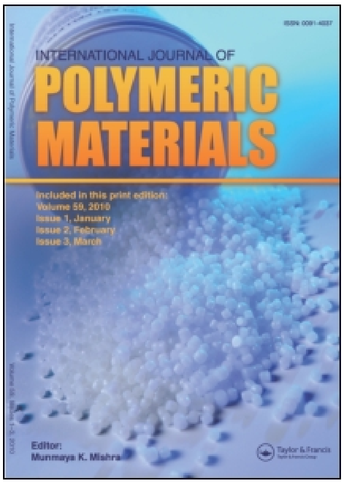

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

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To cite this Article Suthar, Bhikhu , Parikh, Nilesh and Patel, Nimish(1991) 'Interpenetrating Polymer Networks from Castor Oil Based Polyurethanes and Poly(Methyl Methacrylate) XX', International Journal of Polymeric Materials, 15: 2, 85 — 91

To link to this Article: DOI: 10.1080/00914039108031525

URL: http://dx.doi.org/10.1080/00914039108031525

Intern. J. Polymeric Mater., 1991, Vol. 15, pp. 85–91
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Printed in the United Kingdom

Interpenetrating Polymer Networks from Castor Oil Based Polyurethanes and Poly(Methyl Methacrylate) XX

Dedicated with a profound sense of admiration and gratitude to the memory of late Prof. Dr. Herman Kauffman

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(Received June 15, 1990)

Two component interpenetrating polymer networks (IPNs) of castor oil based polyurethanes and poly(methyl methacrylate) were prepared by sequential polymerization. The liquid polyurethanes were formed by reacting the hydroxyl group of castor oil with diphenyl methane diisocyanate at different stoichiometric NCO/OH ratios. These polyurethanes were swollen in methyl methacrylate monomer and subsequently polymerized by radical polymerization initiated with benzoyl peroxide in presence of crosslinkers ethylene glycol dimethacrylate and 1,3-propanediamine. Novel interpenetrating polymer networks PU/PMMA IPNs were obtained as films by transfer molding technique. These IPNs were characterized in terms of crosslink density and mechanical properties. The morphology was studied by transmission electron microscopy. Thermal stability was assessed from the thermogravimetric data.

KEY WORDS: Interpenetrating networks, castor oil, polyurethanes, PMM, properties, structure.

INTRODUCTION

Pioneering work on castor oil based interpenetrating polymer networks has led to the development of industrially useful materials.[1–5] Preliminary reports on castor oil based IPNs showed high strength, good resiliency and resistance to abrasion and hydrolysis.[6,7] The aim of our work has been to prepare and characterize the interpenetrating polymer networks from castor oil based polyurethane and poly(methyl methacrylate) and to investigate their properties. Some of these studies were previously reported.[8] Although PU/PMMA IPNs have been previously investigated, an attempt is made in present study, to correlate the variations of crosslink density with the resulting changes in mechanical properties of IPNs. These findings are further supported by the results of morphological and thermogravimetric studies.

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EXPERIMENTAL

Materials

Chemicals used in the present investigation are described and abbreviated in the following Table.

Chemicals	Description	Source	Code
Castor oil[a]	Triglyceride of ricinoleic acid, experimental hydroxyl value 132	Local market	—
Diphenyl methane diisocyanate	Density = 1.239 g cm^{-3}	Schuchardt M	DMDI
Methyl methacrylate	Density = 0.940 g cm^{-3}	Fluka	MMA
Ethylene glycol dimethacrylate	Acrylic crosslinker	Fluka	EGDM
Benzoyl peroxide	Initiator recrystallized from chloroform	Aldrich	BZO
Polyurethane	Polyurethane from castor oil and diisocyanate with different NCO/OH ratios	Our laboratory	PU

[a] Castor oil is triglyceride of glycerol and ricinoleic acid having hydroxyl group at the 11-position. Castor oil should give a theoretical hydroxyl value of 164, corresponding to the three hydroxyl groups. The experimental hydroxyl value of 132 obtained in the present work would correspond to 2.19 OH groups per mole of castor oil.[9,10]

Synthesis of polyurethane

A mixture of castor oil (10.11 g; 0.0108 mol) and diphenyl methane diisocyanate, DMDI (8.87 g; 0.03547 mol) with NCO/OH ratio of 3.0, was stirred vigorously for 10 min at 35°C and 1 h at 45°C. This "prepolymer" was a thick liquid and was immediately used for IPN synthesis. Following the above procedure, the other polyurethane (PU) with varying ratios of NCO/OH were prepared.

Synthesis of IPNs

The polyurethane PU (castor oil + DMDI) "prepolymer" in various proportions was swollen in stabilizer-free methyl methacrylate containing 1% EGDM crosslinker and the mixture was stirred at room temperature for 5 min to form homogeneous mixture. Benzoyl peroxide (0.5%) was added and the temperature was raised to 60°C to initiate radical polymerization of methyl methacrylate along with added crosslinker. After stirring for 1 hr at this temperature, the solution was poured into the glass mold kept in a preheated air circulating oven maintained at 60°C. It was kept at this temperature for 24 hr and at 120°C for 4 hr. The film thus formed was cooled slowly and removed from the mold. A series of IPNs (IPN-1 to IPN-9) of different composition were obtained.

