

Interpenetrating Polymer Networks from Polyurethanes and Poly(methyl Acrylate)

HARRY L. FRISCH,* LINFU WANG,* WEIYU HUANG,* YAO HE HUA,[†]
HAN X. XIAO,[†] and KURT C. FRISCH^{†*}

Department of Chemistry, State University of New York at Albany, Albany, New York 1222

SYNOPSIS

Simultaneous two-component interpenetrating polymer networks (IPNs) of polyurethane (PU)–poly(methyl acrylate) (PMA) were prepared, as well as the corresponding pseudo-IPNs. A comparison was made between the full IPNs, pseudo-IPNs, and the respective homopolymers. Their ultimate mechanical properties were obtained and the dynamic glass transition temperatures (T_g 's) were found using a thermomechanical analyzer. At all compositions, a single T_g (except 50–50 wt %) was found.

INTRODUCTION

Simultaneous or sequential interpenetrating polymer networks (IPNs) are a special type of chemical combination of different polymer networks held together by permanent entanglements^{1–17} with essentially no graft covalent bonds between the networks. They are not only intrinsically interesting as examples of macromolecular chemical to topological isomerism, but also are, in practice, useful means of controlling mutual miscibility and phase morphology in crosslinked polymers. Interest in these materials has mounted steadily and, since 1969–1985, has resulted in several hundred literature citations.¹⁸ In this paper we report the synthesis and characterization of the simultaneous interpenetrating polymer networks based on polyurethane and poly(methyl acrylate).

EXPERIMENTAL

Materials

The raw materials used and their descriptions are listed in Table I. Poly(oxytetramethylene) glycol

(Terathane 1000), 1,4-butanediol (1,4-BD), and trimethylolpropane (TMP) were dried at 60°C for 5 h under a vacuum of 2 mm Hg. Methyl acrylate (MA) and divinyl benzene (DVB) were washed with 5% aqueous potassium hydroxide solution, followed by washing with distilled water, dried over 4A molecular sieves, and distilled at 30°C under a vacuum of 80 mm Hg and at 40°C under 20 mm Hg, respectively, to remove inhibitor. 4,4'-Diphenylmethane diisocyanate (MDI), dibutyltin dilaurate (T-12), and benzoyl peroxide (BPO) were used without further purification.

Preparation of Homopolymers, IPNs, and Pseudo-IPNs

A resin kettle, equipped with a nitrogen inlet, stirrer, thermometer, and reflux condenser, was charged with 2 eq MDI. To this was added slowly with stirring 1 eq Terathane 1000. The reaction was carried out under nitrogen at 75–80°C until the theoretical isocyanate content (determined by the di-*n*-butylamine titration method¹⁹) was reached. The prepolymer was stored inside a desiccator before use. One equivalent of the PU prepolymer was heated to 80°C, and then homogeneously mixed with 1 eq of a mixture of 1,4-BD and TMP (4:1 eq ratio) for 5 min using a high torque stirrer. The air entrapped during mixing was removed by applying a vacuum for 5–10 min. The mixture was cast in a closed aluminum mold (with polypropylene lining for easy de-

* Department of Chemistry, State University of New York at Albany, Albany, NY 12222.

[†] Polymer Technologies, Inc., University of Detroit, MERCY, 4001 W. McNichols Road, Detroit, MI 48221.

[‡] To whom correspondence should be addressed.

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Table I Raw Materials

Material	Description	Supplier
Terathane 1000	Poly(oxytetramethylene) glycol	E.I. DuPont deNemours & Co.
MDI	4,4'-Methylene bis(phenyl isocyanate)	Mobay Chemical Co.
TMP	Trimethylolpropane	Aldrich Chemical Co., Inc.
1,4-BD	1,4-Butanediol	GAF Corp.
T-12	Dibutyltin dilaurate	M & T Chemicals, Inc.
MA	Methyl acrylate	Aldrich Chemical Co.
DVB	Divinylbenzene	Aldrich Chemical Co.
BPO	Benzoyl peroxide	Fisher Scientific Co.

molding) at 80°C for 16 h and 110°C for 1 h on a platen press under 350 psi pressure to obtain polyurethane elastomers. A resin kettle equipped with a nitrogen inlet, stirrer, thermometer, and reflux condenser was immersed in a water bath. It was charged with 90 g of distilled MA monomer, 10 g of distilled DVB, and 1 g benzoyl peroxide (BPO). The mixture was stirred until the BPO was dissolved. The reaction was carried out until 10–15% conversion and stopped by rapid cooling of the reaction product. The reaction mixture was cast in the same mold as used for the PU preparation and cured at 80°C for 16 h and 110°C for 4 h under 350 psi of pressure to obtain poly(methyl acrylate). In order to obtain IPNs, 1 eq PU prepolymer was heated to 80°C and then homogeneously mixed with 1 eq of the 1,4-BD/TMP mixture (4 : 1 equivalent ratio) for 5 min. The mixture of MA monomer, DVB, and BPO (9 : 1 : 0.1 weight ratio) was added in varying weight ratios and homogeneously mixed for 3 min using a high torque stirrer. The air entrapped during mixing was removed by applying a vacuum for 30 s. The mixture was then cast in the same manner as described above. The pseudo-IPNs were prepared in the same manner as described in the IPN preparation except that the PU was left as linear chain by omitting the crosslinker (TMP).

