

Interpenetrating Polymer Networks Composed of Castor Oil-Based Polyurethane and 2-Hydroxy-4-Methacryloyloxy Acetophenone

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ABSTRACT: 2-Hydroxy-4-methacryloyloxy acetophenone, a vinyl monomer, was prepared by reacting 2,4-dihydroxy acetophenone with methacryloyl chloride in presence of triethylamine in methyl ethyl ketone. The vinyl monomer was characterized by Fourier transform infrared spectra and Proton magnetic resonance spectra to confirm the various functional groups in the monomer. The liquid prepolyurethanes obtained from castor oil, toluene-2,4-diisocyanate, and hexamethylene diisocyanate, varying the NCO/OH ratio, were interpenetrated with the above vinyl monomer containing ethylene glycol dimethacrylate, using radical polymerization initiated by benzoyl peroxide. The interpenetrating polymer networks were obtained as transparent tough films by transfer moulding. They were characterized for thermal behavior with evaluation of kinetic parameters. From the kinetic data, it is clear that the degradation process of the interpenetrating networks is slower in the temperature range of 270–390°C and faster in the range of 390–510°C. Thermal stability also varies with the change in diisocyanates. The morphology was examined by scanning electron microscopy (SEM). The resulting two-phase morphology was found to be sensitive to change in monomer concentration. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 75: 1487–1492, 2000

Key words: castor oil; hexamethylene diisocyanate; interpenetrating polymer networks; morphology; polyurethane; thermal property; toluene-2,4-diisocyanate; vinyl monomer

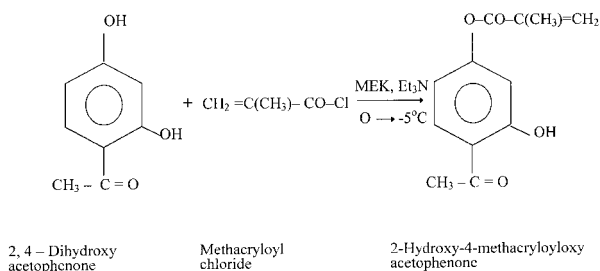
INTRODUCTION

Interpenetrating polymer networks (IPNs) composed of two chemically different components are the youngest polymers used as engineering materials. IPNs represent a new approach to the problem of mutual incompatibility of polymers. The trifunctional castor oil molecule used for polyurethane (PU) synthesis provides low molecular weight as the molecular weight build up may be influenced by the secondary hydroxyl groups flanked by alkyl groups.^{1,2} The low mo-

lecular weight oligomers (PU) have been successfully utilized in the synthesis IPNs.^{3–5} Notable research on IPNs and their utility have been substantiated by the works of Sperling^{6–9} and Frisch.^{10–13} This communication deals with the synthesis and characterization of a vinyl monomer¹⁴ containing a bulky aromatic ring and some castor oil-based IPNs prepared from it, and the study of thermal impact of bulky aromatic ring of the vinyl monomer. As the formation of IPN involves two steps, the degree of cross-linking induces changes in the properties of IPN. The importance and effect of cross-linking and type of monomer, are very much established by the morphologic study.

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Scheme 1

EXPERIMENTAL

Materials

All the chemicals were of analytical grade. Castor oil was obtained locally and dried in a vacuum oven at 100°C for 2 h. Its hydroxyl value (2.83 meq/g) was estimated by standard procedure. Benzoyl peroxide was recrystallized from chloroform-methanol mixture. Benzoyl chloride essential for the preparation of methacryloyl chloride was used without further purification. Methacrylic acid and methyl ethyl ketone (MEK) were used after distillation. Ethylene glycol dimethacrylate (EGDM), hexamethylene diisocyanate (HMDI), and toluene-2,4-diisocyanate (TDI) from E. Merck (Calcutta, India) were used without further purification. 2,4-Dihydroxy acetophenone was obtained from Sisco Research Laboratories (Mumbai, India). Methacryloyl chloride was prepared as reported.¹⁵

