Chapter II

SYNTHESIS

Most of the IPNs synthesised so far are based on an elastomeric phase and a glassy phase. In the present system under investigation, polyurethane based on castor oil acts as the elastomeric phase and the glassy phase consists of an unsaturated polyester.

POLYOLS

The polyols used for the polyurethane as well as IPN synthesis were based on castor oil. Two different hydroxy terminated polyols designated as R60 and R92 were employed in the study and were supplied by H K Agencies, Ahmedabad, India They differ in their hydroxyl number, which was measured by the standard ASTM method as discussed below

Hydroxyl number

The hydroxyl number is defined as the number of milligrams of potassium hydroxide equivalent to the hydroxyl content of 1g of the polyol. It is generally determined by reacting the polyol with a known excess of acetic anhydride in pyridine and titrating the excess reagent with standard KOH solution[1] In the actual experiment, about 1g of the polyol was weighed accurately into a standard joint flask 5 ml of freshly prepared acetylating mixture (mixture of pyridine and acetic anhydride in the ratio 4.1) was added to the flask and the contents were boiled gently for about an hour with a condenser attached to it. The flask was allowed to cool to about 50°C and about 5 ml of distilled water was added through the sides of the condenser The mixture was again heated gently for another 5 min with occasional shaking. The contents of the flask were cooled to room temperature and washed the walls and neck of the condenser with n-butyl alcohol (Sisco Chem , India) before detaching it from the flask The solution was made homogenous by adding excess of n-butyl alcohol and the clear solution was titrated against standard alcoholic KOH solution using phenolphthalein as the indicator. The similar procedure was adopted for a blank experiment without the sample and the volume of KOH required for both actual and blank experiment were found out The hydroxyl number was calculated using the formula

$$\text{Hydroxyl number} = \frac{56.1 \times N \times V}{w}$$

where

N = Normality of alcoholic KOH solution

V = Volume of KOH consumed (blank - actual)

w = Weight in gm of sample used

The equivalent weights of polyols were also calculated and the values are given in Table 2.1

Table 2.1 · Specification of polyols

Polyols	Hydroxyl groups/mole	Equivalent weight	Brookfield viscosity (cP)
CO	2 5	373	530 ± 5
R60	5 0	220	620 ± 6
R92	6.0	190	700 ± 10

FTIR spectra

Both the polyols were characterized by FTIR spectra (Canon, Michelson Series, Model MB 104) using KBr coating technique Representative plot for R60 polyol is shown in Fig 2 1 A broad band at around 3500cm^{-1} shows the presence of hydroxyl end groups Another sharp band at ~ 1740cm^{-1} is attributed to the carbonyl stretching of ester group in the chain backbone The medium absorption band at around 1650cm^{-1} is attributed to the C=C stretching vibration

UNSATURATED POLYESTER

Unsaturated polyester resins (UPE) in their commercial form are a mixture of an unsaturated polyester polymer with a vinyl monomer, usually styrene In the commercial resins, the ratio of the unsaturated polyester polymer to the styrene monomer is usually varied to accommodate the diverse applications in the plastic industry The formation of the rigid three dimensional network that characterizes these materials comes from the free radical polymerization of the double bond functionalities of the UPE resin and the styrene monomer. Polyester resins are generally prepared by condensing a glycol with both a saturated and an unsaturated carboxylic acid. The unsaturated acid provides a site for subsequent crosslinking while the saturated acid reduces the number of sites for crosslinking by spacing out the double bonds and thus reducing the crosslink density

Synthesis

In the present study, two UPE resins based on isophthalic and orthophthalic acids have been synthesized and designated as 'IPE' and 'OPE' in the following chapters Maleic anhydride was used to provide unsaturation along the chain

Materials and method

Isophthalic and orthophthalic acids (S.d Fine, India) and maleic anhydride (Sisco Chem , India) were used as received Propylene glycol (Qualigens, India) was dried over 4Å molecular sieves before use

