CHAPTER - 2

Raw Materials, methods for coating and film characterization methods
As the aim presented in an earlier chapter the present chapter comprises the peer review about the reaction of castor oil, with various isocyanated terminated polyurethanes (ICOPU) and various DGEB epoxy resin, methods of coating techniques used for the characterization of the prepared blends. The adopted experimental procedures explained in this chapter.

2.1 Castor oil

Castor oil is derived from the beans of the castor plant (Recinus Cunnunis L.) and it is belonging to the family of Euphorbiaceae. It is also known as resinous oil, oil of Palma Christi, Tangantangan oil and Neoloid. Typical of most fats the oil is triglycerides of fatty acids what is the unique is that the fat contains 87-90% ricinoleic acid. IUPAC name of the acid is cis-12 hydroxy octadac-9-enoic acid, \[\text{CH}_3(\text{CH}_2)_5\text{CH(OH)CH}_2\text{CH}==\text{CH(C}_2\text{H}_5)\text{COOH}\]. A rare source of an eighteen carbon hydroxylated fatty acid with one double bond. Castor oil sometimes described as a triglyceride of ricinoleic acid, is one the few naturally occurring glycerides that approaches being a pure compound.

A rare source of an eighteen carbon hydroxylated fatty acid with one double bond. Castor oil sometimes described as a triglyceride of ricinoleic acid, is one the few naturally occurring glycerides that approaches being a pure compound.

The pale yellow and viscous, with a slight characteristic odour and nearly tasteless but familiarly unpleasant through its minor use as a purgative. The industrial uses of castor oil are extensive.

<table>
<thead>
<tr>
<th>2.1.1 Composition of Castor oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>The average fatty acid composition of castor oil is as follows:</td>
</tr>
<tr>
<td>Ricinoleic acid</td>
</tr>
<tr>
<td>Dihydroxystearic acid</td>
</tr>
<tr>
<td>Palmitic acid</td>
</tr>
<tr>
<td>Steric acid</td>
</tr>
<tr>
<td>Oleic acid</td>
</tr>
<tr>
<td>Linoleic acid</td>
</tr>
<tr>
<td>Linolenic acid</td>
</tr>
<tr>
<td>Eicosanoic acid</td>
</tr>
</tbody>
</table>

The industrial quality standards of castor oil as specified by the ASTM are given in Table 2.1.

The oil is distinguished from other triglycerides by its high specific gravity, viscosity and hydroxy value. Another unique feature is its solubility in alcohol: one Volume of
castor oil dissolved in volume of 95% ethanol at room temperature and the oil is miscible in all proportions with absolute alcohol and also the oil is typically soluble in polar organic solvents and less soluble in aliphatic hydrocarbon solvents. It slight miscibility in pet. Ether is as characteristic which distinguishes it from other oils.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid value, max</td>
<td>2.0 mg of KOH/gm.</td>
</tr>
<tr>
<td>Clarity</td>
<td>Clear</td>
</tr>
<tr>
<td>Gardner color, max</td>
<td>2</td>
</tr>
<tr>
<td>Hydroxyl value</td>
<td>160-168 mg of KOH/gm.</td>
</tr>
<tr>
<td>Loss on heating, max 96</td>
<td>0.2</td>
</tr>
<tr>
<td>Refractive index, 25°C</td>
<td>1.4764-1.4778</td>
</tr>
<tr>
<td>Saponification value</td>
<td>176-184</td>
</tr>
<tr>
<td>Solubility in alcohol a</td>
<td>Complete</td>
</tr>
<tr>
<td>Specific gravity,25°C</td>
<td>0.957-0.961</td>
</tr>
<tr>
<td>Unsaponifiable, max 96</td>
<td>0.7</td>
</tr>
<tr>
<td>Viscosity, cm²/s (stokes)</td>
<td>6.5-8.0</td>
</tr>
<tr>
<td>Iodine value</td>
<td>84-88</td>
</tr>
</tbody>
</table>

- Courtesy of the American Society for testing and Materials

a Soluble in 1:2 in 95% ethanol 3A (SDA) at 20 °C.

2.1.2 Chemical Modification

The unit processes involved in converting castor oil to such products include dehydration, sulfonation, alkali fusion, oxidation, pyrolysis, saponification and others of a more complex nature. The chemical reactions taking place in castor oil are shown in Table 2.2.

