

Interpenetrating Polymer Networks from Castor Oil-Based-Polyurethanes and Poly(ethyl Acrylate). VII.

MAYUR PATEL and BHIKHU SUTHAR,* *Chemistry Department, Sardar Patel University, Vallabh Vidyanagar, 388 120, Gujarat, India*

Synopsis

Liquid prepolyurethanes were synthesized from castor oil and toluene-2,4-diisocyanate (TDI) under different experimental conditions and varying NCO/OH ratios. All these prepolyurethanes were subsequently reacted with ethyl acrylate/ethylene glycol dimethacrylate mixtures by radical polymerization using benzoyl peroxide as initiator to obtain interpenetrating polymer networks (IPNs) by transfer molding. The novel polyurethane/poly(ethyl acrylate) IPNs are found to be tough films. These IPNs are characterized in terms of their resistance to chemical reagents, thermal behavior (DSC, TGA), mechanical behavior including tensile strength, Young's modulus, and elongation. The dielectric properties, namely electrical conductivity (σ), dielectric constant (ϵ'), dielectric loss (ϵ''), and loss tangent ($\tan \delta$) were computed. The mechanothermal behavior was analyzed by dynamic mechanical spectroscopy. The morphological behavior was studied by scanning electron microscopy.

INTRODUCTION

Since the historical synthesis by Millar,¹ and the major works of Sperling and co-workers,²⁻⁵ and Frisch and co-workers,⁶⁻⁹ interpenetrating polymer networks (IPNs) have been the subject of great importance from the technological point of view. Although IPNs are the youngest polymers in the field of polymer blends and composites, they have proven to be excellent engineering materials. Sperling and co-workers¹⁰⁻¹² reported on the IPNs from castor oil based polyurethanes and styrene monomer. They found that the mechanical properties of these IPNs were increased by increase in TDI content of the castor oil based polyurethanes. They also reported on IPNs from castor oil, TDI, and sebacic acid interpenetrated with polystyrene and found that elastomeric as well as plastic IPNs are tougher than the corresponding homopolymers.¹³

To investigate the properties of elastomeric castor-oil-based polyurethanes with other vinyl monomers, the present work was undertaken. The synthesis of IPNs from castor-oil-based polyurethanes from toluene-2,4-diisocyanate (TDI) and interpenetrated with polymerizing ethyl acrylate containing 1% ethylene glycol dimethacrylate (EGDM) is reported. The IPNs were characterized by their thermal, mechanical, mechanothermal, morphological, and dielectric properties.

*Correspondence author.

TABLE I

Materials	Description	Source	Code
Castor oil	Triglyceride of ricinoleic acid, hydroxyl value 124, $-\text{OH} = 2.27$ per mole of castor oil	Local	---
Toluene-2,4-diisocyanate	Density $1.22 \text{ (g mL}^{-1}\text{)}$	Fluka (Switzerland)	TDI
Ethyl acrylate	Density $0.923 \text{ (g mL}^{-1}\text{)}$	Schuchardt M (West Germany)	EA
Ethylene glycol dimethacrylate	Acrylic crosslinker	Schuchardt M (West Germany)	EGDM
Benzoyl peroxide	Initiator recrystallized from chloroform	Aldrich (USA)	Bz ₂ O ₂
Prepolyurethane	Prepolyurethane from castor oil + TDI	Our laboratory	PPU

EXPERIMENTAL

Materials

See Table I.

Synthesis of Prepolyurethane

Castor oil (55 g, 0.55 mol) was reacted with TDI (17.38 g, 0.099 mol) in order to maintain an NCO/OH ratio of 1.6 to give an isocyanate-terminated prepolyurethane. The reaction was carried out at 45°C with continuous stirring for 1 h. The polymer was isolated as a thick syrup. Following the above procedure, the other prepolyurethanes (PPU) with varying NCO/OH ratio were prepared.