A dry process was employed for the synthesis, in which a reaction kettle equipped with a mechanical stirrer and provision for nitrogen flushing, was charged with propylene glycol (2 1mole) and maleic anhydride (1 mole) along with isophthalic or orthophthalic acid (1mole) The temperature was raised slowly with continuous stirring and was maintained at 200°C for about 6 h The water formed during the reaction was removed from top of the air condenser The acid value of the contents were measured periodically A gradual decrease showed the progress of the reaction The reaction was finally stopped at an acid value of around 20-25 The final traces of water was removed from the resin by continuously applying vacuum along with bubbling of inert gas, nitrogen The resin was cooled to about 40°C and was mixed with reactive diluent styrene (35% by weight) and 0 1% quinhydrone as inhibitor, and was stored at low temperature. The resins were characterized by FTIR spectra The acid values of both of the resins were determined using the following method

Acid value

It is defined as the number of milligrams of KOH required to neutralise the acid groups present in 1 g of the resin In the actual experiment[2], about 1 g of the resin was accurately weighed into a conical flask and was dissolved in 50ml of dry toluene The contents were gently swirled till the resin was dissolved completely This clear solution was titrated against standard alcoholic KOH solution (0 5N) using phenolphthalein as the indicator A similar procedure was adopted for the blank reading The acid value was calculated using the formula

$$\text{Acid value} = \frac{V \times N \times 56.1}{w}$$

where

N = Normality of KOH solution used

V = The volume of KOH consumed (actual - blank)

w = The weight in gm of sample used

The values obtained for IPE and OPE are respectively 20 6 and 26 4

FTIR Spectra

Both the polyester resins were characterized by FTIR spectra (Caon, Michelson Series, Model MB 104) using KBr coating technique Fig 2 1B shows the FTIR spectrum of IPE resin A strong band at