TABLE I

Data on IPN synthesis

Polymer code	NCO/OH ratio of DMDI and castor oil	Polyurethane content[a] (wt %)	Methyl methacrylate content (wt%)
IPN-1	2.0	15	85
IPN-2	2.0	25	75
IPN-3	2.0	35	65
IPN-4	2.5	15	85
IPN-5	2.5	25	75
IPN-6	2.5	35	65
IPN-7	3.0	15	85
IPN-8	3.0	25	75
IPN-9	3.0	35	65
PU	3.0	100	—
PMMA	—	—	100

[a] Content of polyurethane >35 wt.% does not afford film formation as the islands of PU and PMMA are formed during IPN synthesis.

Characterization

Mechanical properties were measured according to the appropriate ASTM procedures. Crosslink densities of the IPNs were determined by its equilibrium compression modulus of immersed IPN discs in toluene using the test method described in the literature.[11,12] Transmission electron microscopy of the IPN was generously done by ELM laboratories, Cumbria (UK). The thermal stability was measured with a Du Pont 951 thermal analyzer at a heating rate of 10°C/min.

RESULTS AND DISCUSSION

Hydroxyl groups of castor oil were reacted with diphenyl methane diisocyanate at different stoichiometric NCO/OH ratios and yielded isocyanate-terminated polyurethanes "prepolymers" as mentioned in the experimental part. The structure of the prepolymer has been established from the infrared evidence.[8] The liquid polyurethane was used immediately for further interpenetration with methyl methacrylate, otherwise it continues to crosslink until it results into an insoluble mass in organic solvents. No further characterization of the prepolymers could be made because of their insolubility. Thus castor oil based polyurethane and poly(methyl methacrylate) networks are allowed to form in situ through independent condensation and radical polymerization techniques respectively. These reactions are made to progress in presence of the appropriate crosslinkers (1,3-propanediamine for PU and EGDM for PMMA) and both of them are simultaneously completed by transfer moulding technique. Thus obtained PU/PMMA IPNs were semi-transparent films. These IPNs are insoluble in common organic solvents: alcohols, aromatic solvents, chloroform, carbon tetrachloride, dioxane, pyridine, dimethyl formamide and dimethyl acetamide.

Mechanical properties

Sperling and his coworkers[3,5] reported the synergistic behaviour of IPNs from castor oil based polyurethane from toluene-2,4-diisocyanate and polystyrene component networks. Mechanical properties of PU/PMMA IPNs in the present investigation were studied in terms of tensile strength, Young's modulus, elongation at break (%) and Shore A hardness and further correlated with their crosslink densities. Mechanical properties of the IPN-1 to IPN-9 presented in Table II reflect the structure-property relationships for this system. It is shown that incorporation of the poly(methyl methacrylate) component into an elastomeric polyurethane increases the Young's modulus from a value of 6.47 to 235.44 MN/m^2, depending upon the content of poly(methyl methacrylate). Only minor changes are observed in the elongation at break, thus it may be concluded that in the present set of IPNs, toughness in the elastomeric PU increases with the increase in the PMMA content of the IPNs.

The crosslink densities of these samples were determined by equilibrium compression technique and are given in Table II. The variation of crosslink densities with the different NCO/OH ratio of the polyurethane as well as with the amount of plastic component PMMA in the present IPNs is shown in Table II. It is evident that an increase in the NCO/OH ratio of the prepolyurethane (PU) increases the crosslink density. This may be explained on the basis of the increased possibilities of crosslinking between the segments of isocyanate-terminated polyurethanes with increase in the NCO/OH ratios. Similarly there is also an increase in the crosslink density with the decrease in the PMMA content of the IPNs. An attempt to determine crosslink density of 100% PMMA film has been made but it failed because of the deterioration of PMMA film in toluene. There is a close similarity between the crosslink densities and tensile strengths of the IPN films (Table II).