2.1.2.1 Dehydration

Catalytic dehydration of castor oil yields oil called dehydrated castor oil (DCO). It is used extensively by the coating industries. Although the reaction was known for a long time, its commercial application became significant during World War II in making a substitute of tung oil. In the dehydration reaction the 12-hydroxyl group is removed with a nearby hydrogen atom to form water and a new double bond.

Further reaction yields both conjugated and non-conjugated linoleic acid isomers. The reaction is first order with activation energy of about 188 J/mol (43 cal/mol) [60].
Analysis of commercial dehydrated castor oil indicated that using sulfuric acid as the catalyst about 30% of the linoleic acid double bonds are conjugated in the 9,11 position. Practical dehydration processes are the subject of extensive publications and patents. They deal with improvement of color, reduction of the after-tack after drying and increased conjugation. The common catalysts are sulfuric acid and its acid salts [61], oxides, and activated clay [62]. In a typical process, castor oil is heated to 230-380 °C under vacuum and 3-5% diluted sulfuric acid is added to it at a controlled rate. The viscosity of the product is regulated by the degree of dehydration, reaction time and temperature.

The fatty acids of dehydrated castor oil are obtained by hydrolysis or by saponification followed by the acidification of the oil. The conjugated acid content of the products remains the same as in the oil itself. Much higher conjugated acid contents, 50% and above, are obtained by dehydration of ricinoleic acid. Usually, the crude acids are distilled under vacuum to obtain a light-colored high quality product.

2.1.2.2 Sulfonation

Sulfonated castor oil, also known as Turkey red oil, represents one of the earliest chemical derivatives of castor oil. The traditional method of preparing Turkey red oil is to add concentrated sulfuric acid to maintain a temperature of 25-30 °C, followed by washing to remove surplus acid and then neutralization with either aqueous sodium hydroxide, potassium hydroxide, ammonia or an amine such as ethanolamine.

Sulfonation results largely in esterification of the hydroxyl group of ricinoleic acid. Side reactions that can take place include attack of the double bond to produce an ester of hydroxysulfonic acid [63]. Hydrolysis of the esters during the reaction and subsequent treatment forms sulfuric acid and hydroxyl acids which can further sulfated at the –OH group. Despite the many side reactions most commercial products seem to be similar in properties.

Commercially sulfated castor oil contains 8.0-8.5% combined SO₃, indicating that the only one of the reactive sites in the unsaturated, hydroxyl bearing triglycerides has been sulfated. The sulfate group imparts excellent wetting emulsification and
dispersing characteristics. The product is used in the textile industries for fiber wetting ability and as dye agent to obtain bright, clear colours.

Sulfonation of castor oil with anhydrous SO$_3$ (2 mol) at temperatures higher than the sulfuric acid treatment produces a product also containing only 8 to 8.5 % combine SO$_3$, which has better hydrolytic stability [64] and contain less inorganic salts and free fatty acids.

2.1.2.3 Alkali fusion

Depending upon condition two different sets of products can be formed [65, 66]. At 180 to 200 °C, using 1 mole of NaOH or KOH, 1Mylethyl ketone and 10-Hydroxydecanoic acid result. This reaction is favored by the presence of unhindered primary or secondary alcohol, such as 1 or 2 octanol and 10-Hydroxydecanoic acid is also form in good yield when methyl ricinoleate [67, 68] is used. Two moles of alkyl per mole of ricinoleate at 250-275 °C and with a shorter reaction cycle produce 2-Octanol and sebacic acid. Hydrogen is also form with excess alkali [69].

Sebacic acid is used in the manufacture of nylon-6, 10 by reaction with hexamethelene diamine. Nylon-6, 10 has better molding properties and resistant to moisture then adipic acid base (6, 6) nylon and is use in molding filament bristles and some textiles fiber applications. Sebacic acid eaters are used as plasticizer and bis-(2-ethylhexyl) sebacate is a high performance lubricant forget engine.
2.1.2.4 Hydrogenation

The hydrogenation of castor oil can be performed in a number of ways to produce derivatives. The largest use of hydrogenated castor oil is in the manufacture of multipurpose greases.

Simple double bond hydrogenation at 140 °C in the presence of raney-Ni catalyst produces glyceryl tris (12-hydroxystearate), m.p. 86 °C [70-71]. Care is necessary to avoid decomposing of the sensitive hydroxyl group. The synthetic wax is use commercially in waxes, polishes, cosmetic and paper coating. Al thought it lack the gloss of some high natural waxes it is preferred in specific application where its ability to impart grease-proofness is required. Partial hydrogenation in waxes modified properties.