Preparation of 2-Hydroxy-4-Methacryloyloxy Acetophenone

2,4-Dihydroxy acetophenone (7.6 g), triethyl amine (9.5 mL), MEK (100 mL), and hydroquinone (0.5 g) were taken in a three-necked flask equipped with a magnetic stirrer, thermometer, and a separating funnel. The contents were cooled to 0 to -5°C. Then methacryloyl chloride (3.4 mL in 50 mL of MEK) was added drop-wise with constant stirring and cooling. The reaction mixture was then stirred for another 2 h at room temperature and the quaternary ammonium salt was filtered off. The filtrate was thoroughly washed with distilled water, dried over anhydrous sodium sulfate, and MEK was evaporated. The crude 2-hydroxy-4-methacryloyloxy acetophenone was recrystallized from petroleum ether (melting point: 59–62°C). The reaction path is shown in Scheme 1.

Preparation of Polyurethane

Castor oil (4.66 g, 0.005 mol) was reacted with HMDI (1.9 g, 0.0113 mol) to maintain a NCO/OH

ratio 1.6. A similar reaction procedure was followed with varying the amount of TDI maintaining NCO/OH ratio of 1.6. This resulted in an isocyanate-terminated polyurethane. The reaction was carried out at 45°C with continuous stirring for 1 h in a nitrogen atmosphere. The polymer was isolated as thick syrup. Following the above procedure, other PU with varying NCO/OH ratios were prepared.

IPN Synthesis

The polyurethane was taken in different proportions into a round, bottom flask. A mixture of 2-hydroxy-4-methacryloyloxy acetophenone, EGDM (1% based on methacrylate weight in MEK, and benzoyl peroxide (0.5%) were added. The mixture was stirred at room temperature for 10 min to form a homogeneous solution. The temperature was then raised to 60°C to initiate polymerization. After stirring for 1 h, the solution was poured into glass mold and kept in an air-circulated 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. Six IPNs prepared out of different diisocyanates by changing the NCO/OH ratio and PU/HMA are referred to as IPN-1 to IPN-6.

Measurements

Fourier transform infrared (FTIR) spectrum of the monomer was recorded with a Nicolet Magna-IR 550 Series II spectrometer on KBr pellets. ¹H NMR spectrum of the monomer was scanned in CDCl₃ with the help of Bruker dpx 300 spectrometer at 300 MHz. Thermal analysis was carried out using Perkin-Elmer 7-series thermal analyzer at a heating rate of 10°C/min. Scanning electron micrographs (SEM) were taken employing a Cambridge Stereoscan 250 MK III model electron microscope.

CHARACTERIZATION

FTIR Spectra

The FTIR spectrum of 2-hydroxy-4-methacryloyloxy acetophenone (Fig. 1) shows a peak at 3084 cm⁻¹, which may be assigned to phenolic—OH stretching. The peak is lower than expected because of intramolecular hydrogen bonding, which is presumed to be formed with the ketonic oxygen. The C—O stretching for phenol is characterized

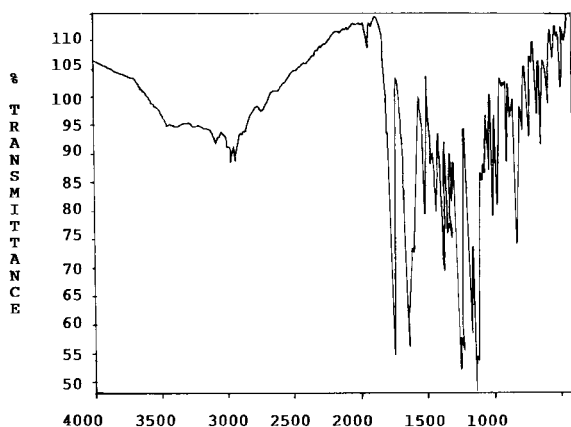


Figure 1 Fourier transform infrared spectrum of 2-hydroxy-4-methacryloyloxy acetophenone.

