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Preparation and properties of semi-interpenetrating polymer networks based on polyurethane ionomer/polyvinyl chloride

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Semi-Interpenetrating polymer networks (IPNs) of polyurethane anionomers (IPU) with Polyvinylchloride (PVC) were synthesized and characterized by Fourier-transform infrared spectrophotometer (FT-IR), thermogravimetric analysis (TGA) and mechanical studies. The synthesized semi-IPNs were found to be compatible. The hydrogen bonding interactions and the thermal stabilities are discussed based on FT-IR analysis and thermogravimetric analysis (TGA). Tensile strength and hardness increase with increasing NCO/OH ratio and ionic content of the polyurethanes. © *2000 Kluwer Academic Publishers*

1. Introduction

Interpenetrating polymer networks (IPNs) are a type of polymer alloys consisting of two or more polymer networks. In the IPN system, two networks are fixed together by permanent entanglements. Several methods are used to synthesise IPNs [1, 2]. Simultaneous IPNs, Sequential IPNs and latex IPNs are the main types [3].

IPNs of different types with a wide range of properties have been reported elsewhere [4–6]. In our earlier work, we have reported the morphological and mechanical properties of ternary semi-IPNs based on nitrocellulose [7], Poly(vinyl chloride-co-vinyl acetate)[8] and polyurethane derived from castor oil [9]. Most of the polymer pairs are generally immiscible or partially miscible. For improving the miscibility and thus the degree of interpenetration of the components, one often tries to introduce attractive interactive groups between the components. For example, Frisch *et al.* prepared IPNs from polymer with ionic groups [10]. The introduction of relatively small number of ionic moieties into polyurethane backbone significantly alters the properties of the materials [11–13]. In the present study, ionomeric IPNs are prepared with the PVC and PU anionomers and their extent of interaction examined through FT-IR, thermal and mechanical studies.

2. Experimental

2.1. Materials and preparation

Toluene diisocyanate (TDI; System name: methyl phenylene diisocyanate) (a mixture of 80% 2,4 and 20% 2,6 isomers) of specific gravity 1.225 was supplied by Fluka, polycaprolactone diol (PCDL) (M.Wt of 2000), was dried at 80°C under vacuum for 4 hrs , dibutyltin dilaurate (DBTDL) and polyvinylchloride (PVC) Aldrich were used as received. 2,4-dihydroxy benzoic acid (DHBA), triethylamine (TEA) and Tetrahydrofuran (THF) S. D. fine Chem, India were purified and used.

Polyvinyl chloride was dissolved in THF and polyurethane prepolymer was prepared at 70°C in an inert atmosphere in a stirred-glass reaction vessel with reflux condenser. Polycaprolactone diol (PCDL) was added into the vessel containing PVC in THF and heated up to 50°C. Then the calculated amount of TDI in THF was added slowly, to yield NCO terminated prepolymers. When the NCO content of 5.51% was reached as determined by the di-*n*-butylamine method, calculated amount of DHBA in THF was added slowly to the prepolymer at 50°C. The reaction temperature was raised to 70°C and continued till all the NCO groups were reacted as confirmed by the disappearance of IR absorption at 2270 cm^{-1}. Quaternization of the -COOH groups in DHBA was carried out by the addition of TEA (*Scheme*). The reaction mixture was then cast on a glass mold and heated under vacuum at 110°C for 2 hours and dried.

2.2. FT-IR analysis

Thin films were cast from the IPN reaction mixture over glass plates for FTIR studies after complete drying, the films were taken out without distortion and FT-IR spectra were recorded using Nicolet Impact 400 FT -IR spectrophotometer.

2.3. Morphological studies

Morphological features were deduced from Reichert-Jung optical microscope with a magnification at 100×. IPN films were placed between two thin glass plates, and photographs were taken using a Pentax 35 mm camera.

2.4. Thermal studies

The thermal stability of the synthesized IPNs was determined by Mettler TA 4000 system at a heating rate of 20°C/min. in N_2 atmosphere. The samples were heated from room temperature to 600°C.

2.5. Swelling studies

Swelling was determined by a known weight of specimen (W_0) immersed in toluene as solvent at room temperature. After obtaining constant weight of the swollen specimen (W^1) the swelling ratio (q) is calculated as follows.

$$q = \frac{(W^1 - W_0)}{W_0} \times 100$$

2.6. Mechanical studies

Dumb-bell shaped specimens, with the narrow part of which was 2.2 cm long and 0.4 cm wide, were cut from the films for tensile measurements and mounted on cardboard. The tensile properties were measured on an Instron, Universal Testing Machine [UTM], (UK, Model 4501), at a rate of 100 mm/min. The test was carried out as per ASTM D: 638 (1977). Hardness was measured as per ASTM D: 2240 test procedure.