Synthesis of IPNs

IPNs were synthesized by pouring the PPU in different proportions into a round bottom flask. To this, the mixture of ethyl acrylate, 1% EGDM, and 0.5% benzoyl peroxide was added. The mixture was stirred at room temperature for 5 min to form a homogeneous solution. The temperature was then raised to 60°C to initiate ethyl acrylate polymerization. After stirring for 1 h the solution was poured into a glass mold kept in a preheated air-circulating oven maintained at 60°C. It was kept at this temperature for 24 h and at 120°C for 4 h. The film thus formed was cooled slowly and removed from the mold. Nine different IPNs were synthesized with different compositions and abbreviated as IPN-1-IPN-9 (Table II). It is worth mentioning here that prepolyurethane content beyond 45 wt % did not yield IPN film.

Characterization

Resistance to chemical reagents was measured according to ASTM D 543-67 (1978). Tensile properties were measured on a universal Instron testing ma-

TABLE II
Composition of IPNs

Sample	Prepolyurethane (wt %) ^a	Ethyl acrylate, (wt %)	Density (g/mL)	T_g^c
IPN-1	25	75	1.08	38
IPN-2	35 (1.6) ^b	65	1.10	40
IPN-3	45	55	1.18	41
IPN-4	25	75	1.16	39
IPN-5	35 (1.8) ^b	65	1.16	38
IPN-6	45	55	1.14	41
IPN-7	25	75	1.14	40
IPN-8	35 (2.0) ^b	65	1.27	39
IPN-9	45	55	1.00	40
PPU	—	—	Liquid	Liquid
PEA	—	—	—	-20

^a Contents of prepolyurethane > 45 wt % was not possible due to experimental difficulties.

^b NCO/OH ratio of castor oil and TDI.

^c T_g from DSC in air at a heating rate of 5°C/min.

chine according to ASTM D 638 (1977). Shore A hardness was measured according to ASTM D 785 (1965). Dielectric properties were measured according to ASTM D 1531 (1962). The thermal stability was assessed on a DuPont 950 thermal analyzer at a heating rate of 10°C/min in air. Scanning electron microscopy (SEM) was made with a Phillips EM-400 equipped with S(T) EM System PW-6585 scanning attachment. The cryogenically fractured film in liquid nitrogen was mounted vertically on an SEM stub using silver adhesive paste. The specimen was coated with gold using a Carl Zeiss Vacuum System EP 5 at about 10^{-5} torr. The mechanothermal analysis was made on DuPont 951 dynamic mechanical analyzer.

RESULTS AND DISCUSSION

PPU / PEA IPNs

All the IPNs were prepared as tough films. Table II represents the experimental conditions for the formation of IPNs. The prepolyurethanes were obtained from castor oil and TDI and characterized elsewhere.¹⁴ The densities of IPNs at room temperature were measured using the hydrostatic technique (Table II). The IPNs were insoluble in the following solvents: acetone, carbon tetrachloride, chloroform, methanol, R-spirit, ethyl acetate, dimethyl formamide, tetrahydrofuran, dimethyl acetamide, dioxane, pyridine, benzene, toluene, xylene, etc. It was observed that there was no weight loss when IPNs were kept in the stated solvents.

Chemical Resistance

Solvent resistance of PPU/PEA IPNs films to a series of standard reagents, namely, 25% H₂SO₄, 15% HCl, 5% HNO₃, 5% NaOH, 10% NH₄OH, 25% acetic acid, 5% H₂O₂, 40% NaCl, methylethyl ketone, distilled water, carbon tetra-

TABLE III
Thermogravimetric Data of IPNs

Sample	Percent weight loss ($\pm 2\%$) at different temperatures ($^{\circ}\text{C}$)					
	300	350	400	450	500	550
IPN-1	8	30	55	70	85	93
IPN-2	8	29	57	70	85	93
IPN-3	7	31	56	70	83	93
IPN-4	7	31	56	71	83	94
IPN-5	9	31	55	69	84	94
IPN-6	8	29	54	71	84	95
IPN-7	7	29	55	70	84	95
IPN-8	7	30	55	70	85	94
IPN-9	7	31	56	71	85	95
Homopolymer poly(ethyl acrylate)	15	35	62	86	—	—

chloride, and toluene was studied according to ASTM D 543-67 (1978) procedure. The pieces of IPN ($20 \times 20 \times 0.78$ mm) were put in 100 mL standard reagents for 7 days. After exposure to chemical reagents, each of the IPN pieces was examined on the basis of physical appearance such as discoloration, loss of gloss, decrease in weight, and change in thickness. These IPNs were stable in all of these reagents except methyl ethyl ketone, toluene, and carbon tetrachloride in which the IPNs lost their gloss and became brittle.