by the presence of a peak at 1241 cm^{-1} . The $\text{C}=\text{O}$ stretching for ester and ketonic groups are characterized by the presence of strong peaks at 1749 and 1685 cm^{-1} respectively. This monomer was confirmed to be aromatic by the presence of medium peaks for $\text{C}=\text{C}$ stretching of aromatic ring at 1638 , 1502 , and 1415 cm^{-1} . Medium peaks at 3000 and 2927 cm^{-1} are due to $\text{C}-\text{H}$ stretching of methyl group. The strong peaks at 1175 and 1138 cm^{-1} are due to $\text{C}-\text{C}(=\text{O})-\text{O}$ stretch and $\text{O}-\text{C}-\text{C}$ asymmetric stretching respectively as the $\text{C}-\text{O}$ stretching vibrations of esters composed of the above two asymmetric coupled vibrations.

Proton Magnetic Resonance Spectra

From the proton magnetic resonance spectrum (Fig. 2) of 2-hydroxy-4-methacryloyloxy acetophenone, a sharp singlet at 12.3 ppm confirms the presence of $-\text{OH}$ group that is almost completely

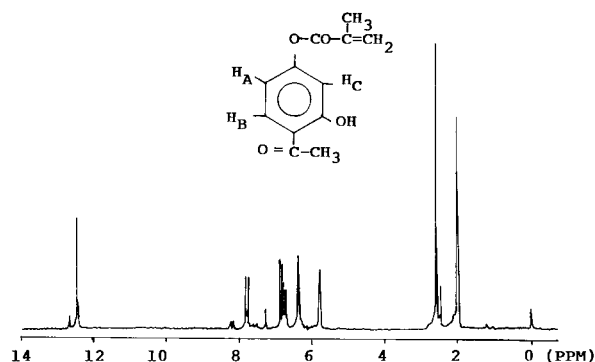


Figure 2 ^1H NMR spectrum of 2-hydroxy-4-methacryloyloxy acetophenone.

invariant with concentration because of intramolecular hydrogen bonding with the carbonyl group. Singlet at 6.3 ppm is due to $-\text{CH}_3$ proton of side chain. Singlets at 5.7 and 2.6 ppm correspond to $-\text{CH}_2$ protons and $-\text{CH}_3$ protons of the carbonyl group respectively. Three nonequivalent protons of the benzene ring resonate at different δ values. H_A proton appears as a multiplet at 6.7 ppm , proton H_B as a doublet at 7.7 ppm , and H_C proton appears as a singlet at 7.2 ppm .

Thermal Analysis

The kinetics of thermal decomposition of IPN have been studied by using Lotus 1-2-3 package developed by Rao and Mohanty¹⁶ using Coats and Redfern method for the determination of kinetic parameters.

Coats and Redfern method is given by the following equation:

$$\ln[g(\alpha)/T^2] = \ln \frac{A \cdot R}{\beta \cdot E} \left(1 - \frac{2RT}{E} \right) \cdot \frac{E}{2.3R} \frac{1}{T}$$

Table I Feed Composition and Thermal Decomposition Data of IPNs

Sample Code	System ^a	NCO/OH	PU/HMA	% Wt Loss Up to Various Temperatures °C		
				150–270	270–390	390–510
IPN-1	CO + TDI + HMA	1.6	25 : 75	15	42	87
IPN-2	CO + TDI + HMA	1.6	35 : 65	13	40	84
IPN-3	CO + TDI + HMA	1.8	25 : 75	12	39	85
IPN-4	CO + TDI + HMA	1.8	35 : 65	14	37	83
IPN-5	CO + HMDI + HMA	1.6	25 : 75	22	47	92
IPN-6	CO + HMDI + HMA	1.8	25 : 75	20	44	90

^a CO = castor oil; TDI = toluene-2,4-diisocyanate; HMA = 2-hydroxy-4-methacryloyloxy acetophenone; HMDI = hexamethylene diisocyanate.