2.1.2.5 Pyrolytic decomposition

Pyrolysis of castor oil at 340-400 °C split the ricinoleate molecule at the hydroxyl group to form hepta aldehyde and undecylenc acid. Hepta aldehyde is use in manufacture of synthetic flavors and fragrances. It also is converted to heptanoic acid by various oxidation techniques and 2-heptly alcohol by catalytic hydrogenation. When helt aldehyde react with benzaldehyde by aldol reaction, alpha-amyl cinnamic aldehyde C6H3CH=C(C6H11) CHO is produce. 10-undecylenic acid and its derivatives are used primarily for their fungicidal and bactericidal properties. A combination of undecylenic acid and Zn undecylenate is used in the treatment of athlete's foot infection. The Cu salt has been compounded in to ointments use in treating facial and body infection.

2.1.2.6 Alkoxylation

Ethylene oxide and propylene oxide react with the hydroxyl group of castor oil to yield a varieties of polyoxyalkylene derivatives. The reaction is carried out at 120-180 °C and 0-105 KPa (0-4 atm). Using alkaline catalyst such as NaOH free radical acid catalyst are also use at lower temperature and pressure [72].

The ethoxylated derivatives of the castor oil and hydrogenated castor oil are non-ionic surface active agents with varied degree of hydrophobic-hydrophilic properties. The low-level ethoxylated derivatives are water emulsifiable and are used as defoamers and
de-emulsifier for petroleum emulsions. The highly ethoxylated products are excellent solubilizers for water insoluble oils in cosmetic compositions [73-74]. They are also used as components in detergents, lubricants, and cutting oils and hydraulic fluids [75], textile finishing compositions and as antistatic agents [72, 76] for nylon carpets and apparel. The propoxylated derivatives of castor oil are mineral oil soluble and useful in lubricant oils and hydraulic fluid composition.

2.1.2.7 Oxidation

Oxidized (blown) castor oil is clear viscous oil resulting from controlled oxidation by intimate mixing (blowing) of castor oil at 80-130 °C with air or oxygen, with or without the use of catalyst. The reaction is combination of oxidation and polymerization promoted by transition metal like Fe, Cu, and Mn [77]. The viscosity, acidity, color and other properties are highly dependent on the reaction condition and a variety of products can be prepared.

Oxidized castor oil is excellent non-migrating, non-volatile plasticizer for cellulose resins, poly (vinyl butyral), polyamides, and shellac, natural and synthetic rubber. The high viscosity products are also used as tackifiers in gasket compounds and as adhesives because of their good oil and solvent resistance. They also serve as excellent pigment grinding media and as a base for lubricating and hydraulic oil [78].

2.1.3 Uses

Castor oil known primarily for its medical use as a cathartic is now used primarily as an industrial raw material for the preparation of chemical derivatives used in coatings, urethane derivatives, surfactants and dispersants, cosmetics, lubricants etc.

2.1.3.1 Urethanes

Castor oil and its many derivatives have been successfully used for at least twenty years as polyols for the preparation of polyurethanes, particularly in the preparation of polyurethanes coatings [79-85], adhesives casting compounds [86-88]. Urethanes are prepared by the reaction of polyhydroxy compounds such as castor oil with polyfunctional isocyanates. Urethanes prepared from castor based polyols are
characterized by their excellent hydrolytic stability and shock absorbing and electrical insulating properties [89-93].

Trans-esterification (alcoholysis) of castor oil [94-96] with polyols such as trimethylol propane or propylene glycol results in castor oil polyols with higher or lower hydroxyl value functionality. Polymerization of castor oil, chemical or oxidative, results in higher viscosity or bodied oils, which are more useful in urethane coatings than the unreacted castor oil. Other derivatives used to prepare urethanes are amides prepared by reaction of castor oil with alkanilamines, amides of ricinoleic acid with long chain di- and triamines and butanediol dicinoleate [97]. Other methods of preparing castor based polyols are by acetylation, dehydration, epoxidation and hydrogenation.