Thermal Behavior

Frisch and his co-workers¹⁵⁻¹⁷ assessed the thermal stability of the various IPNs and found that they possessed greater thermal stability than their component networks. The thermal stability of all these IPNs was compared with homopolymer poly(ethyl acrylate) in terms of percent loss in weight at different temperatures from the TG thermograms and the results are reported in Table III. It is evident that all the IPNs are stable up to approximately 300°C , lose weight rapidly around 400°C , and decomposes completely beyond 550°C . However, the thermal stability of all the IPNs does not change with increase in the contents of poly(ethyl acrylate) in the IPNs. Their thermal stability is much greater than that of the homopolymer poly(ethyl acrylate). The enhancement in weight retention of IPNs may be explained on the basis of the miscibility of two component networks.¹⁸

Mechanical Properties and Morphology

The mechanical properties namely tensile strength, Young's modulus, elongation at the breaking point, and Shore A hardness are presented in Table IV. These IPNs exhibit good mechanical strength as compared to homopolymer of poly(ethyl acrylate). Thus the IPNs from elastomeric PPU and plastic PEA have quite different properties from their individual homopolymers. The dynamic mechanical properties of IPN-2, IPN-4, and IPN-7 are shown in Figures 1-3. The dynamic storage modulus (E') vs. temperature for the IPNs shows the general modulus response to the content of ethyl acrylate as well as

TABLE IV
Mechanical Properties of IPNs

Sample	Tensile strength (MN/m ²)	Young's modulus (MN/m ²)	Elongation at break (%)	Hardness Shore A
IPN-1	3.41	1.64	194	79
IPN-2	3.66	2.17	182	83
IPN-3	2.85	1.90	188	95
IPN-4	3.37	3.67	148	81
IPN-5	7.10	3.01	225	73
IPN-6	6.38	2.99	200	80
IPN-7	9.38	4.67	183	86
IPN-8	10.60	4.13	186	87
IPN-9	8.67	3.84	178	79
PEA	62.30	2500	16	92

temperature. The damping factor ($\tan \delta$) vs. temperature for these IPNs showed one peak corresponding to only one T_g of the compatible interpenetrated PPU and PEA polymers. Because the T_g of the homopolymer poly(ethyl acrylate) is below 0°C, it was not compared in the present study. The present IPNs reflect the synergistic behavior in which modification in the

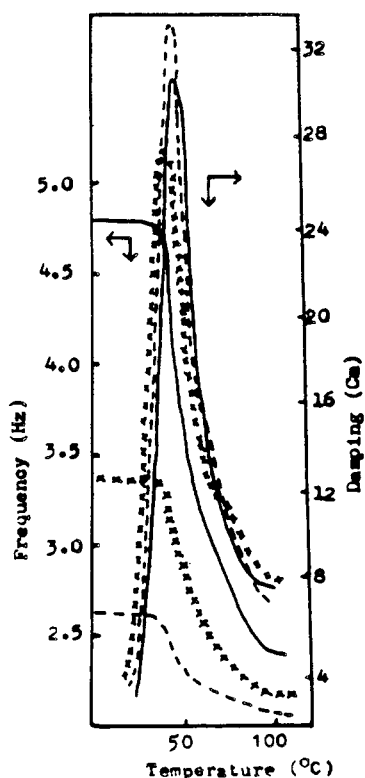


Fig. 1. Frequency (Hz) and damping (cm) vs. temperature: (xxx) IPN-2; (—) IPN-4; (---) IPN-7.