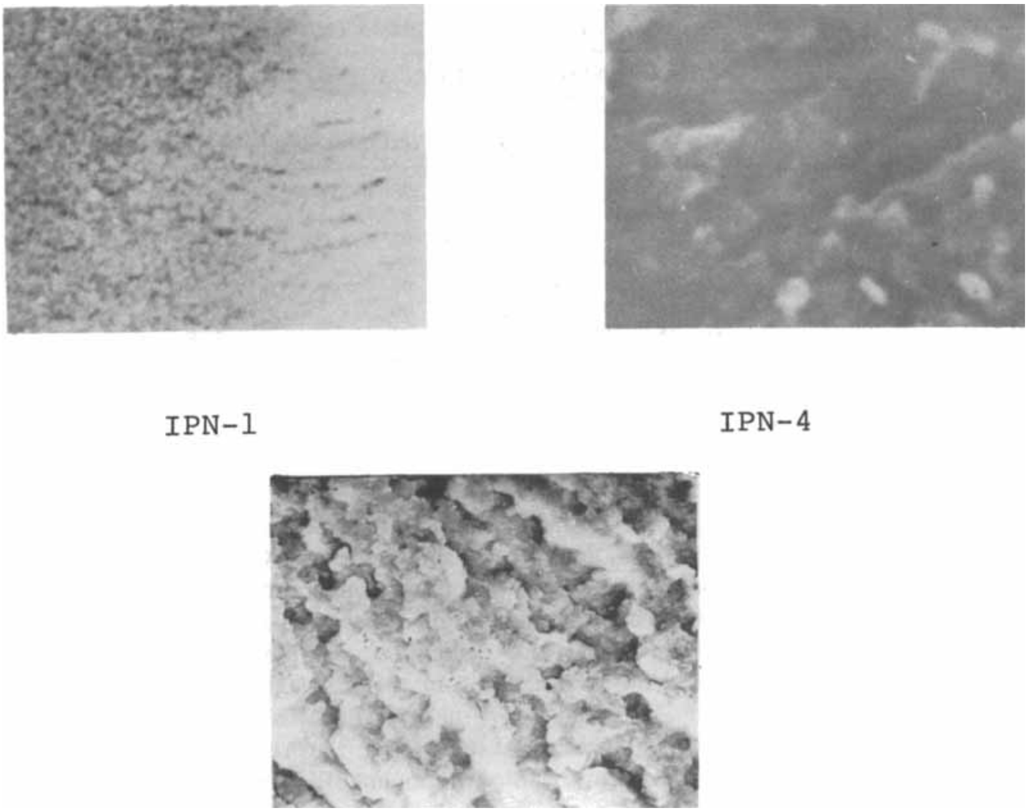
Morphology

Sperling *et al.*[5] observed that PU/PS IPNs have distinct phase separation of the individual PU and PMMA component networks. It is further established that the

TABLE II

Mechanical properties of PU/PMMA IPNs

Polymer code	Tensile strength MN/m^2	Young's modulus MN/m^2	Elongation at break (%)	Crosslink density $\times 10^4$ mole cm^{-3}	Shore A hardness
IPN-1	0.75	8.70	94	0.652	96
IPN-2	0.88	9.81	80	0.664	81
IPN-3	1.07	14.71	88	0.669	92
IPN-4	1.96	71.83	78	1.213	86
IPN-5	2.35	89.69	52	1.307	83
IPN-6	2.67	127.48	70	1.398	91
IPN-7	2.94	151.70	74	2.123	85
IPN-8	3.51	186.01	80	2.470	80
IPN-9	3.92	235.44	64	2.598	78
PU (100%)	1.37	6.47	72	14.30	86
PMMA (100%)	2.17	154.74	12	Deteriorates	99



IPN-1 IPN-4

FIGURE 1 Transmission electron micrographs of:

phase domain of the initial component, i.e., polyurethane, becomes continuous phase during the synthesis of IPNs by interpenetration of the second component.[5] The transmission electron micrographs of selected IPN-1, IPN-4 and IPN-7 in the present investigation are shown in Figure 1. The morphology of these IPNs has indicated that there is an appreciable mixing of PU and PMMA component networks. As a result the initial polyurethane phase controls the phase separation.[13,16] In the present IPNs, PU is continuous phase in which second component PMMA is entangled in the matrix of polyurethane. This is agreement with the literature data.[17]

Thermal behaviour

Thermogravimetric analysis of IPNs has revealed that the IPNs possessed much greater thermal stability than their less stable (PMMA) component network.[18–20]

TABLE III

Thermogravimetric data of PU/PMMA IPNs

Polymer code	Percent weight loss (±2%) at a different temperature °C								Activation energy kcal mol^{-1}
	250	300	350	400	450	500	550	600	
IPN-1	—	6	20	39	68	83	90	98	19.3
IPN-2	—	3	16	31	58	78	85	97	21.2
IPN-3	—	3	14	28	54	73	89	95	18.4
IPN-4	—	6	24	39	62	76	81	96	19.6
IPN-5	—	3	20	35	58	75	82	93	17.5
IPN-6	—	—	14	29	51	66	71	90	16.5
IPN-7	—	6	15	31	52	76	84	97	14.9
IPN-8	—	2	18	28	45	65	76	89	19.3
IPN-9	—	2	15	27	39	50	57	71	13.3
PU (100%)	—	—	19	30	40	66	73	91	16.9
PMMA (100%)	7	35	80	97	—	—	—	—	14.8

The thermal stabilities of PU/PMMA IPNs were assessed on the basis of percentage weight retention at different temperatures from TG thermograms and compared to those of homopolymers: 100% polyurethane and 100% poly(methyl methacrylate) respectively. The IPNs are found to be stable up to 290°C, lose their weight rapidly around 450°C and decompose completely beyond 600°C (Table III). It is evident that the difference in thermal stability of component homopolymers I (PU) and II [poly(methyl methacrylate)] is not reflected in an additive manner in the thermal stability of their IPNs. Surprisingly, their thermal stability is close to that of the more stable component (PU). Similar effects have been previously reported.[21]

Acknowledgement

Dr. Douglas Hourston, Director, Polymer Centre, Lancaster University, U.K., is gratefully acknowledged for useful research facilities and discussion.

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