Castor oil and its polyol derivatives have found to be very useful in the preparation of the rigid, semi-rigid and flexibility urethane foams. These foams are resistant to moisture, shock absorbing and have good low temperature flexibility. Castor based urethane foams have been used in the manufacture of foam packaging, in application requiring high shock absorbing properties, in clothing interliners and filters. High density semi-rigid castor based urethane foams have also been used for potting electrical components where their excellent electrical and shock absorbing properties as well as their excellent hydrolytic stability are utilized.

Castor oil resistance to hydrolysis, pigment dispersion ability and compatibility with polyether polyols has also made it useful as modifier for polyether-based foams. Foams based on castor oil are semi-rigid at low densities and become more rigid as the foam density increases. These foams generally possess an open cell structure [98].

Castor oil can also be used to formulate commercially acceptable rigid polyurethane foams for such uses as thermal insulation and structural support [99]. Superior rigid polyurethane foams have been prepared from hydroxymethylated polyol esters of castor acids [100]. Recently considerable emphasis has been placed on developing fire-retardant urethane foams. Brominated castor oil has been investigated as a modifier for preparing fire-resistant urethane forms [101,102].
2.1.3.2 Coatings

Dehydrated castor oil (DCO) fatty acids have been copolymerized with acrylic esters or allowed to react with hexamethoxy methylolated melamine resin and neutralized with ethylamine to give an aqueous solution reportedly useful as water-soluble resin for electrodepositing coatings [103].

Sulfated castor oil and an emulsifiable polyethylene can be used to make a creamy paste pigment-dispersing agent. This paste can be blended with resins and pigments in high flash naphtha to develop white baking enamel with good non-setting readings after three months [104].

Castor oil condenses with triethylenetetramine to give diamides which when neutralized with H$_3$PO$_4$, act as emulsifiers for nitrocellulose lacquers [105].

The quality of poly (phenylene sulfide) coatings was improved by using polyoxyethylated castor oil as a surfactant (e.g. Emulphor EL-620 or Emulphor EL-719) [106].

Castor oil fatty acid reacts with Phthalic acid using a tetra isopropyl titanate catalyst to give castor oil fatty acid adduct from which an amide hardener is made using diethylenetetraamine (DETA). This hardener can be mixed with Epikote 1001 epoxide resin coating compound to give an anticorrosive film-forming coating compositions [107]. The adduct can also be used with commercial epoxy resin EPN 740 with triethylamine in mixed solvents. This will produce a thick anticorrosive film on rusted steel sheet with good salt-water resistance [108].

A vinyl chloride-vinyl propionate copolymer varnish at 40% solids with TiO$_2$, baraytes, dioctyl phthalate (DOP) in ethyl acetate-xylene can be mixed with castor wax and Gelton 50 (acid treated CaCO$_3$) to yield a stable coating for spray coating glass plate, giving a 30 µm thick sag-free film [109].

Many other coating applications have been reported [106-113].

2.1.3.3 Surfactants and Dispersants

A Sulfated derivative of castor oil is used as a dispersant for plaster of Paris. It reduces the amount of water needed to form plastic slurry [114]. Sulfated and sulfonated
derivatives have been used in electroplating zinc [115], as softeners in dishwashing compounds [116] and in glass cleaning [117].

A hydrolysis-sensitive biocide was stabilized using an ethoxylated castor oil as the emulsion stabilizer for use in a pesticide [118]. Alkylene oxide-modified castor oil has also been used in ink for pigment dispersion [119].

Polyoxyethylated castor oil (42 moles of ethylene oxide) has been approved by FDA as an emulsifier in nitrocellulose coatings for paper and paperboard intended for use in contact with fatty foods at a maximum level of 8% of the coating solids [120].

Emulsified noncreosotic pine oil disinfectant compositions were prepared using <7% of an emulsifier mixture and soaps of castor oil and mixture of soaps of tall oil [121].

A partially saponified castor oil surfactant was prepared by reaction of an ethoxylated castor oil with alkali metal hydroxide. The product had excellent detergency, low forming characteristics, stability in alkali and acid solutions, complete water solubility and no cloud point in typical aqueous use solutions [122].

2.1.3.4 Lubricants

Non-toxic lubricating cutting oil for metals at 700-1200 °C can be prepared from aluminum powder, graphite, potassium soap and castor oil [123].

Oils suitable as lubricants for rolling of steels as high temperatures are prepared by mixing castor oil, alkylene oxide-containing castor oil and C₄-C₂₄ fatty acid esters [124].