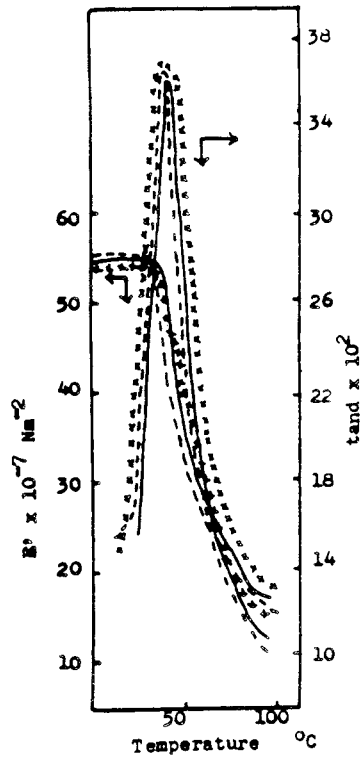


Fig. 2. Storage modulus (E') and damping factor ($\tan \delta$) vs. temperature: (xxx) IPN-2; (—) IPN-4; (---) IPN-7.

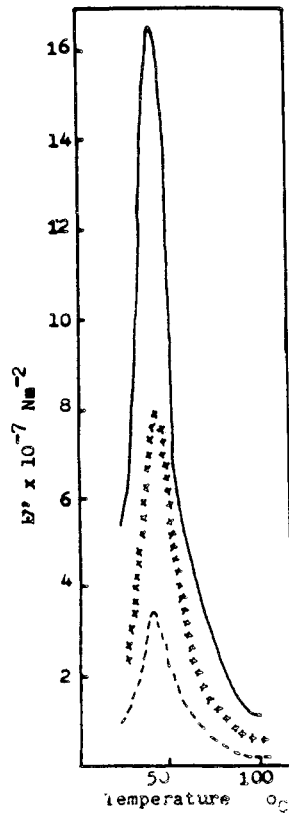


Fig. 3. Loss modulus (E'') vs. temperature: (xxx) IPN-2; (—) IPN-4; (---) IPN-7.

