Chapter 2

Materials and Methods

2.1 PREVIEW

This chapter deals with description of different materials, the experimental procedures for polyols synthesis and various techniques used for the characterization of polyols. This chapter also deals with materials used for the polyurethanes synthesis and also their characterization.

2.2 MATERIALS

Castor oil received from Jayant Oil Mills, Vadodara, India was used after drying for preparation of ricinoleic acid. Ethylene glycol, diethylene glycol and triethylene glycol (Merck, USA) were used directly for polyol prepartions with ricinoleic acid. Epoxy resin (Diglycedyl ether of bis phenol A, DGEBA) mol wt. 392 g/mole was received from Atul Industries, Valsad, India for synthesis of novel polyol. Triethylamine and Di butyl tindilaurate (DBTDL) was procured from Merck, USA and used directly as catalyst for novel polyol synthesis and for Polyurethane respectively. Toluene diisocyanate (TDI) is received from Merck, USA and used without further purification for non-toxic adduct prepartions. Polyethylene glycol (PEG) of molecular weight 200, 400 and 600 used in this study were obtained from Sisco Chem Industries, Vadodara, India and were dried over anhydrous Na_2SO_4. 2-hydorxyl ethyl methyacrylate (HEMA) was procured from Fluka, Switzerland. Azo bis isobutyronitrile (AIBN) was received from Suvidhinath Laboratory, Vadodara and used after recrystallization. Solvents xylene, toluene, butyl acetate, methyl ethyl ketone, methanol, ethanol, n-butanol, ethyl acetate, dioxane were received from Suvidhinath Laboratory, Vadodara, India and were distiilled and dried with molecular sieves (size 4Å) prior to use. Potassium hydroxide was received from Qualigens, India and used directly. R-60 resin (castor oil derivative) received from Hardik Agencies, Ahmedabad, India having five free hydroxyl groups per mole and hydroxyl equivalent weight 220 was used after drying in oven at 100^0C under vacuum for two days.

2.3 EXPERIMENTAL METHOD

2.3.1. Hydrolysis of Castor oil:

In 500 ml beaker 10% of alcoholic KOH was prepared by dissolving 25 g of KOH in 250 ml added to a three necked flask containing 125 g of castor oil under stream of nitrogen gas. The mixture was then refluxed at 65^{0}C for 4 h. to complete hydrolysis reaction. The reaction mixture was poured in 250 ml water with stirring, followed by acidification with dil HCl to adjust pH to 6. From resulting two layers the upper fatty acids layer was then separated and washed with 3 % acetic acid and two to three times with water. The fatty acid mixture was fractionated by differential freezing method (freezing point of ricinoleic acid is 5.5 ^{0}C while that of other fatty acids is in the range of 0 ^{0}C). Freezing procedure was repeated thrice. The pure ricinoleic acid thus collected was used for synthesis of polyols The physical properties of these ricinoleic acid was determined i.e. Acid value, hydroxyl value etc. and are shown in Table 1.

Table 1 : Physical Properties of Ricinoleic acid

	Acid value	Hydroxyl value (mg. KOH/gm.)	% NVM	Viscosity FC B-IV (s)
Ricinoleic Acid	175	150	99.78	75

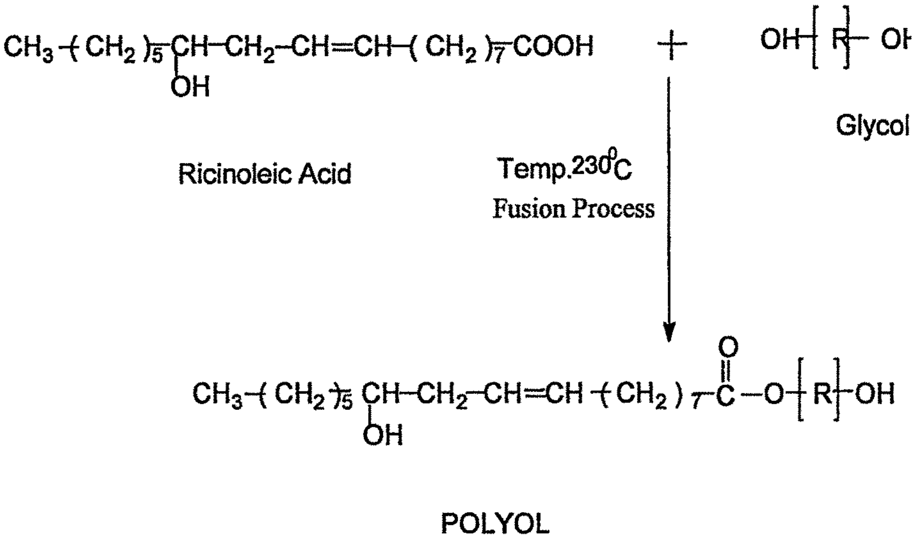
2.3.2. Preparation of polyester polyols:

A dry process (Fusion Process) was employed for the synthesis of polyols, in which a reaction kettle equipped with a mechanical stirrer and provision for nitrogen flushing; was charged with dry ricinoleic acid (0.5 mole) and 0.5 mole of respective glycols.(For synthesis of polyol A, B and C ethylene glycol, diethylene glycol and triethylene glycol were charged respectively, 1:1 molar ratio). The temperature was raised slowly with contininious stirring and was maintained at 230 ^{0}C for 3h. The water formed during the reaction was removed from the top of condenser by vacuum evaporation. The acid value of the contents was measured periodically. A gradual decrease in acid value showed the progress of reaction. The reaction was finally stopped at an acid value near to zero. The final traces of water were removed from the resin by continuously applying vacuum along with bubbling of nitrogen gas. Finally polyol was cooled to 40^{0}C and the acid value was determined. The reaction is shown in scheme 1. The properties of the polyols such as hydroxyl value, non-volatile matter and viscosity, are presented in Table 2.

Table 2 : Composition Code and Physical Properties of Castor Oil-based Polyester polyols.

Designation of polyols	Hydroxyl value (mg. KOH/gm.)	Hydroxyl equivalent weight (gm.)	Viscosity at 30 ^{0}C FC B-IV (s)	NVM (%)
Polyol A	306	183	124	99.1
Polyol B	265	210	137	99.5
Polyol C	249	225	168	99.3