A metal working lubricant useful for drawing aluminum tubing can be prepared by mixing sulfur-free woo wax, aluminum stearate, castor oil and 1,1,1-trichloroethane at 39-49 °C [125].

Aviation oils were prepared by esterification of thermally treated or oxidized castor oil with alcohols in the presence of H₂SO₄ or HCl [126].

Highly stable oil was prepared by the reaction of castor oil with an epoxy compound (e.g. ethylene oxide, butadiene oxide, styrene oxide). The product was hydrogenated and dispersed in oils or water to yield highly stable rolling oil [127].
2.1.3.5 Textiles

Different polyamide fibers with different affinities for anionic dyes are dyed level shades by pretreatment with aqueous acidic solutions containing sulfated castor oil [128].

Readily dispersible antistatic agents are prepared by reaction of polyoxyalkylated-hydrogenated castor oil or dialky oxalate or malonate. A mixture of poly (ethylene terephthalate) is spun with this product to give fibers having static discharge properties [129].

2.1.3.6 Cosmetics

Ethoxylated castor oils (Cremophor EL) or ethoxylated castrowaxes (Cremophor RH, a 40/60 ethoxylated-hydrogenated castor oil) are used as solubilizers of hydrophobic substances such as perfumes in cosmetics. Ethoxylated castor oil was the best solubilizer in a multicomponent system and the hydrogenated oil was more effective than the unsaturated oil. Other ethoxylated triglycerides were not as effective as castor oil. Ethoxylated castor oil was also a good solubilizer for vitamin A palmitate [130].

Castor oil and hydrogenated castor oil impart emollient and lubricant properties to ointments and cosmetic preparations [131].

2.1.3.7 Miscellaneous Uses

Castor oil and polychlorinated biphenyl (PCB) were principal impregnates used in energy storage capacitors. Castor oil is better than PCB for pulshed applications [132].

A Cigarette filter with improved nicotine and tar absorption characteristics is obtained by spraying glycercyl triacetate on crimped acetate fiber tow and subsequently applying castor oil and 75% poly (vinyl alcohol) [133].

Stable protease-containing tablets can be prepared with ethoxylated castor oil [134].

Looking to the reactions of castor oil above, it is evident that castor oil is mostly used in the form of its modified derivatives [135]. The numbers of reactions have been adopted modify castor oil. The reaction of –OH group and epoxy is well feasible under normal conditions. Having three –OH groups in castor oil can react easily with epoxy resin as epoxy group is susceptible to active H atom. Such reaction product may have good surface coating properties due to the presence of epoxy segment. The literature survey also reveals that reaction of castor oil with epoxy resin
i.e. DGEBA has found with few instances [136,137]. Hence it was thought interesting to extend these study castor oil-epoxy resin reaction products. The present chapter comprises the synthesis of COERs products.

2.2 Experimental

2.2.1 Materials

Castor Oil:

It was purchased from local market. Its characteristics are:

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Appearance</td>
<td>Pale yellow in color and clear</td>
</tr>
<tr>
<td>Density</td>
<td>0.95 gm./cc</td>
</tr>
<tr>
<td>Viscosity (By Ford cup B IV at 28°C)</td>
<td>130 sec.</td>
</tr>
<tr>
<td>Hydroxyl Value</td>
<td>160 mg of KOH/gm.</td>
</tr>
<tr>
<td>Number of –OH Groups</td>
<td>2.45 per mole of oil</td>
</tr>
<tr>
<td>Number of unsaturation</td>
<td>2 per mole of castor oil</td>
</tr>
</tbody>
</table>

Hydroxyl value [138] and number of hydroxyl groups of castor oil [139] were estimated using acetylation method as described in literature. Estimation of unsaturation was carried out by reported process [140].