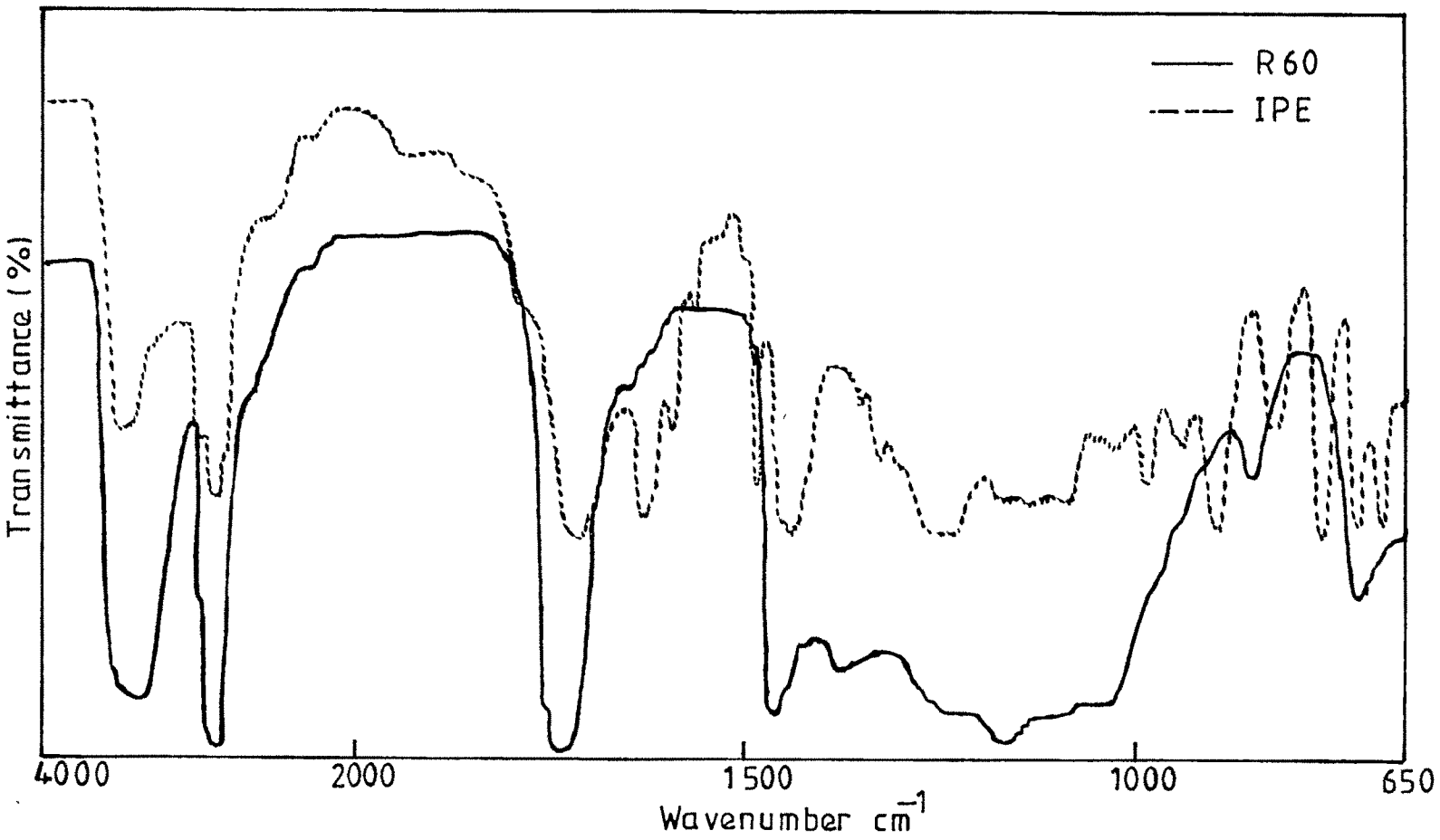


Fig 2.1 FTIR spectra of R60 polyol (—) and IPE (-----)

1740 cm^{-1} corresponds to the carbonyl stretching of ester group The medium absorption bands at 1648 cm^{-1} and 1634 cm^{-1} were assigned to the C=C stretching from the styrene and maleic anhydride respectively The bands at 915 cm^{-1} are related to the -CH=CH- absorption due to styrene The band at 982 cm^{-1} correspond to the absorption of both styrene and polyester double bonds A broad band at around 3500 cm^{-1} indicates the presence of hydroxyl groups at the chain end of polyester

SYNTHESIS OF IPN

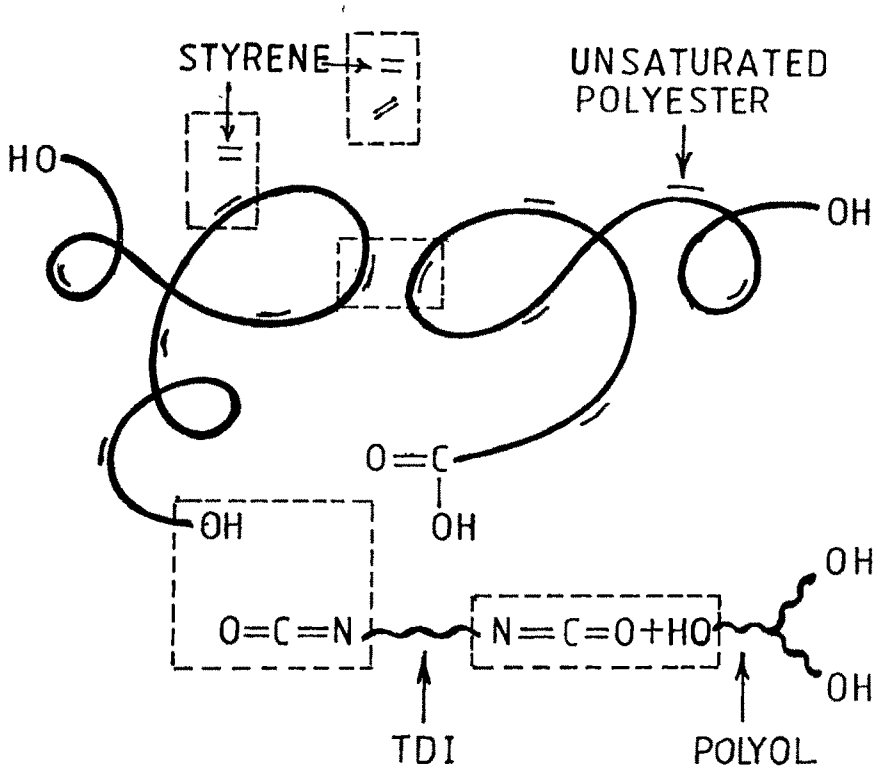
IPNs were synthesized by a simultaneous polymerization method by the interpenetration of polyurethane based on above mentioned polyols (R60 and R92) and unsaturated polyester resins (IPE and OPE)