Scheme 1



R = CH_2-CH_2 for Polyol A

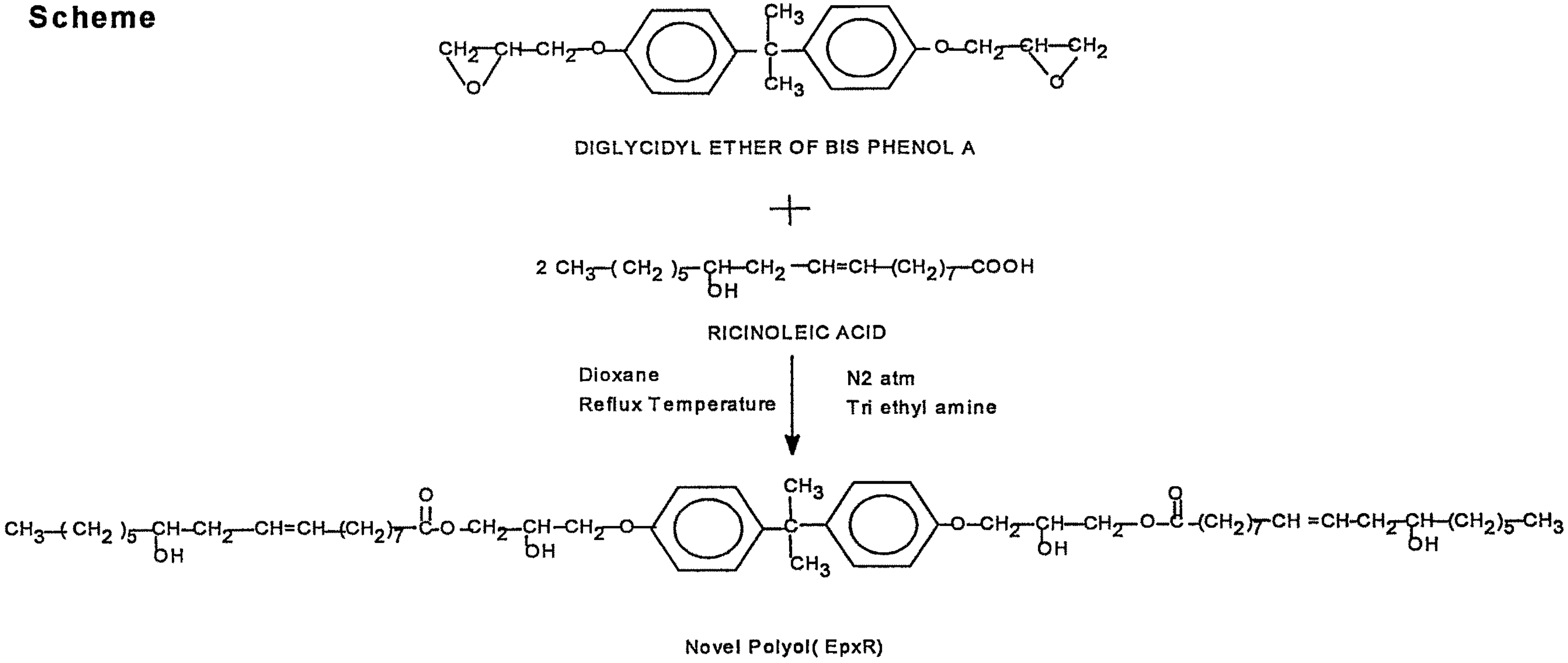
$CH_2-CH_2-O-CH_2-CH_2$ for Polyol B

$CH_2-CH_2-O-CH_2-CH_2-O-CH_2-CH_2$ for Polyol C

2.3.3. Synthesis of novel polyol:

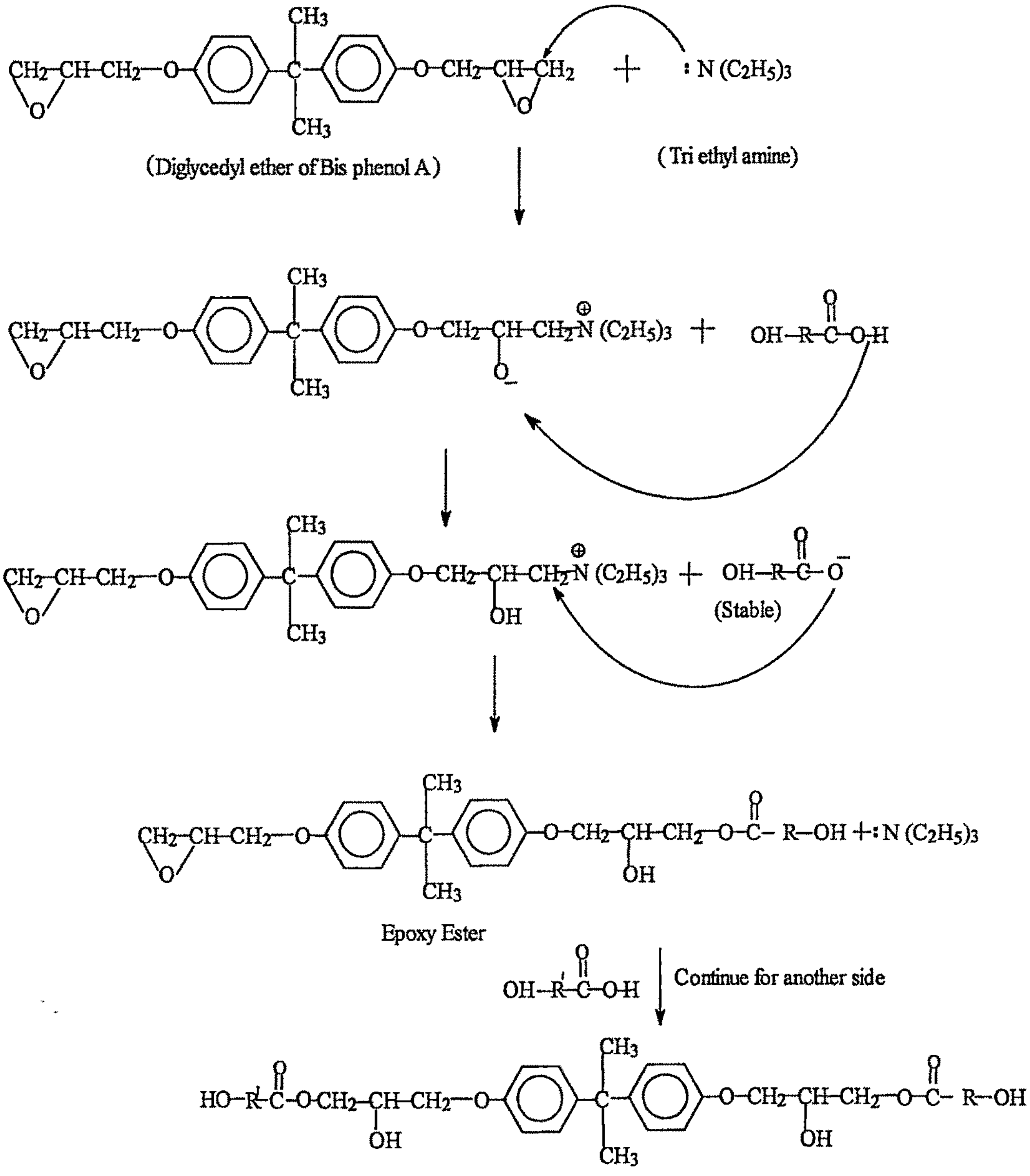
Reactive novel polyol was synthesized by reacting castor oil derivative ricinoleic acid (2 mole) having free carboxyl group with epoxy resin (1 mole) in three necked round bottom flask equipped with nitrogen inlet and water condenser. 0.05 mole of triethyl amine as a catalyst was added along with 100 ml of dioxane in the flask. The reaction was continued at reflux temperature of dioxane for 2h. After completion of reaction dioxane was distilled out from the flask. At the end of reaction a viscous liquid was collected in cleaned glass stoppered bottle. The reaction and mechanism are shown in scheme 2a and 2b respectively. Various physical properties like viscosity, hydroxyl value, acid value, percentage of non-volatile matter were determined and are given in Table 3.