Epoxy Resins:

Two epoxy resins mentioned bellow:

Epoxy resins i.e. DGEBA and DGEBF (structure shown below) were obtained from Atul Industries Limited, Atul. Then specifications are:
<table>
<thead>
<tr>
<th>Appearance</th>
<th>Water white in color and clear</th>
</tr>
</thead>
<tbody>
<tr>
<td>Epoxy Equivalent Weight</td>
<td>190</td>
</tr>
<tr>
<td>Epoxy Equivalent Weight</td>
<td>160</td>
</tr>
<tr>
<td>Viscosity at 25°C</td>
<td>9000-11000 cps</td>
</tr>
</tbody>
</table>

**Isocyanated terminated castor oil polyurethane**

<table>
<thead>
<tr>
<th>Appearance</th>
<th>Pale yellow in color and clear</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>0.98 gm./cc</td>
</tr>
<tr>
<td>Viscosity (By Ford cup B IV at 30°C)</td>
<td><strong>145 sec.</strong></td>
</tr>
<tr>
<td>Number of unsaturation</td>
<td>1 per mole of castor oil</td>
</tr>
</tbody>
</table>

### 2.3 Synthesis of Castor Oil-Epoxy Resin

**Reaction Products (COERs) I & II**

250 gms. (0.268 mole) of castor oil was taken in a three necked round bottom flask equipped with a mechanical stirrer and placed in a water-bath where temperature was maintained about 70-80°C. Under continuous stirring desired amount of epoxy resin was added gradually and depending upon amount of epoxy resin, generally 0.05% of epoxy resin weight, triethyl amine was added as a catalyst. During the reaction temperature was not allowed to rise above 85°C. At the regular interval of time, a sample was withdrawn from the reaction mixture using siphoning device and test for epoxy group [141] was carried out to check the progress of reaction. When a sample showed the negative test for epoxy group, reaction was stopped and reaction mixture was allowed to cool to room temperature after which it was subjected to preliminary characterization.

Three different types of COERs with varying proportions of epoxy resin were prepared by following the above procedure. The proportions (moles) of reactants used and designations of resultant COERs are presented in Table 2.3.
2.3.1 Characterization of Castor Oil-Epoxy Resin Reaction Products (COERs)

The three COERs were characterized first for their appearance visually and then the preliminary characterization was carried out, results of which are given in Tables 2.3 and 2.4.

Table 2.3 Preliminary Characterization (Physical) of COERs-I

<table>
<thead>
<tr>
<th>Type of COER</th>
<th>Appearance</th>
<th>Viscosity by Ford Cup B IV at 28 °C in sec.</th>
<th>Sp. Gravity at 28 °C in gm/cc</th>
</tr>
</thead>
<tbody>
<tr>
<td>COER-1</td>
<td>Pale yellow and clear</td>
<td>135</td>
<td>0.98</td>
</tr>
<tr>
<td>COER-2</td>
<td>Dark yellow and clear brownish</td>
<td>260</td>
<td>1.01</td>
</tr>
<tr>
<td>COER-3</td>
<td>Yellow and clear</td>
<td>N/A</td>
<td>1.05</td>
</tr>
</tbody>
</table>

Table 2.2 Castor oil-Epoxy Resin Reaction Products (COERs)

<table>
<thead>
<tr>
<th>Moles of reactants taken</th>
<th>Designation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Castor oil</td>
<td>Epoxy resin</td>
</tr>
<tr>
<td>0.268</td>
<td>0.314</td>
</tr>
<tr>
<td>0.268</td>
<td>0.268</td>
</tr>
<tr>
<td>0.268</td>
<td>0.402</td>
</tr>
</tbody>
</table>
Table 2.4  Preliminary Characterization (Chemical) of COERs-II

<table>
<thead>
<tr>
<th>Type of COER</th>
<th>Hydroxyl Number</th>
<th>Hydroxyl value in mg of KOH/gm.</th>
<th>% Hydroxyl</th>
<th>Number of unsaturation per molecule</th>
</tr>
</thead>
<tbody>
<tr>
<td>COER-1</td>
<td>~3</td>
<td>145</td>
<td>4.56</td>
<td>2</td>
</tr>
<tr>
<td>COER-2</td>
<td>~3</td>
<td>130</td>
<td>3.89</td>
<td>2</td>
</tr>
<tr>
<td>COER-3</td>
<td>~3</td>
<td>113</td>
<td>3.37</td>
<td>2</td>
</tr>
</tbody>
</table>

Viscosity of various COERs was measured using Ford cup B IV at ambient room temperature (28 °C) and flow time was reported in seconds as a measure of viscosity. In case of COER-3, the sample was much viscous and so the viscosity could not be measured accurately with Ford cup B IV.

Specific Gravity of COERs increase as the amount of epoxy resin increases in the COERs.

From the above results it is evident that the number of hydroxyl groups in all three COERs is 3 but hydroxyl value and % hydroxyl decreases as the moles of epoxy resin increases.

