

Interpenetrating polymer networks based on polyol modified castor oil polyurethane and poly(2-hydroxyethylmethacrylate): Synthesis, chemical, mechanical and thermal properties

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Abstract. Interpenetrating polymer networks (IPNs) of glycerol modified castor oil polyurethane (GC-PU) and poly[2-hydroxyethylmethacrylate] (PHEMA) were synthesized using benzoyl peroxide as initiator and N,N-methylene bis acrylamide as crosslinker. GC-PU/PHEMA interpenetrating polymer networks were obtained by transfer moulding. These were characterized with respect to their resistance to chemical reagents and mechanical properties such as tensile strength, per cent elongation and shore A hardness. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were undertaken for thermal characterization. The changes in NCO/OH ratio and GC-PU/PHEMA composition on the properties of the IPNs were studied.

Keywords. Transesterification; glycerol modified castor oil polyurethane; poly[2-hydroxyethyl methacrylate].

1. Introduction

Interpenetrating polymer networks (IPNs) are a new class of polymer blends in network form in which at least one component is polymerized and/or crosslinked in the immediate presence of the other (Sperling 1981). IPNs possess several interesting characteristics in comparison to normal polyblends, because the varied synthetic techniques yield IPNs of such diverse properties that their engineering potential spans a broad gamut of modern technology (Sperling 1981). IPNs from castor oil based polyurethane and methacrylate polymers have been reported by many researchers (Carraher and Sperling 1981; Sperling *et al* 1981; Sperling and Manson 1983; Tan and Xie 1984; Sperling 1986, 1993; Patel and Suthar 1987, 1990; Nayak *et al* 1993; Mallu *et al* 2000). Though voluminous literature is available on modified castor oil polyurethane, the study of IPNs of modified castor oil polyurethane has not been paid due attention.

As a part of our free radical polymerization studies (Sherigara *et al* 1999; Rai *et al* 2000; Yashoda *et al* 2000, 2001; Prashantha *et al* 2001), we present here the synthesis of sequential IPNs from glycerol modified castor oil polyurethane and poly(2-hydroxyethylmethacrylate). Evaluation of their chemical, mechanical and thermal properties and the effect of NCO/OH ratio of the polyurethane

prepolymer (PPU) on these properties have been presented.

2. Experimental

2.1 Characterization methods

2.1a Infrared spectra: Infrared spectra of the synthesized IPNs in KBr pellets were obtained from Shimadzu FTIR 4200 series spectrophotometer. Whereas in case of PPU, being a liquid, a thin film was cast over the NaCl block and its FTIR was recorded.

2.1b Glass transition temperatures: The glass transition temperatures were determined on a Mettler TA4000 DSC. Temperature and energy calibration were carried out with indium. Samples weighing between 12 and 15 mg were used in all cases. The scan rate was 10°C/min in air. The glass transition temperature (T_g) was calculated as the inflection point of the jump of heat capacity.

2.1c Mechanical properties: The tensile strength and elongation at break were measured at room temperature using Instron Houns-Field universal testing machine model 4204 as per ASTM D-638 method. Hardness measurements were made on Shore A hardness test apparatus using ASTM-2240 method.

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2.1d *Resistance to chemical reagents*: Acid, alkali and solvent resistance were estimated according to ASTM-D-543-67 method. Samples were hung in the reagent for seven days and tested for change in weight and for their film appearance.

2.1e *Thermogravimetric analysis*: Thermograms were obtained on Mettler TA 4000 TGA at a heating rate of 10°C/min in air.

2.2 Materials

British Standard Specification (BSS) grade castor oil (hydroxyl value 160–162 mg KOH/g) was used without any purification. Hexamethylene diisocyanate (HMDI) and 2-hydroxyethylmethacrylate (HEMA) were obtained from E. Merck (Germany). Triethanolamine and benzoyl peroxide were obtained from S.D. Fine (India). N,N-methylene bis acrylamide was procured from Loba Chemie (India). Benzoyl peroxide was recrystallized from chloroform and monomer, HEMA was freed from the inhibitor before use. All other reagents were of analytical grade and used without further purification.

2.3 Synthesis

2.3a *Transesterification castor oil using glycerol (GC-polyol)*: A resin kettle equipped with thermometer, stirrer, nitrogen inlet and reflex condenser were charged with one equivalent each of castor oil and glycerol along with catalyst litharge (0.05%). Reaction was carried out at 240–250°C for 2 h. Progress of the reaction was monitored by thin layer chromatography (Das and Nirvan 1994) (solvent system: petroleum ether, diethylether and acetic acid in the ratio of 85 : 15 : 1 by volume, respectively). The resultant polyol was dried at 80°C under vacuum and had hydroxyl value 290 mg KOH/g, acid value 2.0 mg KOH/g and the viscosity (at 30°C) 483 cps (Athawale and Kolekar 1998) (scheme 1).