Scheme


DIGLYCIDYL ETHER OF BIS PHENOL A
+
2 CH3–(CH2)5–CH–CH2 –CH=CH–(CH2)7–COOH
OH
RICINOLEIC ACID
Dioxane
Reflux Temperature
N2 atm
Tri ethyl amine
Novel Polyol(EpxR)

Scheme 2 b

Mechanism:



EpxR Polyol

Table 3: Physical properties of novel polyol (EpxR)

Polyol	Hydroxyl value	Acid value mg/KOH	Hydroxyl equivalent weight	Viscosity 30^{0}C Brookfield viscometer *cP* (5rpm)	NVM (%)
EpxR	231	2.3	243	13320	99.20

2.3.4. Synthesis of Acrylated polyol:

In a three necked round bottom flask, 20 gms of EpxR polyol was dissolved in 60 ml of toluene. The mixture was stirred using a mechanical stirrer at 45°C temperature for homogenous solutions in thermostated water bath. Two different separating funnels containing (a) 0.01 gm AIBN (Azo bis iso butyronitirle) dissolved in 10 ml of toluene and (b) 1 gm of 2-hydroxy ethyl methacrylates (5 %) dissolved in 10 ml of toluene, were attached to the necks of the round bottom flask. Both these solutions were added drop wise simultaneously from these funnels. The temperature was maintained at 75^{0}C and the reaction mixture was stirred for 5h in nitrogen atmosphere. After the completion of reaction, excess toluene was distilled off and the synthesized polyol was washed with acetone at room temperature, and dried at 60^{0}C under reduced pressure. Polyols containing 10, 15 and 18% HEMA were synthesized by same process, and were characterized by various physical properties like hydroxyl value, % Non-volatile matter, viscosity etc and are presented in Table 4. Number average molecular weight of these polyols was also determined by GPC.

Table 4: Physical properties of acrylated polyol

Acrylated Polyol	Hydroxyl value	Hydroxyl equivalent weight	Viscosity 30^0C Brookfield Viscometer cP (10rpm)	NVM (%)
EpxR (0%)	231	243	6320	99.2
EpxR(5%)	245	228	7502	98.2
EpxR (10%)	258	217	9563	96.0
EpxR (15%)	267	210	10236	95.3
EpxR (18%)	278	201	--	96.4

2.4 CHARACTERIZATIONS OF POLYOLS:

2.4.1. Hydroxyl Value:

The hydroxyl value or hydroxyl number is defined as the number of milligrams of potassium hydroxide equivalent to the hydroxyl content of the 1 g. of 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 1 g. of the polyol was weighed accurately into a flask with a standard joint. 5ml 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 one hour with a condenser attached to it. The flask was allowed to cool to about 50 ^{0}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 falsk were cooled to room temperature and the walls and neck of the condenser were washed with n-butyl alcohol 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 an indicator. The similar procedure was adopted for a blank experiment without the sample and the volume of KOH required for both actual and blank experiments were found out. The hydroxyl value was calculated using the formula.

$$\text{Hydroxyl value} = \frac{56.1 \times V \times N}{W}$$

where,

N = Normality of alcoholic KOH solution

V = Volume of KOH consumed (blank – actual) ml.

W = Weight in g. of sample used.

The equivalent weight was also calculated.

2.4.2. Acid Value:

It is defined as the number of milligrams of KOH required to neutralize the acid groups in 1 g of resin. In the actual experiment [2], about 1 g. of resin was accurately weighed into a conical flask and was dissolved in 50 ml of dry acetone. The contents were gently swirled till the resin was dissolved completely. This clear solution was titrated against standard alcoholic KOH solution using phenolphthalein 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 alcoholic KOH solution

V = Volume of KOH consumed (blank – actual) ml.

W = Weight in g. of sample used

2.4.3. Viscosity:

Viscosity of the surface coating resins is one of the most important characteristics as it dictates the method of processing and also affects several application and performance properties of surface coatings. Viscosity is mostly used as a quality control procedure for polyol and resins. As the viscosity of a polyol is dependant on temperature and this particularly applies to polyols, it must be measured at a fixed and closely controlled temperature. The temperature most commonly used is 25^0C. Flow cup can be used. A measured quantity of polyol is allowed to flow through a defined orifice on the conical base of the container and the time (s) for the discharge noted. This is proportional to the viscosity. One example of this type of measuring viscosity is Ford cup B IV (FC B –IV). Another, rotational type such as Brookfield viscometer (model RTV) was used to measure the viscosities of polyol. It is a rotating disk type viscometer with a motor that can rotate a disc in a liquid at a range of revolutions per minute (shear rates). The resulting torque was measured as a dial reading and using standard equation, viscosity was measured in terms of centipoises (c*P*).

2.4. 4. Non-volatile Matter (NVM):

Non-volatile contents of any resin or polyol are evaluated to ascertain the film build and the related characteristic [3]. The solid contents of each polyol was determined by weighing a small amount of polyol in petri dish and heating it in oven at 120^0C for 2h to drive off the volatile components, subsequent weighing gives the weight of the residual non volatile matter. The percentage of solid in the original samples hence was calculated.

2.4. 5. IR spectroscopy:

IR spectral measurement of polyols is considered to be one of the useful methods of characterization. In principle, it provides qualitative and quantitative information about the structural details of the polyol under examination. IR spectra are measured either on the solid state in the form of KBr pellet or in the form of film in suitable solvent. One of the most popular applications of IR spectral study is detection of functional group in the polymer chain.

In recent years, with the introduction of commercial Fourier Transform Infra Red (FT-IR) spectrometers, that are operable over the entire IR frequency range, many applications of IR analysis that were impossible or at least extremely difficult using conventional dispersive instruments are now readily accomplished [4].

FTIR spectrum of polyol samples was recorded on a Perkin Elmer RX 1 spectrophotometer (range 400 to 4000 cm^{-1}). Polyols were characterized by FTIR spectra using KBr coating technique.

IR spectrum of Castor oil , Ricinoleic acid, Polyols (A, B, C), EpxR polyol, Acrylated polyol (5%), Acrylated polyol (10%) are given in Fig. 1,2,3,4,5 and 6 respectively.

Fig 1 is the representative spectrum of castor oil. The spectrum shows typical bands corresponding to C=O at 1756 cm^{-1}, hydroxyl groups at 3400 cm^{-1}, presence of C-O-C linkages at 1080 and 1252 cm^{-1} and C-H of alkyl groups at 2871 cm^{-1}.The medium absorption band at around 1688 cm^{-1} is attributed to the C=C stretching vibrations [5] .

Fig 1: FTIR spectrum of Castor oil

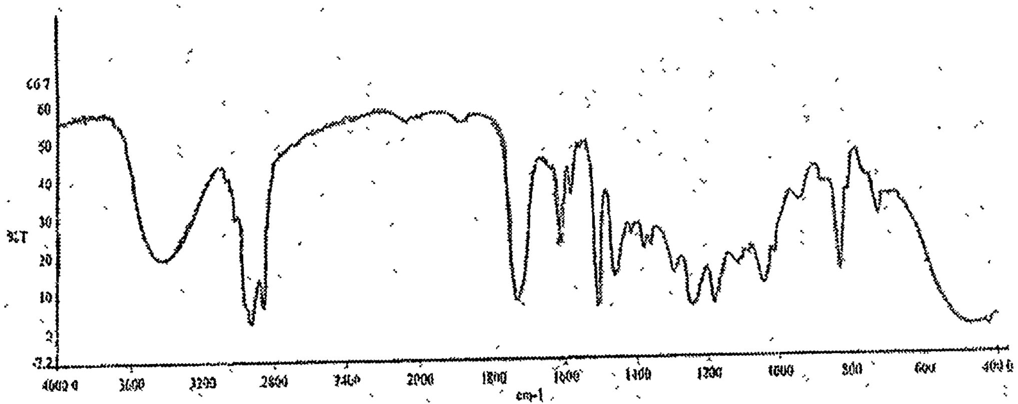


Fig 2 is the representative spectrum of Ricinoleic acid. The spectrum shows –O-C-O linkages of acid at 1732 cm^{-1}, a medium band at around 3400 cm^{-1} shows the presence of hydroxyl end group, and C-H groups is attributed at 2925 cm^{-1} . The strong intensity band observed at 1732 cm^{-1} is due to the presence of acid groups