From the unsaturation test it is clear that the number of unsaturation per molecule in each COER is 2 which are same as that of castor oil. It means that the reaction of epoxy resin has not occurred at double bond of castor oil.

2.3.1  Synthesis of isocyanated terminated castor oil polyurethane (ICOPU):
This was prepared by method reported in literature [142]. To a well stirred castor oil (1 mole) the hexamethylenediasocyanate (3-5 mole) was added gradually. The resultant syrup was immediately used for next step.

2.3.2  IR Spectral Study of COERs:

The IR spectra of these three COERs and castor oil were scanned neat on KBr pellets. The spectra are shown in Figs. 2.1 to 2.4.
Fig 2.1 IR Spectrum of Castor oil

Fig 2.2 IR Spectrum of COER-1
Interpretation of IR spectra of COERs reveals characteristic group frequencies. A broad band around 3500-3300 cm\(^{-1}\) can be assigned to intermolecular and intramolecular H-bonding in hydroxyl functionalities. Symmetrical stretching frequencies around 2930-2830 cm\(^{-1}\) due to aliphatic alkenes are observed.

A well resolved sharp band at 1746 cm\(^{-1}\) indicates the presence of carbonyl group of ester linkage in triglyceride structure. A series of bands at 1460, 1410 and 1366 cm\(^{-1}\) are observed due to asymmetric stretching vibrations of aliphatic moieties.
A distinct but weak band around 1250 cm\(^{-1}\) and well resolved bands around 1180 and 1120 cm\(^{-1}\) can be ascribed to C-O linkages in castor oil molecule. Presence of distinct bands around 3020, 1500 and 960 cm\(^{-1}\) confirms the unsaturation, due to C-H stretching, C=C stretching and in-plane bending vibration frequencies respectively. In the IR spectra of COERs, band at 910 cm\(^{-1}\) is not observed which indicates the absence of epoxy group. Bands due to aromatic rings are observed at their respective positions.

### 2.4 Techniques Used for the Coatings

#### 2.4.1 Application of Coating Materials

Several properties demands’ of a coating material can be full filed only if the coating materials form films with considerable physical integrity. The process of film formation, the conversion of liquid composition into an adherent and durable film, comprises three main steps: Application, Fixation and curing [142].

Coatings can be applied on substrate by various methods like brushing, spraying, electro deposition, Dipping etc. The method of application of coating depends upon nature of composition and substrate on which coating has been applied [143].

After application of coating material, their come the fixation step in which coating is stabilized on substrate against any tendency of run off or to form an uneven film. This depends upon many factors like film thickness, rate of solvent evaporation and rheological properties of coating materials. The rate of solvent evaporation should be controlled carefully as it causes rapid film viscosity build up resulting in fixation. Thus fixation is controlled mainly by rheological properties of coating materials.

The final stage of film formation process is drying or curing in which film is converted into durable coating. Depending up on nature of resin, drying process can be either chemical drying or physical drying.

Physical drying mainly takes place due to solvent evaporation and film integrity obtained by chain entanglements. Very high molecular weight polymers provide more chain entanglements which in turn result in better film integrity and finally durable coatings.

In case of chemical drying, some types of chemical reactions at room temperature or at elevated temperature are always encountered. These chemicals
reaction yields high molecular weight polymers with three dimensional networks to obtain a durable film. These reactions are generally termed as cross linking reaction. Cross linking reaction can occur either due to auto-oxidation of unsaturation present in resin structure or due to condensation reaction between the functional group present in the same resin or other resin or even between the functional group present in additive and resin. In the latter case the additive is termed as curing or crosslinking agent.

2.4.2 Auto oxidative Drying and its mechanism

The film formation in case of drying oil or oil modified resin contain unsaturated fatty acid take place due to oxidative drying. Several workers have reported their work in this area [144,145]. During drying the most important reaction of drying oil involved is with atmospheric oxygen which results in isomerism, polymerization and degradation of C-C bond and formation of oxidation product. A number of structural features of oil affect the oxidation of oils, the most important being [146]:

A) Number of unsaturation / double bonds.
B) Either conjugated or non-conjugated double bonds
C) Geometric arrangement of substituent groups around double bond.