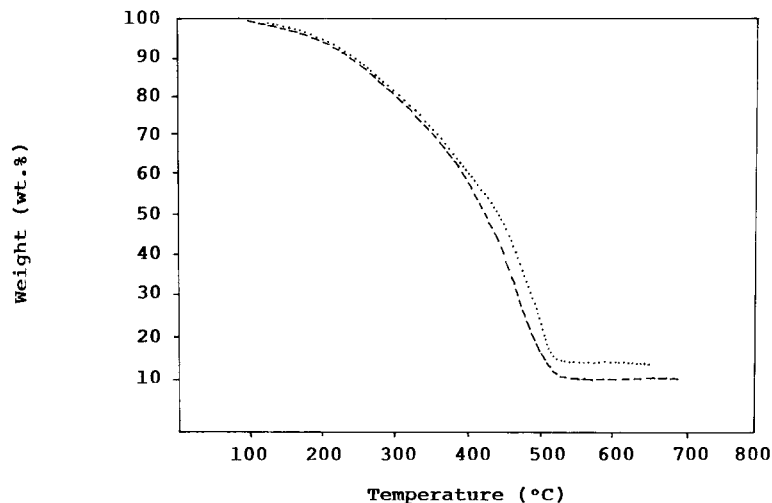


Figure 3 Thermogravimetric curves of IPN-1 (---) and IPN-2 (....).

where α is the rate of heating, β is a constant, R is the universal gas constant, A is the collision frequency, and E is the activation energy. E is calculated from the straight line obtained by plotting $\ln(\alpha/T^2)$ versus $1/T$ and $\ln A$ can be obtained from the intercept.

The chemical composition and thermal decomposition data of IPNs are given in Table I. The patterns of decomposition at various temperatures are represented in Figures 3–5. From the thermograms it is clear that all IPNs decompose in three steps. Taking a close look at the percentage of thermal decomposition at various temperature ranges, a remarkable change is noted in the extent of decomposition for the two systems involving two different diisocyanates. From the

thermograms it is observed that for the IPNs prepared from TDI-based polyurethanes, the initial weight loss occurs at a comparatively low temperature than that in the case of HMDI-based polyurethanes. In case of IPN-1, only a 15% loss in weight is observed in the temperature range of 150–270°C, whereas 22% of weight loss is observed for IPN-5. In determining the kinetic parameters for the thermal degradation process with the help of Coats and Redfern method, the best out of 14 models having R^2 value close to unity has been chosen. From Table II it is seen that the activation energy values for the TDI-based IPNs are much higher than HMDI-based IPNs. For both the systems the initial slowness of the degradation process is due to the loss of some

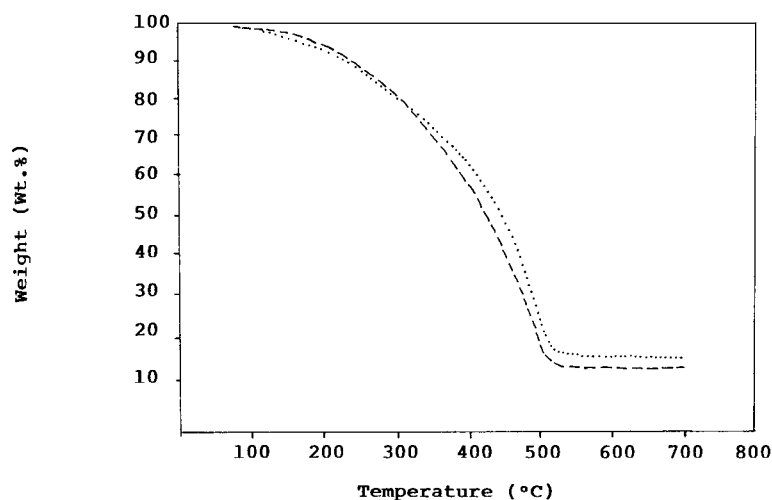


Figure 4 Thermogravimetric curves of IPN-3 (---) and IPN-4 (....).