Fig 2: FTIR spectrum of Ricinoleic acid

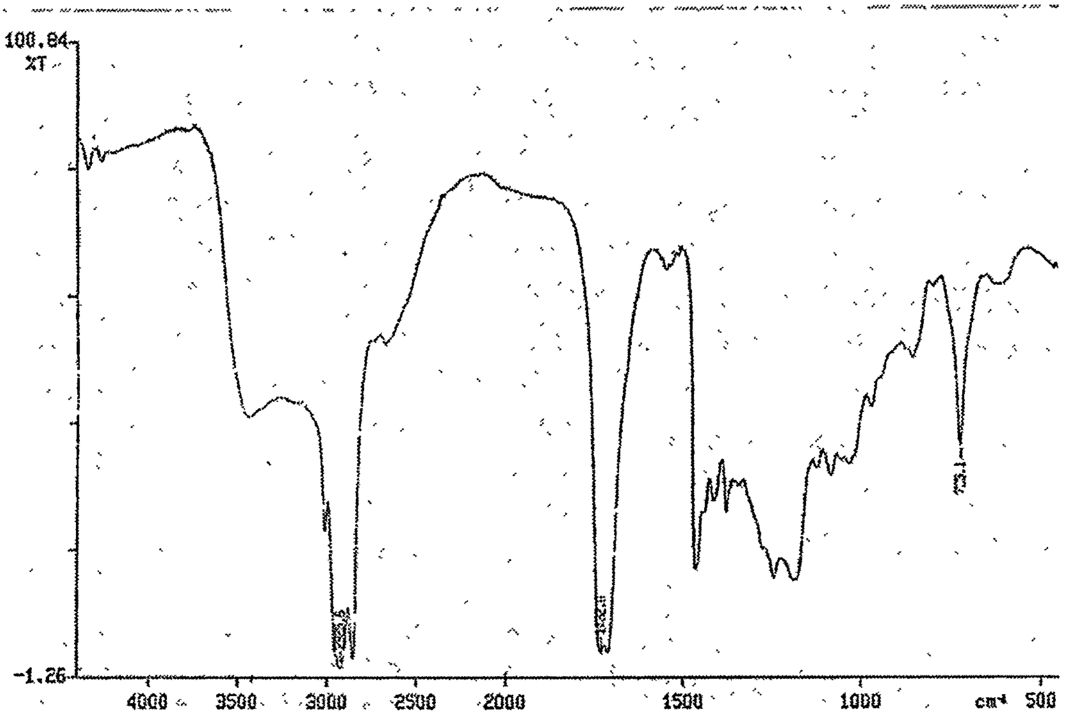


Fig 3 is the representative spectrum of polyols A B and C respectively. The spectrum shows the double bond in the polyol moieties. This was observed as a medium intensity peak at 1635 cm^{-1}. The OH stretching band at 3400 cm^{-1} indicated the presence of free hydroxyl groups [6]. In the cases of diethylene glycol and triethylene glycol, the presence of C-O-C ether linkage is indicated with a band observed at 1904cm^{-1}. The band observed at 2949 cm^{-1} is due to the -CH stretching.

Fig 4, it is the representative spectrum of EpxR polyol. The spectrum shows the characteristic peak of terminal epoxy group [7] was not observed at 920 cm^{-1}. The disappearance of this peak indicates that breakage of epoxy linkage and formation of secondary hydroxyl group at 3400cm^{-1}.The double bond moieties in polyol correspond to the medium intensity peak of 1635 cm^{-1}.

Fig 5 and 6 are representativeive spectra of acrylated polyol 5% and 10% respectively. The strong band observed at 3400 cm^{-1} is due to presence of hydroxyl groups in acrylated polyol. Intensity of the characteristic band of vinyl group (-C=C-) at 1620 cm^{-1} decreased in these polyols, confirms grafting at conjugated double bond. The strength and broadness of peak around 3400 cm^{-1} confirms increase of hydroxyl group due to incorporations of hydroxyl functional groups from HEMA. Broadness of spectra around 1700 cm^{-1} increased due to increased ester linkage density.

Fig 3: FTIR spectra A, B C of Polyol A, B and C respectively.

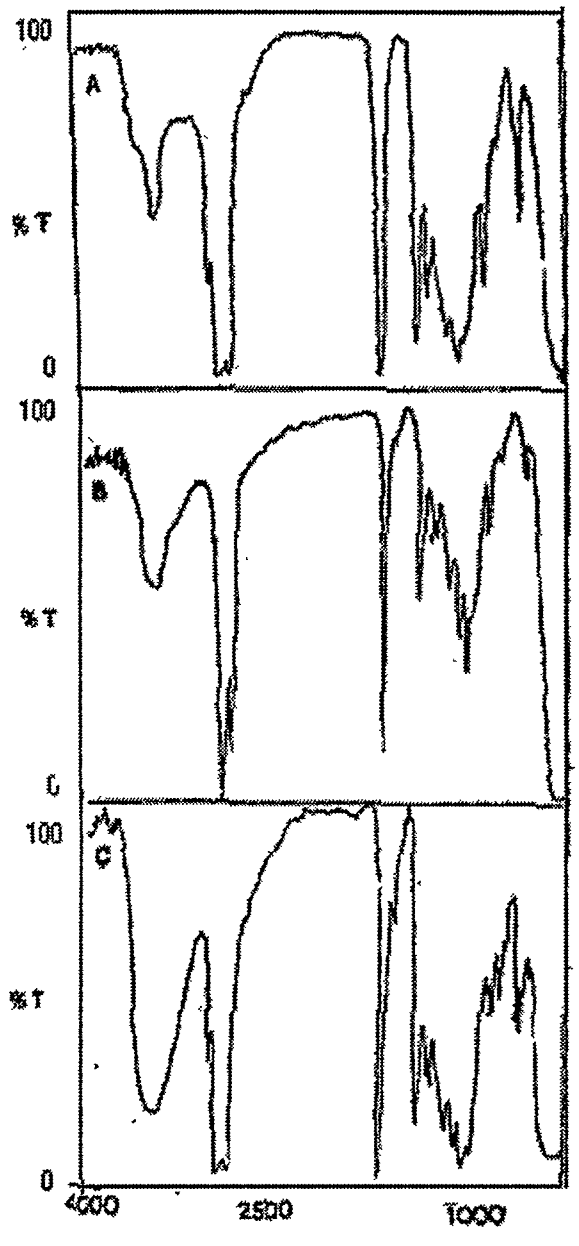


Fig 4: FTIR spectrum of EpxR-polyol.