Materials and method

The system can be divided into two phases; polyurethane phase and the polyester phase The urethane phase consists of castor oil based polyols, R60 or R92 Toluene diisocyanate (Fluka, Switzerland, an 80 20 mixture of 2,4 and 2,6 isomers) was used as the crosslinker along with dibutyltin dilaurate, DBTDL (Fluka) as the catalyst for this phase The UPE phase consist of both IPE and OPE resins along with the initiator, methyl ethyl ketone peroxide, MEKP (Aldrich), a 30 weight % solution in dimethyl phthalate, and the accelerator cobalt naphthanate Both R60 and R92 were dried at 60°C under vacuum for about 10 h to make them completely moisture free before the synthesis

The moisture free polyols (R60 or R92) along with IPE or OPE were introduced into a reaction kettle equipped with an inert gas inlet and stirrer The content was stirred vigorously to make it homogenous Calculated quantities of TDI, MEKP and cobalt naphthanate were introduced into the kettle and stirring was continued, when the temperature of the reaction mixture started rising The catalyst for the PUR phase, DBTDL was added and the mixture was stirred vigorously for few more seconds, the bubbles formed were removed by applying vacuum and the homogenous mixture was transferred into a preheated levelled glass mold kept at 60°C in an oven It was maintained at this temperature for about 10 h. for complete curing to take place The post curing was done at 100°C for about 5 h The samples were removed from the mold and stored under vacuum

Homopolymer polyurethane networks were prepared following the similar procedure by combining either of the polyols, TDI and DBTDL in required proportions Unsaturated polyester networks were prepared by crosslinking the liquid resin using MEKP and cobalt naphthanate The following scheme illustrates the formation of a PUR/UPE IPN



Thus different sets of samples were prepared by varying the following parameters

(a) Weight composition of polyols and unsaturated polyester resins

(b) Crosslink density (NCO/OH ratio) of polyurethane

(c) Type of polyol (R60 and R92)

(d) Type of polyester (IPE and OPE)

The list of samples along with experimental variations are summarised in the following chart

System	NCO/OH Ratio	Weight composition of components (PUR : PE)						
PUR60/IPE	1 2	100 00	80.20	60 40	50 50	40 60	20 80	00.100
	1 5	,,	,,	,,	,,	,,	,,	,,
	2 0	,,	,,	,,	,,	,,	,,	,,
PUR92/IPE	1 2	100:00	80:20	60 40	50 50	40 60	20 80	00 100
	1 5	,,	,,	,,	,,	,,	,,	,,
	2 0	,,	,,	,,	,,	,,	,,	,,
PUR60/OPE	1 2	100 00	80 20	60 40	50 50	40 60	20 80	00 100
	1 5	,,	,,	,,	,,	,,	,,	,,
	2 0	,,	,,	,,	,,	,,	,,	,,
PUR92/OPE	1.2	100 00	80 20	60 40	50 50	40 60	20.80	00 100
	1 5	,,	,,	,,	,,	,,	,,	,,
	2 0	,,	,,	,,	,,	,,	,,	,,

In the text, an IPN is represented as [Type of polyurethane(NCO/OH ratio) / Type of polyester, composition of components] For example, PUR60(1 2)/IPE 80.20 IPN means that, the sample is prepared from polyurethane based on R60 polyol having NCO/OH ratio1 2, and isophthalic acid based polyester with weight composition of components, polyurethane (80%) and unsaturated polyester (20%)

REFERENCES

1 C Hepburn, Polyurethane elastomers, Applied science publishers, London,1982

2 C L Mantell, C W Kopf, J L Curtis and E M Rogers, Technology of natural resins, Wiley, New York, 1942