure 2. In all cases there are two separate transitions for the semi-1-IPNs. The one at about 15°C is the copolymer glass transition, and it occurs at the same temperature as the copolymer itself. As with other semi-1-IPNs,^{13,16} there is a slight shift of the PU glass transition to higher temperature. This shift is more prominent in Figure 3, which shows the dynamic loss modulus E'' against temperature plots. These shifts indicate that some molecular mixing occurs between the constituent polymers. Phases of pure copolymer also exist. The dynamic storage modulus E' against temperature plots of the semi-1-IPNs and the homopolymers (Fig. 4) support the above morphological conclusions.

Figure 5 is a plot of V_L vs. composition. A straight line can be drawn through the data points for all three semi-1-IPNs, but not through the datum point for the copolymer. This is taken to mean¹⁸ that the PU component is present as a continuous phase even for the 20 PU-80 PMA/PEA material.

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