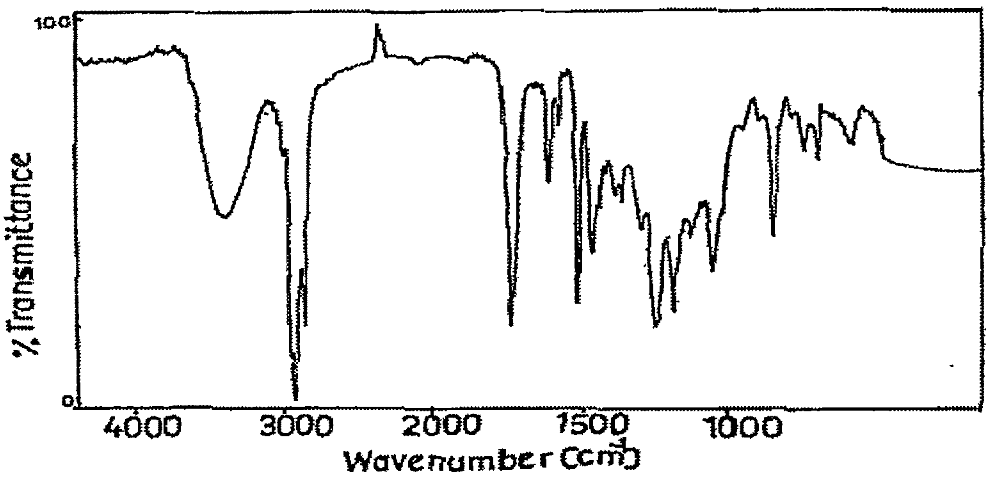


Fig 5: FTIR spectrum of acrylated polyol (5 %)

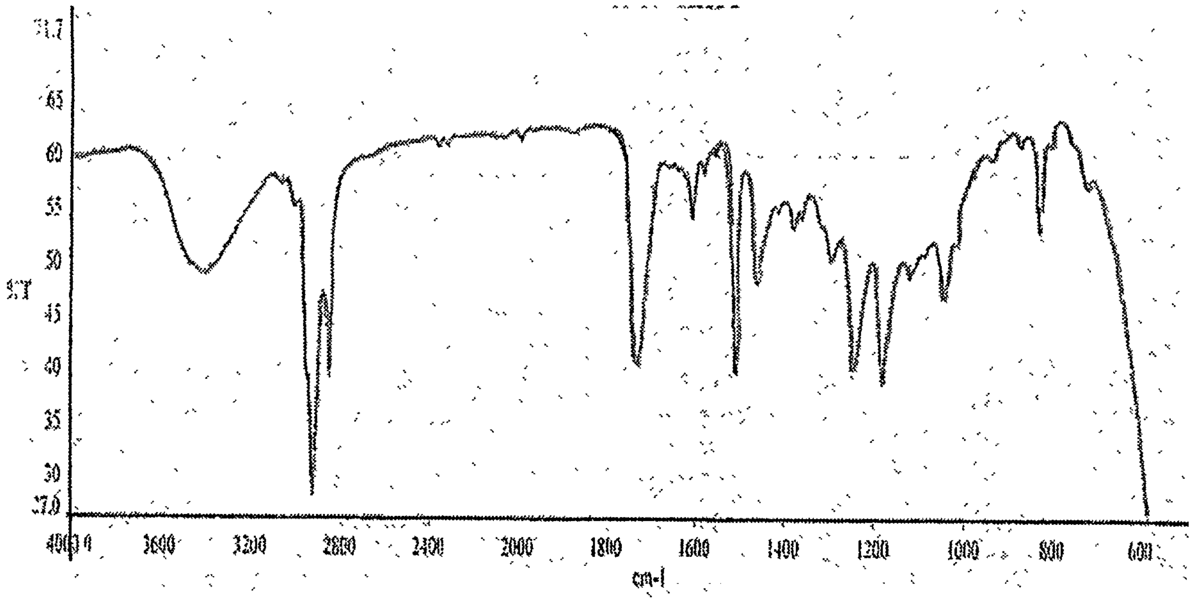
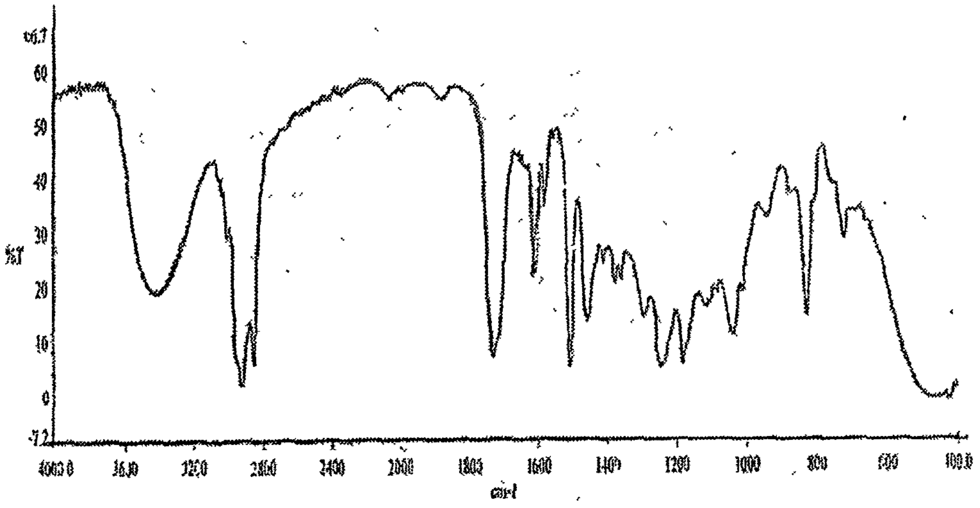


Fig 6: FTIR spectrum of acrylated polyol (10 %)

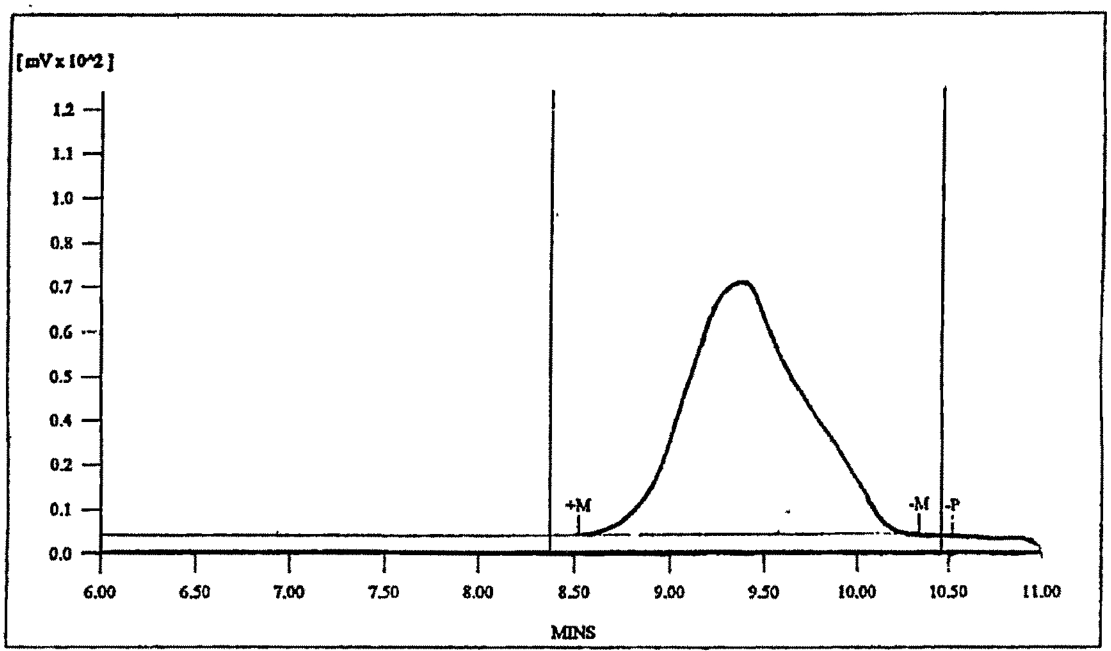


2.4.6. *Gel permeation Chromatography:*

Average molecular weight of polyols were obtained by GPC (mol wt range 500 to 500000 g/mole) unit consisting of a solvent delivery pump (Perkin Elmer series 200), Refractive index detector (Perkin Elmer spectra series 200). Columns filled with poly (styrene- divinyl benzene) were used. Standard reference sample was polystyrene. 20 µl of THF solution of novel polyol were introduced in to the system using flow rate 1 ml/min. with a pressure of 17 bar. Only polyols with molecular weight above 500 were measured by GPC