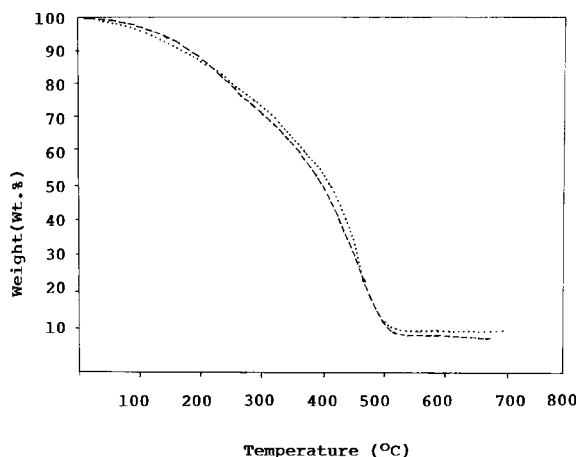


Figure 5 Thermogravimetric curves of IPN-5 (---) and IPN-6 (....).

simple associated molecules and the activation energy for the last step shows a much difficult path because of the rigidity of the molecule. This indicates the stability of TDI-based IPNs, as in agreement with the reported observations.¹⁷ The presence of aromatic rings could be the reason for slow weight loss.

Morphology

The SEM micrographs of IPNs are represented in Figure 6a and 6b. The morphology of these IPNs

indicates that there are two distinct phases due to individual component networks. Partial crystallinity of PU is evident from the micrograph of the IPN-2 shown in Figure 6a whereas Figure 6b represents the SEM micrograph of IPN-1. As cross-linking takes place in the second step, extent of cross-linking depending mostly on monomer concentration leads either to a continuous or discontinuous phase having more homogeneity or heterogeneity respectively. It is observed that when the monomer concentration becomes more

Table II Coats and Redfern Treatment of Kinetic Parameters of the IPNs

Sample	$g(\alpha)$	Temperature (°C)	R^2	E (kcal/mol)
IPN-1	D ₃	150–270	0.977889	16.72
	D ₂	270–390	0.977407	12.63
	D ₂	390–510	0.991943	32.74
IPN-2	MPL ²	150–270	0.991587	16.26
	MPL ¹	270–390	0.993741	10.57
	D ₂	390–510	0.989384	30.98
IPN-3	MPL ⁰	150–270	0.998053	17.69
	D ₂	270–390	0.992568	13.35
	D ₃	390–510	0.996354	31.67
IPN-4	D ₃	150–270	0.995426	18.23
	MPL ⁰	270–390	0.998969	11.89
	MPL ¹	390–510	0.993663	31.87
IPN-5	MPL ¹	150–270	0.999676	12.27
	D ₂	270–390	0.996216	10.71
	D ₃	390–510	0.990454	23.92
IPN-6	MPL ¹	150–270	0.995348	13.32
	D ₂	270–390	0.996375	9.91
	MPL ⁰	390–510	0.996473	25.21

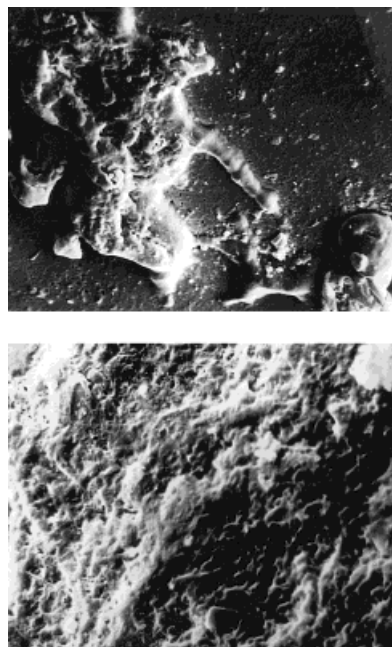


Figure 6 SEM micrograph of (a) IPN-2, and (b) of IPN-1.

we get a continuous phase having more homogeneity. So homogeneity of IPNs increases with increase in monomer concentration.

CONCLUSIONS

Increasing the NCO/OH ratios in the IPNs, the thermal stability increases, because of more cross-linking. A distinct thermal stability possessed by TDI-based IPNs over HMDI-based ones is due to presence of aromatic ring in the former and the bulky aromatic ring of the monomer. From the micrographs of IPNs it is observed that nature of homogeneity of the phase increases with increase in the monomer content.

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