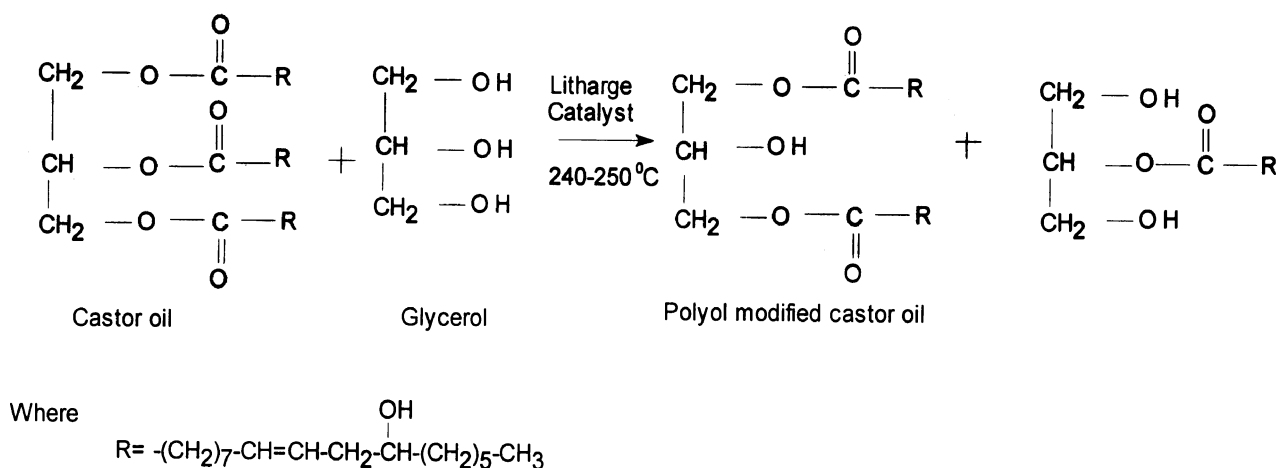
2.3b *Polyurethane prepolymer (PPU)*: A reaction kettle, under dry nitrogen, was charged with HMDI and GC-polyol of varying ratio of NCO/OH were added slowly with stirring. The reaction was carried out at 45°C for 2 h.

2.3c *Sequential interpenetrating polymer network (IPNs)*: IPNs were synthesized by charging the isocyanate terminated polyurethane prepolymer in different proportions and different NCO/OH ratio along with 1% triethanolamine (for chain extension and curing) to the mixture of HEMA, 1% N,N-methylene bis acrylamide crosslinker and benzoyl peroxide (0.5% based on HEMA) in a reaction kettle. The mixture was stirred at room temperature for 15 min to form a homogeneous solution. The temperature was increased to 60°C to initiate HEMA polymerization. After stirring for 1 h, the solution was poured into a glass mold kept in a preheated oven maintained at 60°C. It was kept at this temperature for 24 h and at 120°C for 4 h to facilitate the complete network formation. The film thus formed was cooled slowly and removed from the mold. Nine IPNs were synthesized by this method (table 1).

3. Results and discussion

3.1 Infrared spectroscopy (IR)

IR spectra of PPU showed characteristic absorption at 1740 cm⁻¹ and 3410 cm⁻¹ corresponding to urethane amide (–NH stretching). As the prepolymer is isocyanate terminate, an intense and sharp band due to NCO is observed at 2260 cm⁻¹. IR spectra of IPNs showed broad peak at 3220 cm⁻¹ corresponding to the OH stretching of the urethane linkage with finite contribution from extensive hydrogen bonding in the system. Further, IPNs does not show any band at 2260 cm⁻¹ corresponding to NCO



Scheme 1.

because of the reaction of curing agent, 1% triethanolamine with terminated NCO. Therefore, there would be no NCO left for the formation of chemical linkage between NCO and OH group of PHEMA or HEMA.

3.2 Glass transition temperatures (T_g)

The glass transition temperatures of synthesized IPNs lie between the T_g of the PPU and PHEMA (table 2). The appearance of single T_g indicated the formation of an interpenetrating polymer networks and ruled out the formation of any phase separation. With increase in PHEMA concentration in the IPN the T_g of the IPN shifted towards the T_g of PHEMA.

3.3 The compatibility factor (q)

The compatibility factor value is presented in table 2. It was calculated from a theoretical equation of DiBeneditto modified by Xiao *et al* (1983). A decrease in q implies greater compatibility caused by increasing NCO/OH ratio.

3.4 Mechanical properties

Mechanical properties such as elongation at break (%), tensile strength and shore A hardness are furnished in table 3. The NCO/OH has considerable effect on the molecular weight of the PPU and the crosslinking density of the resultant product. It also influences the compatibility between polyurethane and PHEMA, hence the properties of IPNs. High NCO/OH leads to low molecular weight of PPU (Xiao *et al* 1983). From table 3 it is observed that tensile strength and hardness increases whereas, elongation decreases with increasing NCO/OH ratio probably due to low molecular weight of PPU at high NCO/OH ratio. As a result, PU/PHEMA IPNs exhibit higher tensile strength and hardness. However, an exactly reverse trend is observed with increasing PU

composition in PU/PHEMA IPNs. It is observed that glycerol modified castor oil polyurethane and PHEMA IPNs exhibited better mechanical properties as compared to unmodified castor oil polyurethane/PHEMA IPNs (Nayak *et al* 1997). This may be due to the fact that glycerol modification of castor oil results in more crosslinked and stiffer IPNs possessing better mechanical properties over that of unmodified castor oil polyurethane/PHEMA IPNs.