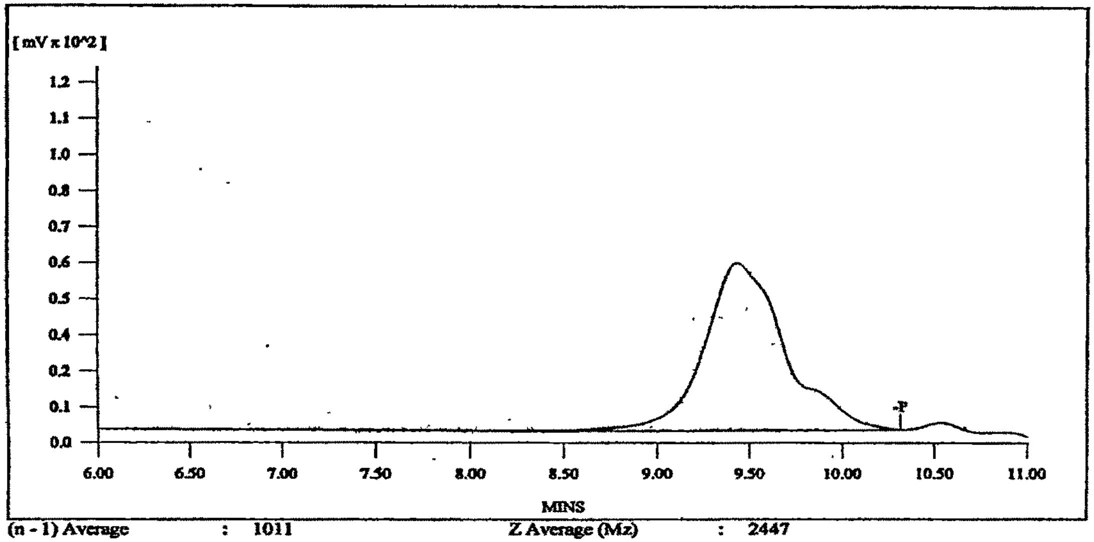
GPC curve of EpxR polyol, acrylated polyol 5% and acrylated polyol 10% are presented in Fig 7, 8 and 9 respectively. From GPC of EpxR polyol, average molecular weight of polyol was found to be 963, which was very well comparable to the end group analysis value (hydroxyl value 231, Molecular weight 972) and with the expected theoretical value (936). Hence it was assumed that the reaction of epoxy resin with ricinoleic acid was completed. GPC analysis of acrylated polyol (5%) indicated the average molecular weight to be 1011 and that of acrylated polyol (10%) to be 1440. Thus increase in percentage of acrylated polyol lead to an increase in percentage grafting of 2 hydroxy ethyl methacrylate on EpxR polyol backbone. Moreover GPC curve of acrylated polyol gave one single retention peak at 9.50 min., suggesting that there was no formation of poly HEMA.

Fig 7: GPC curve of EpxR polyol.



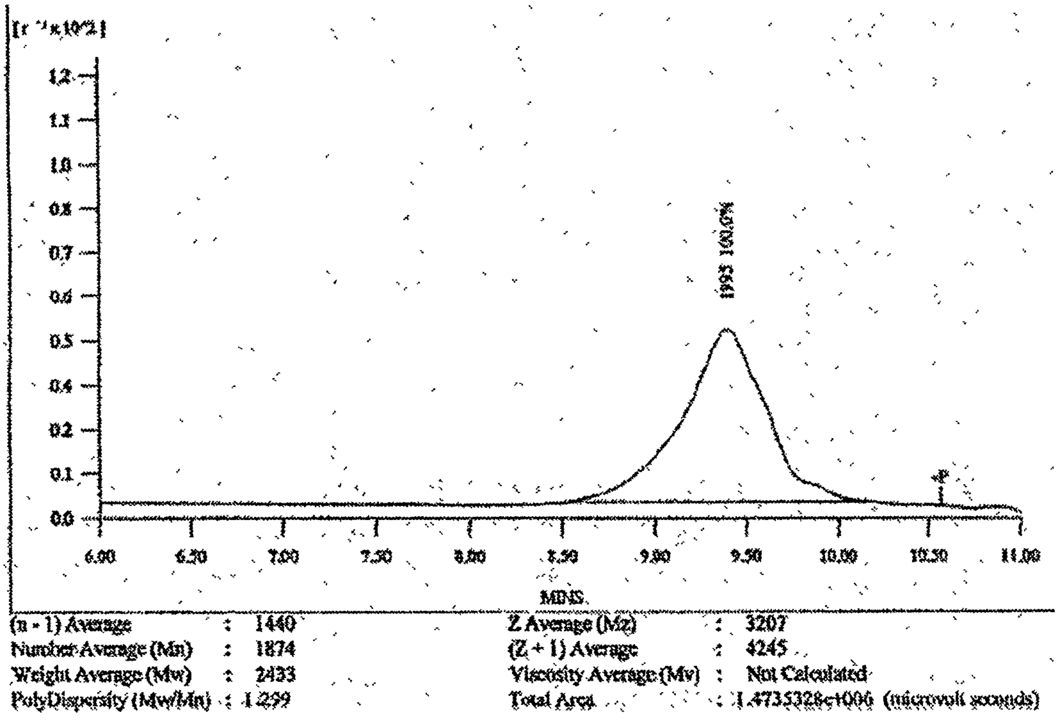
(n - 1) Average	963	Z Average (Mz)	3058
Number Average (Mn)	1510	(Z + 1) Average	3929
Weight Average (Mw)	2247	Viscosity Average (Mv)	Not Calculated
PolyDispersity (Mw/Mn)	1.488	Total Area	2.93694520e+006 (microvolt seconds)

Fig 8: GPC curve of acrylated polyol (5 %)



(n - 1) Average : 1011
Number Average (Mn) : 1405
Weight Average (Mw) : 1849
PolyDispersity (Mw/Mn) : 1.316
Z Average (Mz) : 2447
(Z + 1) Average : 3667
Viscosity Average (Mv) : Not Calculated
Total Area : 1.6943182e+006 (microvolt seconds)

Fig 9: GPC curve of acrylated polyol (10 %)



(n - 1) Average : 1440
Number Average (Mn) : 1874
Weight Average (Mw) : 2433
PolyDispersity (Mw/Mn) : 1.299
Z Average (Mz) : 3207
(Z + 1) Average : 4245
Viscosity Average (Mv) : Not Calculated
Total Area : 1.4735328e+006 (microvolt seconds)

2.5 MATERIAL FOR POLYURETHANES:

Aromatic isocyanate and aliphatic isocyanate were received from Grand Polycoats, Padra, Gujarat, India and characterized for their physical properties, as shown in Table 1. R-60 isocyanate adduct were synthesized in our laboratory and used for the synthesis of polyurethanes.