MEASUREMENTS

Mechanical Properties

The tensile strength (TS) and elongation at break were measured at room temperature on an Instron Tensile Tester (ASTMD 638) at a crosshead speed of 20 in./min for these samples. Shore A hardnesses were also measured.

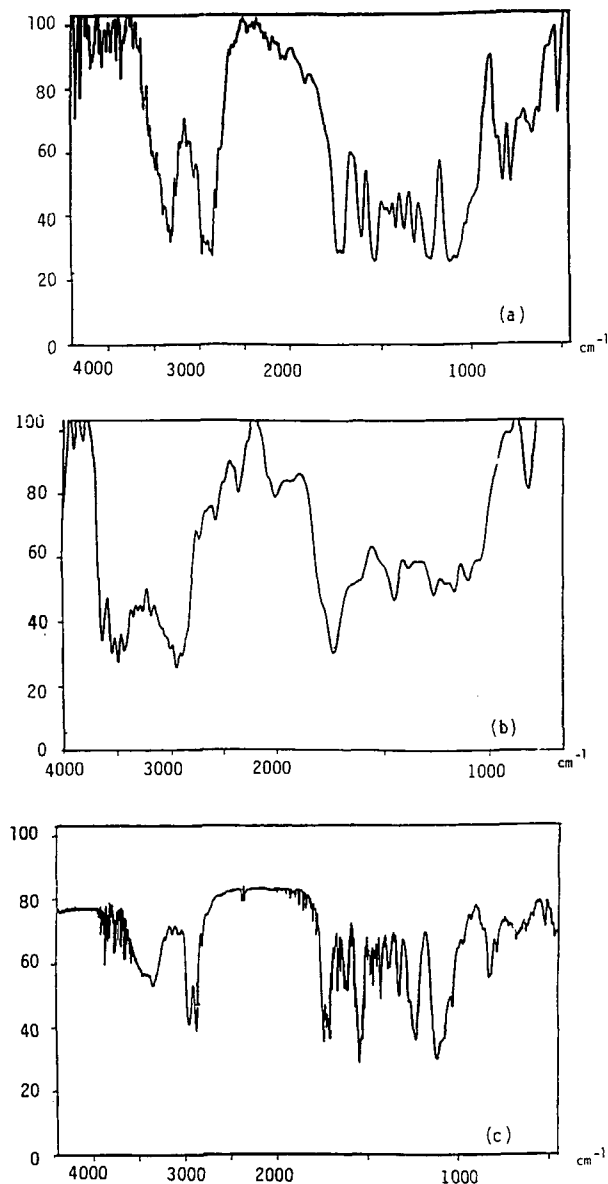


Figure 1 FTIR spectra of PU (a), PMA (b), and IPN (c).

Table II The Wave Length of Absorption Bands of PU, PMA, and IPN

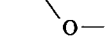
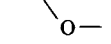
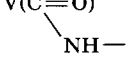
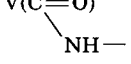
Bands	PU	PMA	IPN
3300 cm ⁻¹	3311 cm ⁻¹ V(N—H)	0	3335 cm ⁻¹ V(N—H)
1730 cm ⁻¹	0	1734 cm ⁻¹ V(C=O) 	1734 cm ⁻¹ V(C=O) 
1700 cm ⁻¹	1701 cm ⁻¹ V(C=O) 	0	1700 cm ⁻¹ V(C=O) 
1540 cm ⁻¹	1533 cm ⁻¹ V(N—C) + δ(N—H)	0	1540 cm ⁻¹ V(N—C) + δ(N—H)

Table III Glass Transition Temperatures (T_g 's) of IPNs, Extracted IPNs, and Pseudo-IPNs by TMA

Composition (% by weight)	IPNs	Extracted IPNs ^a	Pseudo-IPNs
PU/PMA = 100/0	-45.29°C	-28.93°C	—
PU/PMA = 80/20	-29.53°C	-18.49°C	-39.89°C (4.52°C)
PU/PMA = 50/50	-25.19°C (26.47°C)	-22.64°C (18.40°C)	-34.79°C (0.55°C)
PU/PMA = 20/80	-18.37°C	-16.57°C	-19.01°C (25.85°C)
PU/PMA = 0/100	30.06°C	31.26°C	—

^a IPNs Soxhlet extracted by dioxane for 36 h at 70°C.