3.5 Chemical resistance

The percentage weight loss of IPNs were determined in H_2SO_4 , CH_3COOH , HCl , HNO_3 , $NaCl$ and $NaOH$ etc and the results are furnished in table 4. All the IPNs show excellent acid and alkali resistance as compared to unmodified castor oil polyurethane/PHEMA IPNs (Nayak

Table 2. Glass transition temperatures (T_g) of modified castor oil polyurethane/PHEMA IPN systems.

Composition of IPNs PU/PHEMA (wt% ratio)	NCO/OH	T_g (K)		
		By DSC	(Calcd)*	Compatibility factor (q)**
100/0	–	223	–	–
0/100	–	381	–	–
IPN-1	2:0	340	344	0.0117
IPN-2	2:0	323	327	0.0123
IPN-3	2:0	307	312	0.0130
IPN-4	2:2	341	344	0.0087
IPN-5	2:2	324	327	0.0092
IPN-6	2:2	309	312	0.0097
IPN-7	2:4	342	344	0.0058
IPN-8	2:4	325	327	0.0061
IPN-9	2:4	310	312	0.0064

* $T_g = W_1T_{g1} + W_2T_{g2}$, W_1 and W_2 are the weight fractions of PU and PHEMA, respectively.

**Compatibility factor (q) was calculated using the equation: $T_g(DSC) - T_g(calcd)/T_g(calcd) = -q/1 + q$.

Table 1. Data on feed composition of individual IPNs.

Sample code	NCO/OH	Content of polyurethane (wt%)	Content of monomer (wt%)
IPN-1	2:0	25	75
IPN-2	2:0	35	65
IPN-3	2:0	45	55
IPN-4	2:2	25	75
IPN-5	2:2	35	65
IPN-6	2:2	45	55
IPN-7	2:4	25	75
IPN-8	2:4	35	65
IPN-9	2:4	45	55

Table 3. Data on mechanical properties.

Sample code	Tensile strength (MPa)	% Elongation at break	Shore A hardness
IPN-1	29.50	120.0	84
IPN-2	28.42	104.0	81
IPN-3	22.63	92.0	78
IPN-4	34.62	99.0	90
IPN-5	29.64	80.4	88
IPN-6	27.58	58.0	85
IPN-7	37.50	94.6	94
IPN-8	36.91	87.2	90
IPN-9	32.60	92.3	89

Table 4. Chemical resistance test (% weight loss on treatment with different chemical reagents).

Chemical reagents	IPN-1	IPN-2	IPN-3	IPN-4	IPN-5	IPN-6	IPN-7	IPN-8	IPN-9
25% CH ₃ COOH	3.1240	3.0620	3.4310	3.040	3.2340	3.8040	3.1100	3.3240	3.7240
25% H ₂ SO ₄	1.1806	1.2360	1.2410	1.160	1.7620	1.4206	1.1710	1.6240	1.1140
25% HCl	0.6804	0.6511	0.6644	0.630	0.6200	0.6550	0.6640	0.7810	1.7744
5% HNO ₃	0.5410	0.6420	0.4912	0.5510	0.4714	0.4982	1.6440	0.5594	0.6110
10% NaOH	0.5040	0.5410	0.6010	0.5410	0.5510	0.5504	0.5514	0.5591	0.6810
MEK	15.48	16.10	17.24	14.20	14.10	14.72	13.120	13.141	13.244
CCl ₄	20.14	19.22	17.26	12.14	11.26	11.18	10.260	10.78	9.980
Toluene	10.12	8.40	8.18	8.00	7.28	7.01	7.244	6.68	5.928

IPNs are swelled in solvents like methyl ethyl ketone (MEK), CCl₄ and toluene.

et al 1997). It is observed that IPNs irrespective of NCO/OH ratio and PU/PHEMA composition, are stable in acid and alkali whereas, in methyl ethyl ketone, chloroform, carbon tetra chloride and toluene IPNs showed a varying amount of swelling.

3.6 Thermal analysis

From the thermal analysis it is observed that all the nine IPNs decompose within 2–4% weight in the temperature range 0–200°C. About 10% weight loss occurs at 300°C and about 40% weight loss occurs at 400°C. There is a rapid weight loss from 40–90% in the temperature range of 400–500°C. This is due to the decrosslinking of the two network forms of the IPNs (Sperling 1986). In this region, the monomer attached to the backbone of the polyurethane network is most probably detached by a free radical mechanism from the trunk of the main constituent polymer. The final weight loss occurs because of the breakage of the bonds of the homopolymer (PHEMA).

4. Conclusion

Interpenetrating polymer networks prepared from PHEMA and the glycerol modified castor oil polyurethane showed excellent chemical resistance, hardness, elongation, tensile strength properties and higher compatibility. Hence, it can be concluded that using the IPN concept, it is possible to design the most desirable material for a specific end use requirement.

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