2.5.1 Preparation of R-60 adducts:

1 mole of dried R-60 resin (Hardik Agencies, Ahmedabad, India) was taken in a three necked round bottom flask, equipped with nitrogen inlet and mechanical stirrer. Whole assembly was kept in a thermostated water bath at 30^0C. TDI (5 mole) in 50 ml. of toluene was added drop wise using dropping funnel and reaction mixture was stirred continuously for 5h. After completion of reaction the viscous liquid was collected in an airtight bottle. The physical properties of these adduct is reported in table 5.

Table 5: Physical properties of Isocyanate Adducts.

Adduct	Percent Free NCO content*	Isocyanate Equivalent Weight	Specific gravity 30 ^{0}C	Viscosity at 30 ^{0}C by FC-B IV Secs.
Aromatic adduct	12.5	336	1.02	210
Aliphatic adduct	16.5	255	1.05	175
R-60- Adduct	9.9	425	1.35	325

Free NCO groups measured according to reference [8].

2.6 TESTINGS OF THE COATING MATERIAL:

2.6.1 Panel Preparation:

Metals, glass, or wood panels shall be used as specified in different tests methods or in relevant material specifications.

2.6.2 Metal Panels:

Metal panels of mild steel fully finished (confirming to deep drawing quality of BIS [9]) size 150 X 100 X 1.25 mm, free from surface imperfections, such as rolling marks and scores, and scale, and shall be commercially available.

Before use, mild steel panels were cleaned free of excess oil, roughly degrease with petroleum hydrocarbon solvent (confirming to I.S [10] specifications for petroleum hydrocarbon solvents) or xylene confirming to I.S [11] specification for xylol, industrial solvent grade and then brushing uniformly with I.S grit no. 180 emery cloth (confirming to IS specification for coated abrasive, glue bond [12]). Burnish lightly to avoid embedding emery in the surface. The burnishing operation shall be as follows:

Straight across the panel, in a direction parallel to any one side.

Perpendicular to first direction and until all signs of original burnishing have been obliterated.

With a circular motion, of diameter approx. 75 mm until a pattern consisting of circular burnishing marks superimposed one upon another is produced.

Remove the traces of emery dust by wiping with a linen rag. Degrease the panel by swabbing two or three times with a linen rag, soaked in a suitable hydrocarbon solvent. Dry the panels slightly to remove traces of condensed moisture, allow returning to room temperature and then coat without delay. The prepared surfaces should not be touched by hand or otherwise between degreasing and coating.

Tinned mild steel panel shall be clean with suitable and shall be roughened with final paper of I.S. grit no. 100 (2/0) after which the panels shall be rinsed with benzene and wiped dry with a clean rag.

2.6.3 Method of Application:

The main aspects involved in application of coating materials are application of resins and evaluation of properties of the films so formed.

A surface coating system is useful in practical sense only if it forms films with considerable physical integrity, fulfilling several property demands. The conversion of liquid composition into an adherent and durable coating is termed as process of film formation. It comprises three main steps viz. application, fixation and cure [13].

There are various methods of applications of coatings such as spraying, electro deposition, vacuum-impregnation; dipping, brushing etc. the nature of coatings compositions, nature of substrates and the mode of curing dictates the selection of applications methods which can produce a uniform smooth film [14].

Ready mixed coating shall be applied by brushing or spraying as specified in the material specifications.

Brushing:

Flat brush use in the preparation of test panels shall confirm to IS [15] and shall be clean free from loose hair and shall be of a suitable size. The material shall be applied by brushing to obtain an even and uniform coat and shall not be poured or spilled upon the panel.

Fixation is the step of stabilizing the coating on the surface against its tendency to run off or to form an uneven layer. This depends upon number of factors such as film thickness, rate of solvent evaporations and the rheological properties of the compositions. Solvent evaporations causes rapid film viscosity buildup resulting in fixation and hence the rate of solvent evaporations should be carefully controlled. Thus it is evident that the fixation step is controlled mainly by the rheological properties of the coating compositions.

Final conversion of films to durable coatings takes place by curing or drying. Drying processes depending on the nature of resin can be divided in to two main categories physical and chemical drying.

Physical drying mainly involves solvent evaporations and the film integrity is usually obtained by chain entanglements since the chain entanglements is the main criterion for such systems. The resin used should have very high molecular weight to give durable coatings [16].

Chemical drying always involves some type of chemical reactions at room temperature in order to obtain durable film. These chemical reactions cause the formation of high molecular weight three dimensional networks and are often termed cross-linking reactions. These cross-linking reactions can either be due to auto oxidations of unsaturated groups present in the resins or due to condensations reactions between the functional groups present in the same polymer or between the functional groups present in the curing agents and the resin.

Drying due to inter and intramolecular condensations:

Drying involving intermolecular or intramolecular condensation reaction of the functional groups is often called chemical drying. When functional groups undergoing condensations reactions are present on the same polymer molecules, it is termed intra molecular where as it is termed intermolecular if condensations reactions involve functional groups present on the polymer and on added curing agent. These condensation reactions result in the formation of high molecular weight polymers, which in turn, impart film setting. Functional groups most frequently used to bring about these condensation reactions are hydroxyl; carboxyl, isocyanates, epoxy, amides, amines. The curing agents commonly used for this purpose are melamine resin, phenolic resin, di and poly isocyanates, amines amides etc.

2.6.4 Evaluation of Performance of coatings :

Evaluation of mechanical and chemical properties of coatings is of paramount importance in maintaining the protective and decorative properties of the coatings during their service life. Surface coatings are subjected to a great variety of mechanical forces or deformations. They may suffer large forces concentrated on a small surface area for very short time (as in the impact of stones, gravels etc. on car body paints) or they may suffer a succession of slow cycles of deformation in response to change in atmospheric moisture or temperature. Not only do the films suffer a wide variety of mechanical stresses and strains during their service life, but also their mechanical properties of the film. Chemical properties of the films in general, depend upon the chemical composition of the film former , the presence or absence or of free functional groups and, in case of thermosetting resins, the crosslink density of the film [17] .The evaluation of resistance to variety of chemicals, water and solvents by coating is generally dictated by the end use application of the coating. It is, therefore, imperative that the evaluation of mechanical and chemical properties of the film is conducted since these properties determine how long a coating film can preserve its physical integrity and can fulfil its protective role satisfactorily for given application.The most commonly measured properties viz. mechanical and chemical are discussed below.

2.6.4 (1) Adhesion

Adhesion [18] is the state in which force, which may consist of valence attractions, or interfacial forces or a combination of both holds two surfaces together. Interfacial forces are physical bonds whereas valence attractions are chemical in nature. The interfacial forces are too small to be measurable by any mechanical device.

There are two major factors, which affect the adhesion of organic coatings to various substrates

a) The affinity of the solvent and the resin in the coating for the substrate,

i. e. wettability of the substrate by the coating (referred as a specific adhesion).

b) The profile or the roughness of the substrate. The first is referred to as the specific adhesion, the second, the mechanical adhesion (referred as a mechanical adhesion).