3. Results and discussion

The polyurethane prepolymers were synthesized by reacting with TDI and PCDL. The ionic groups were attached to the polyurethanes, referred to as polyurethane anionomers by using dihydroxy benzoic acid with triethylamine. The codes and composition of the IPNs are given in Table I.

Infra-red spectra showed the formation of carboxylic salt, which is the driving force to improve the compatibility between polyurethane anionomer and polvinylchloride IPNs. The carbonyl groups of -COOH shifts from 1748 cm^{-1} to 1580 cm^{-1}, this may be due to the ionomer formation. The spectra of polyurethane anionomer and PVC are given in Fig 1. Broad peaks at 3250–3300 cm^{-1} indicate the presence of inter and intra molecular hydrogen bonding. The C-Cl stretching frequency was observed at 616 cm^{-1} and 692 cm^{-1} for PVC. A shift in the amide band from 1533 cm^{-1} to 1520 cm^{-1} may be either due to dipole-dipole interaction with C-Cl in PVC or H-bonding with hydrogen atom in PVC as shown in Fig 2.

TABLE I Codes and composition of IPU/PVC IPNS

Sample code	NCO/OH ratio	Compositions IPU	PVC	Hard segment (mol %)
IPN 09	0.9	75	25	20
IPN 10	1.0	75	25	21
IPN 11	1.1	75	25	22
IPN 12	1.2	75	25	23
IPN 13	1.3	75	25	23.5
IPN 14	1.4	75	25	24
IPN 15	1.5	75	25	25
IPN 16	1.6	75	25	26
IPN 17	1.7	75	25	27
IPN 18	1.8	75	25	28
IPU 10	1.0	—		—

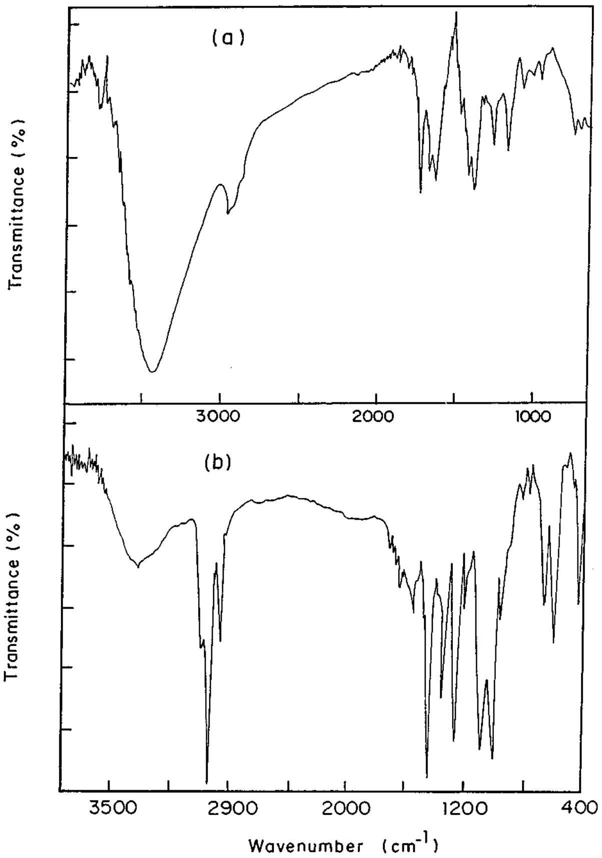

Figure 1 FT-IR spectra of (a) IPU and (b) PVC.

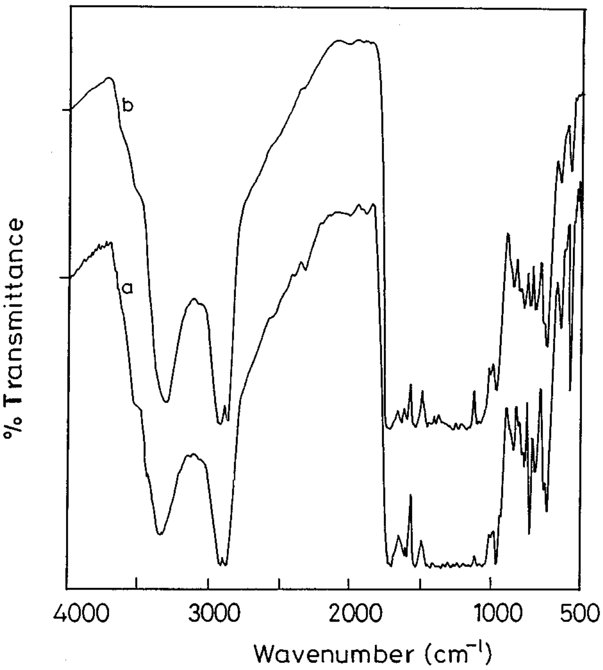

Figure 2 FT-IR spectra of (a) IPN 11 and (b) IPN 13.