Table IV Ultimate Mechanical Properties of Full IPNs

Sample Designation	Composition (wt %)	Tensile Strength			Elongation at Break (%)	Hardness (Shore A)
		at Break (psi)	100% Modulus (psi)	300% Modulus (psi)		
PU	100	2565	558	1021	800	80
PU/PMA	90/10	1941	627	1024	637	81
PU/PMA	80/20	2892	673	1262	717	86
PU/PMA	50/50	2954	921	2048	350	95
PU/PMA	20/80	3524	2855	—	163	98
PMA	100	Too brittle	—	—	—	—

Thermal Properties

Glass transition temperatures were determined on a DuPont 2100 thermomechanical analyzer and measurements were carried out from -100 to 150°C under nitrogen at a heating rate of 20°C/min.

RESULTS AND DISCUSSION

The FTIR spectra of crosslinked PU, crosslinked PMA and full IPNs are shown in Figure 1, and some absorption bands of the chemical components and

Table V Ultimate Mechanical Properties of Pseudo-IPNs*

Sample Designation	Composition (wt %)	Tensile Strength at Break (psi)	100% Modulus (psi)	300% Modulus (psi)	Elongation at Break (%)	Hardness (Shore A)
PU/PMA	90/10	1835	480	844	775	81
PU/PMA	80/20	2022	540	1009	642	85
PU/PMA	50/50	2142	814	1625	484	92
PU/PMA	20/80	2408	2132	—	175	95

* PU was linear, PMA was crosslinked.

Table VI Effect of Degree of Crosslinking on Ultimate Mechanical Properties of Full IPNs

Sample Designation	Composition (wt %)	Tensile Strength at Break (psi)	100% Modulus (psi)	300% Modulus (psi)	Elongation at Break (%)	Hardness (Shore A)
PU/PMA'D5	80/20, DVB 5%	2115	622	895	740	82
PU/PMA'D10	80/20, DVB 10%	2892	673	1262	717	86
PU/PMA'D15	80/20, DVB 15%	3259	716	1366	550	87

their IPNs are listed in Table II. The results are in accord with the expected structures. The T_g 's of the IPNs, extracted IPNs, and pseudo-IPNs by TMA are shown in Table III. All pseudo-IPN samples exhibit two glass transition temperatures which were between the T_g values of PU and PMA, whereas, in most of the IPN samples (except the sample from PU/PMA = 50/50), a single T_g was observed (indicating complete segmental mixing of the two networks). In order to examine the noncrosslinked polymers, we extracted the IPNs with dioxane for 36 h at 70°C. There is a significant difference between the T_g 's of unextracted and extracted samples. This is presumably due to the presence of some noncrosslinked PU and PMA.

The ultimate mechanical properties of full and pseudo-IPNs samples are shown in Tables IV and V. The pure crosslinked PMA was too brittle to cut and no reliable measurements could be obtained. The tensile strengths at break of the full IPNs were higher than those of the pseudo-IPNs pure crosslinked PU except for 90 PU/10 PMA wt % IPN. This may be due to the additional permanent entanglements present in the full IPNs. The tensile strength at break of the full IPNs increased as the content of PMA increased. For full IPNs, a maximum tensile strength was observed at 20/80 of PU/PMA. The tensile strength at the 90/10 of PU/PMA composition was lower than that of pure crosslinked PU. This is probably due to a decrease

Table VII Effect of Solvent Extraction on Ultimate Mechanical Properties of Full IPNs

Sample Designation	Composition (wt %)	Tensile Strength (psi)	Elongation (%)
PU/PMA (D10)	80/20 DVB (10%)	3092	717
EX PU/PMA (D10)*	EX 80/20 DVB (10%)	688	250
PU/PMA (D15)	80/20 DVB (15%)	3259	550
EX PU/PMA (D15)	EX 80/20 DVB (15%)	762	200
PU/PMA	20/80	3524	163
EX PU/PMA	EX 20/80	4276	217

* EX extracted by dioxane for 36 h at 70°C.

in intermolecular hydrogen bonds in the crosslinked PU on addition of the PMA. The elongation at break of the IPNs shows a rapid drop and the Shore A hardness exhibited an increase at around the 50/50 PU/PMA composition. The effects of crosslinking degree and solvent extraction on the ultimate mechanical properties of the full IPNs are shown in Tables VI and VII. The higher the extent of crosslinking degree, the higher the tensile strength and hardness of the full IPNs.

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