In order for a specific adhesion to be formed, there must be an initial interaction between the solvent system and the substrate, followed by an adsorption of the polymeric phase on to the substrate. The manner in which this polymeric phase is formed is crucial to the proper bonding. It is strictly mechanical and in the process, smaller molecules of solvents are replaced by larger molecules of polymers used in the coatings.

It has been shown that presence of low molecular weight fractions in the films can form a weak boundary layer at of near the coating substrate interface, that substantially reduce the apparent adhesion.[19].

The cleanliness of the substrate is a major factor for proper adhesion of any organic coatings. The surface must be free from oils, greases and other foreign materials which can reduce the wettability of the substrate. The coating must be applied to oxide-free surfaces (in the case of metallic substrates) since their presence would prevent the formation of any chemical bond between the metal and the coating.

As adhesion is defined as interfacial forces between coating and substrate, their magnitude can not be measured by mechanical means. Since adhesion can not be measured, as such, it is necessary to determine the forces needed for the removal of the coating from the substrate.

Among the methods for measurement of adhesion, organic coatings are removed by empirical scratching with a sharp blade, by a mechanically operated knife, by exposure to high-speed vibration or by high-speed centrifugal force. The amount of force necessary is then measured and a value for adhesion is ascribed to the coating. Another method is to apply a given force, using a definite instrument or device. The resulting delamination, in quantitative terms, is directly proportional to the adhesion of the coating. Adhesion is measured by forces necessary for the coating's removal, under controlled conditions. Wide range of methods and devices for the purpose has been employed over the years. [20,21]. Adhesion test of coated materials was observed by cross hatch, according to ASTM D 3359 method to determine unacceptable adhesion. The test coatings were cut through the substrate using a sharp razor blade to give parallel lines 2mm apart, forming a 10x10-block grid. The test surface was then brushed lightly to remove loose particles. Adhesive tape (Scotch Brand #810 magic tape or 3M adhesive tape) was pressed on to the scribed area and then pulled off rapidly at 180° angle within 60 seconds. The scribed area was inspected visually with an illuminated magnifier to determine percentage of coating removed.

2.6.4 (2) Flexibility

The term flexibility refers to the characteristics of a coating film to have sufficient elasticity so that it will not split or crack following the shrinkage of the film or movement of the substrate due to weather or service condition The Indian standard specification [22] defines the term flexibility as the degree to which, a film, after drying, is able to conform to movement or deformation of its supporting surface, without cracking or the flexibility depends not only on the elasticity of the applied film, but also on the adhesion of the film to the substrate. It has been shown that well-adhering films have better flexibility than those which adhere poorly. The main external factors affecting flexibility of any coating are humidity, temperature and strain rate.

Flexibility tests are of two basic types. The bend test, in which coated panels are bent around mandrels, and the Erichsen test in which the panel metal is deformed by a large hemispherical ended indenter. Among the most commonly used test is by using conical mandrel apparatus or by bending 1/8″ mendrel apparatus as described in IS : 101—-1989 [23]

2.6.4 (3) Hardness

The hardness of organic coatings [24] cannot be expressed in absolute or intrinsic terms and cannot be expressed quantitatively. The measurement of hardness of organic coatings is based on practical concepts. A material is considered to be hard when it can resist indentation and scratching.

Hardness determination by the use of tests is most widely used. When resistance to indentations is used as measure of hardness, then it is related to rigidity of the material or its elastic modulus. The three widely used tests are:

a) *Pencil Hardness*:

The organic coatings are rated according to their resistance to be scratched or marked by pencils of various hardness [25]. A coated panel placed on a flat horizontal surface and pencil is held at an angle 45° to the film. The pencil is pushed away from the operator in a1/4" stroke. This process is started with the hardest level pencil and is repeated with progressively softer pencil until the pencil did not cut the film. The pencil, which do not cut the film, denotes its hardness. The coating of test formulations whose pencil hardness is measured at 27°C .

b) *Scratch hardness:*

In this method, resistance to scratching under specified load, of a dried film of coating is tested by a mechanized or hand operated apparatus [26].

c) *Pendulum or rocker type hardness:*

This hardness is measured by a pendulum or rocker, the mechanism being the dampening of the oscillations due to the hysterisis losses of the material, rolling friction, shear modulus, and in case of thin coatings, the hardness of the substrate [27].

2.6.4 (4) Impact resistance

From the viscoelastic properties of the coatings it is difficult to present and predict impact resistance due to complicated stress-strain profiles. Timashenko and Goodier [28] have derived a theory of impact which allows the magnitude of the most significant impact parameters to be estimated. Impact test evaluates the ability of coating to withstand extension without cracking when the deformation is applied rapidly [29]. In the measurement of impact resistance, an indenter of low mass is forced against the panel at a specified velocity. The minimum velocity at which damage becomes visible at the point of impact is measured.

In another method determination of impact resistance involves indentation, by an object of specified weight, on to a panel, from the varying height. If the coated side is up, the test is called direct impact test. If the back of the panel is up, the test is called a reverse impact test. The weight is dropped from greater and greater height until the coating on panel cracks. Generally, reverse impact tests where coating is extended as a result of impact, are more severe than direct impact test where coating is compressed. The results are generally reported in *inch -lb* that is the number of inches from which the weight falls times its weight. The thickness, mechanical properties and surface of the substrate substantially affect the results.

2.6.4 (5) Water and moisture resistance:

Surface coatings are invariably designed to control the action of water. They basically function as barriers between substrate and the aqueous environment. The effect of water on paint films and substrate has been extensively studied and reported in the literature [30].

Three basic tests are employed to measure the resistance of coatings to water, viz :

a) Measurement of the water-vapour permeability of the film.

b) Measurement of effect of water that condenses or is splashed on to the film.

c) Determination of the effect of the water vapour being transmitted through a permeable substrate.

Coatings, which are applied to nonporous substrate and are exposed to the atmosphere, must be able to repel and resist the deteriorating effect of water. The laboratory tests designed to determine these effects use water that has been condensed on the substrate, water that has been mechanically sprayed on the substrate or water as the medium for immersion.

Another category of tests is based on the transmission of water vapour through substrate to the paint film.

2.6.4 (6) Chemical resistance

A coating is often formulated to exhibit certain degree of chemical resistance [31]. It is necessary to express the resistively of a coating to varying chemicals. The tests to determine chemical resistance of coating range from the simple spot test to the complicated method requiring sophisticated equipment. The exposure of paint film to various chemicals can reduce its gloss, change colour, or produce a swelling or softening of the paint film. In the extreme case the film can be stripped from the substrate or completely destroyed *by* solvent action.

2.6.4 (7) Resistance to alkalies and acids

Alkali and acid [32] solution can have detrimental effect upon wooden and metal substrates. The test involves immersion of coated panels at room temperature into an alkali solution of sufficient concentration. After the immersion for 24 hours, specimen are rinsed under running water, allowed to dry for 30 minutes at room temperature and examined for various parameters.

The resistance of coating to acids or alkalies, among other factors, mainly depends upon the chemical composition of polymer backbone and the degree of cross-linking in thermosetting films. The films of resins containing hydrolysable groups such as esters, in the polymer backbone are relatively more sensitive to hydrolysis by acids and alkalies. The presence of certain free functional groups also has some deleterious effect on chemical resistance e.g. cured films containing free $-COOH$ or $-NH_2$ groups show poor resistance to alkalies and acids respectively.

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