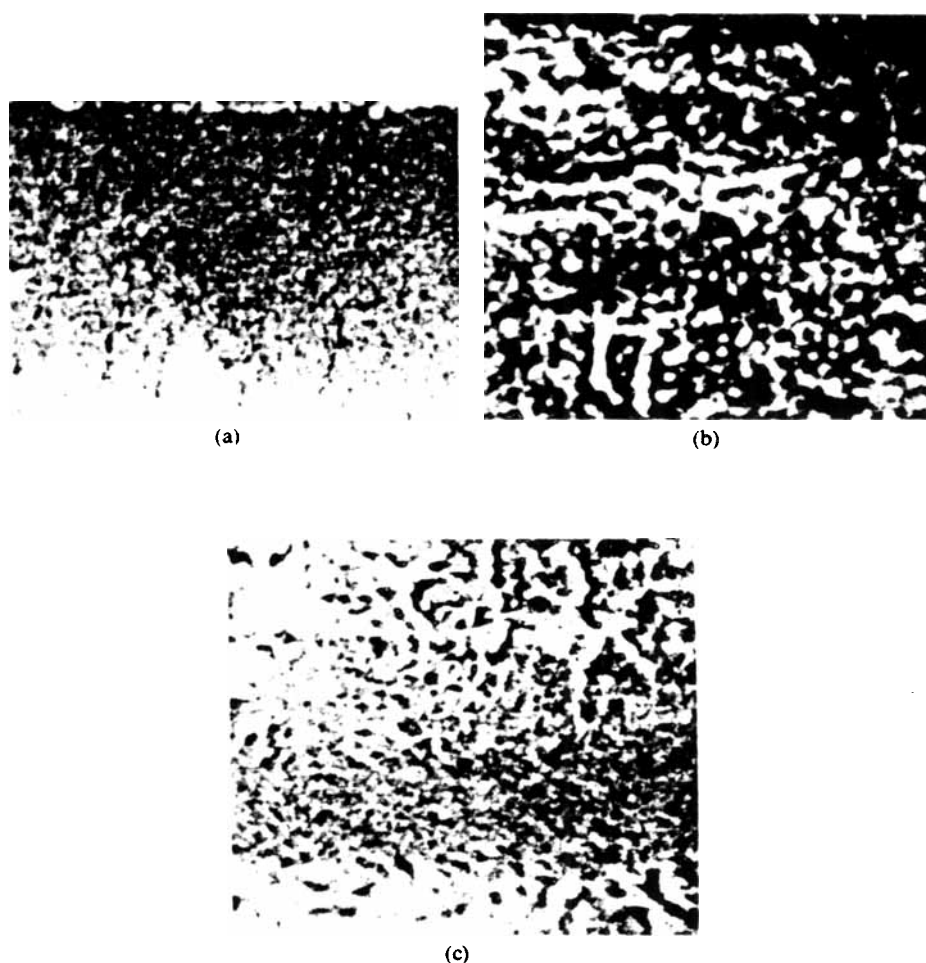


Fig. 4. Scanning electron micrographs with 1200 magnification: (a) IPN-2; (b) IPN-4; (c) IPN-7.

TABLE V
Electrical Conductivity Properties

Sample	Electrical conductivity at room temp, $\sigma(\Omega^{-1} \text{ cm}^{-1})$	Specific conductivity $\sigma_0(\Omega^{-1} \text{ cm}^{-1})$	Activation energy (kJ/mol)
IPN-2	2.6×10^{-14}	2.9×10^{-12}	49.2
IPN-4	1.8×10^{-14}	1.3×10^{-12}	43.7
IPN-7	1.8×10^{-14}	3.8×10^{-12}	61.2
PEA	8.6×10^{-15}	4.5×10^{-13}	79.3

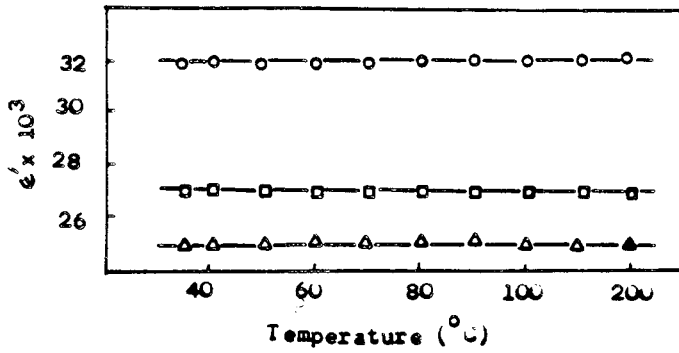


Fig. 5. Dielectric constant (ϵ') vs. temperature: (○) IPN-2; (□) IPN-4; (Δ) IPN-7.

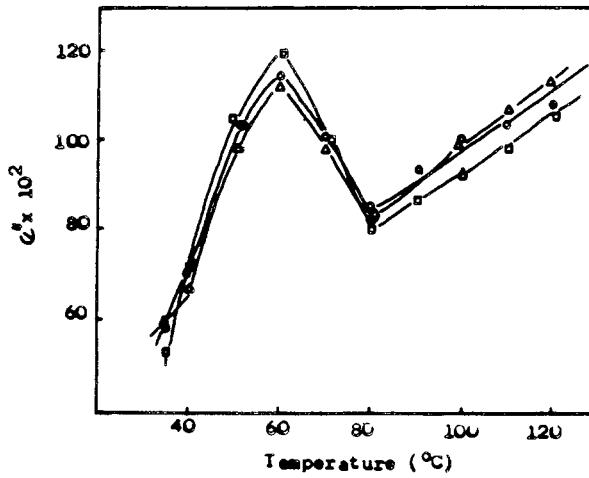


Fig. 6. Dielectric loss (ϵ'') vs. temperature: (○) IPN-2; (□) IPN-4; (Δ) IPN-7.

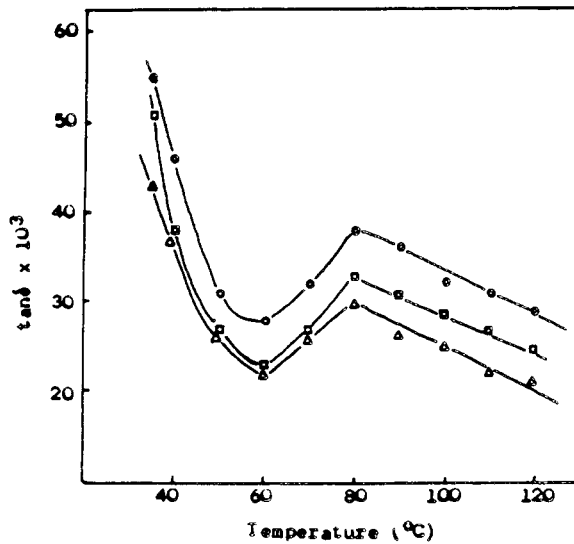


Fig. 7. Loss tangent ($\tan \delta$) vs. temperature: (○) IPN-2; (□) IPN-4; (Δ) IPN-7.