The morphology of synthesized IPNs shows cellular structure. If the two networks are synthesized simultaneously, a different morphology can be expected. Morphological changes take place when introducing

TABLE II Mechanical data of IPU/PVC-IPNS

Sample code	NCO/OH ratio	Ionic content (wt%)	Stress at break (MPa)	Strain (%)	Hardness Shore (Å)	Thickness (mm)
IPN 09	0.9	6.9	3.08	690	65.13	0.39
IPN 10	1.0	6.7	3.78	674	62.83	0.37
IPN 12	1.2	6.3	3.273	663	68.50	0.41
IPN 13	1.3	6.2	3.84	516	72.40	0.44
IPN 15	1.5	5.9	6.83	508	80.66	0.49
IPN 17	1.7	5.7	6.97	467	79.33	0.35
IPN 18	1.8	5.5	8.56	595	81.0	0.35
PVC	—	—	16.78	15	84.16	0.49

TABLE III Thermal data of IPU/PVC-IPNS

		% Weight loss at various temperatures (°C)							
Sample code	NCO/OH ratio	250	300	350	400	450	500	550	600
IPN 09	0.9	3.2	10.0	20.7	54.5	67.5	82.5	90.9	99.3
IPN 12	1.2	1.9	16.6	22.4	46.5	65.6	81.4	87.6	96.1
IPN 15	1.5	2.3	5.7	28.2	45.5	65.5	81.2	87.2	96.0
IPN 18	1.8	2.5	15.8	24.6	45.4	66.2	80.5	81.1	96.0

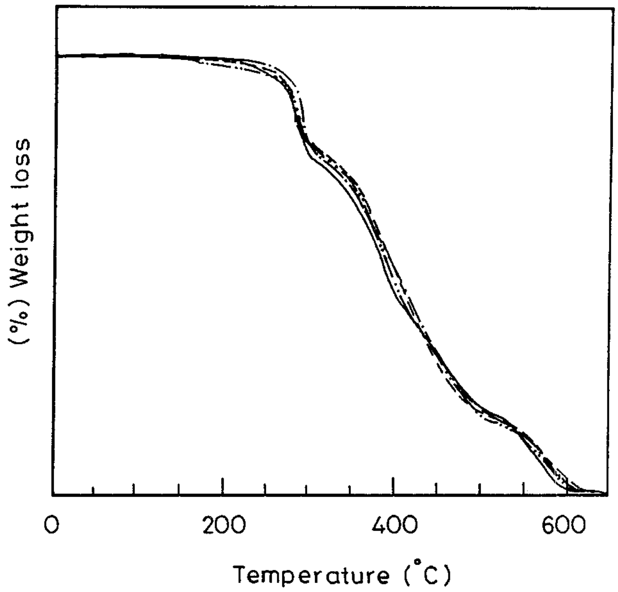

Figure 3 Thermograms of IPN 09(—), IPN 12(−−), IPN 15(−·−) IPN 18(−··−).

ionic groups into the polyurethane in IPU/PVC IPNs. We attempted to use the ionic interaction to control the IPN miscibility in order to obtain a semi-miscible morphology.

The thermal stability of the IPNs and some of their homopolymers were characterized by the initial and maximum decomposition temperature from TGA as shown in Fig. 3 and their decomposition temperatures are listed in Table II. IPNs decompose at higher temperatures than their individual polymers. Fig. 3 shows three decomposition stages of the IPNs, initial decomposition starts at 250°C and complete dissociation at 550°C. It is evident that the thermal stability of the IPNs is much greater than their homopolymers, and this enhancement of thermal stability may be due to interpenetration. Increasing the NCO/OH ratio, the thermal stability of the synthesized IPNs increases, because of the compatibility between hard and soft segment of ionomeric polyurethane (IPU) and polyvinyl chloride.

Tensile strength and percent elongation test results are listed in Table III. As a result of an increase in the ionic content of PUs and increase in the physical entanglement and adhesion at phase boundaries due to interpenetration the enhancement of tensile strength of the synthesized semi-IPNs were noticed. Increasing the NCO/OH ratio, tensile strength and hardness increases. Percent elongation decreases with increasing ionomeric hard segments. Mechanical properties of IPU/PVC-IPNs show improved miscibility.

The swelling analysis of all the semi-IPNs was carried out in toluene at different time intervals. The swelling ratio decreases with increasing NCO/OH ratios, due to high degree of cross-linking. With increasing NCO/OH ratio, the average molecular weight between cross-links (M_c) decreases. M_c depends on the reactivity of the N-H hydrogens.

4. Conclusions

All the ionomeric IPNs are obtained as tough films. The effect of ionic group interaction on the micrograph and tensile properties of the semi-IPNs has been described. Tensile strength and hardness increase with increasing ionomeric hard segment and NCO/OH ratios. Hydrogen bonding interaction and thermal stability of the IPNs increase with increasing ionomeric content of the polyurethane. IPU/PVC IPNs are compatible.

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