properties of component network occurs. The morphological evidence of these IPNs comes from their SEM micrographs shown in Figure 4 for IPN-2, IPN-4, and IPN-7. The observed homogeneity in each specimen indicates the interpenetration of the phase domains of PPU and PEA.

Electrical Properties

The use of polymers as dielectrics is becoming increasingly important and their choice mainly depends upon their dielectric properties. Frisch and co-workers¹⁹ reported on the dielectric properties of three component network of IPNs. The specific electrical conductivity (σ_0), electrical conductivity at room temperature (σ), and the activation energy (E) are compared with the homopolymer poly(ethyl acrylate) (Table V). The dielectrical properties (ϵ' , ϵ'' and $\tan \delta$) at 10 kHz are shown in Figures 5–7. From these dielectrical properties, these IPNs behave like perfect insulators and have properties bordering on those exhibited by semiconductors.¹⁹

CONCLUSION

From the present investigation, it is concluded that the IPNs derived from castor-oil-based PPU and poly(ethyl acrylate) are tough materials having synergistic properties of their corresponding homopolymers.

References

1. J. R. Millar, *J. Chem. Soc.*, **1960**, 1311.
2. L. H. Sperling and D. W. Friedman, *J. Polym. Sci.*, *A-2*, **7**, 425 (1969).
3. L. H. Sperling, J. A. Manson, and M. A. Linne, *J. Polym. Mater.*, **1**, 54 (1984).
4. L. H. Sperling, *Interpenetrating Polymer Networks and Related Materials*, Plenum, New York, 1981.
5. L. H. Sperling and J. W. Widmaier, *Br. Polym. J.*, **16**, 46 (1984).
6. H. L. Frisch, D. Klempner, and K. C. Frisch, *J. Polym. Sci.*, *Part B*, **7**, 775 (1969).
7. D. Klempner and H. L. Frisch, *J. Polym. Sci.*, *Polym. Lett. Ed.*, **8**, 525 (1970).
8. D. Klempner and H. L. Frisch, *Polymer Allows II*, Plenum, New York, 1980.
9. K. C. Frisch, D. Klempner, and H. Xiao, *Polym. Eng. Sci.*, **25**, 258 (1985).
10. J. A. Manson and L. H. Sperling, *Macromolecules*, **12**, 360 (1979).
11. N. Devia, J. A. Manson, L. H. Sperling, and A. Conde, *Polym. Eng. Sci.*, **19**, 869 (1979).
12. N. Devia, J. A. Manson, and L. H. Sperling, *J. Appl. Polym. Sci.*, **24**, 569 (1979).
13. N. Devia, J. A. Manson, L. H. Sperling, and A. Conde, *Polym. Eng. Sci.*, **19**, 869 (1979).
14. M. Patel and B. Suthar, *J. Appl. Polym. Sci.*, **33**, 67 (1987).
15. K. C. Frisch, D. Klempner and S. K. Mukherjee, *J. Appl. Polym. Sci.*, **18**, 689 (1974).
16. K. C. Frisch, D. Klempner, and S. Midgal, *J. Polym. Sci.*, *Polym. Chem. Ed.*, **12**, 885 (1974).
17. K. C. Frisch, D. Klempner, and S. Midgal, *J. Appl. Polym. Sci.*, **19**, 1893 (1975).
18. D. S. Lee and S. C. Kim, *Macromolecules*, **18**, 2173 (1985).
19. E. F. Cassidy, H. X. Xiao, K. C. Frisch, and H. L. Frisch, *J. Polym. Sci.*, *Polym. Chem. Ed.*, **22**, 2667 (1984).

Received October 14, 1986

Accepted January 21, 1987