Many mechanisms are proposed for auto oxidative drying and in most of them it is assumed that oxygen attack either at double bond in case of conjugated system or at methylene groups presents adjacent to the double bond in non-conjugated systems. Farmer and co-workers proposed the reaction occurring during the film drying by auto oxidation in which it is assumed that allylic radicals are first formed by hydrogen abstraction at methylene groups near to the double bonds which subsequently form hydroperoxides. These hydroperoxides being relatively unstable radical break down to generates free radicals. These initial products are then converted to polymers according to the following reaction scheme [147].
During the auto-oxidation termination reactions forming polyperoxides are favored over reactions and afford in carbon to carbon bond due to higher reactivity and concentration of oxygen. These polyperoxides then decomposed to poly ethers.

Rheineck proposed the following steps in film drying by auto-oxidation from linseed oil and other drying oils: [148], (or film drying testing as per BS 3900)

1. Induction stages where antioxidants present in the films are distorted.
2. Oxygen uptake becomes measurable and hydroperoxides and Conjugations are formed.
3. Decomposition of hydroperoxides occurs to form free radicals and reaction becomes auto catalytic.
4. Polymerization and cleavage reactions start leading to formation of high molecular weight cross-linkage polymers and low molecular weight decomposition products respectively.

The presence of certain transition metals increases likelihood of the peroxide break down and also act as oxygen carrier to initiated free radical polymerization. These metals are applied to as dyer and without use of them film formation would very slow. There are three classes of driers [149]:

1. **Primary driers:** These are organic salts generally octoates, talles and naphthenates etc. of transition metals. They directly catalysed the oxidation and their dosage level varies from 0.005 to 0.1 % metal based on resins solid. Their primary function is to promo rapid surface drying of the film.

2. **Secondary driers:** These are organic salts of Zn, Ca, Pb, or Ba. They do not have any direct effect of drying when use alone but when use with a
primary driers, they produce synergistic effect and increase rate of oxygen uptake.

3. **Coordination driers:** They are generally compounds of zirconium or aluminum which help in polymerization presses by forming coordination compounds. Zirconium act through drier.

### 2.4.3 Chemical drying

When drying involves intermolecular or intramolecular condensations reaction of functional groups, it’s termed as chemical drying. When functional groups on the same polymer undergo condensation reaction, it is known as intramolecular condensation and when condensation reactions involve functional groups present on polymer and on cross-linking agents, it is termed as intermolecular condensation. Functional groups generally use to bring about condensations are –OH, -COOH, -NC, -O-, etc. Whereas cross-linking agents employed are melamine resin, phenolic resin, di or poly isocynate, amine etc. These condensation reactions results in the formation of high molecular weight polymers which in turn impart film setting.

### 2.5 Surface coating: Testing and Evolution

It is of prime importance to evaluate mechanical and chemical properties of coatings to assess how long coatings can maintain its protective and decorative values during their service life. During the service life, coatings are subjected to a wide variety of mechanical strains and stresses in different chemical environments which finally affects the ultimate mechanical properties of films. Chemical properties of films generally depends upon chemical composition of film former, presence or absence of free functional groups especially in case of thermosetting resins and cross-link density of film [150]. The most important function of a coating is long term protection of substrate on which it is applied so, evaluation of mechanical and chemical properties of films is essential to know how long a film can maintain its physical integrity and can fulfill its protective role satisfactorily for a said application.

The most common mechanical and chemical properties of a coating film, tested and evaluated, are discussed below:

Film application machine and thickness measurement are shown as per photographs.
2.5.1 Adhesion as per BS 3900

Adhesion [151] can be defined as the state in which two surfaces are held together by the forces. These forces can be either physical or chemical in nature. Physical forces include interfacial forces whereas chemical forces involve valence attractions. The interfacial forces are too weak to be measured by any mechanical means. Adhesion of a coating to substrate is mainly affected by two factors, one is wet ability of substrate i.e. affinity of solvent and resin to substrate and other factor being roughness of substrate. The earlier one is termed as specific adhesion and later one known as mechanical adhesion.

In case of specific adhesion, initially solvent system and substrate must interact with each other and then polymeric phase must be adsorbed on substrate. During the process of formation polymeric phase on substrate. During the process of formation of polymeric phase on substrate, smaller molecules of solvents are replaced by larger molecules of polymers based of polymers used in the coating system. It is found that presence of low molecular weight species largely reduces the adhesion [152] as they form a weak boundary layer at or near coating-substrate interface and reduces the coating-substrate interaction.

To have proper mechanical adhesion, surface of the substrate must be free from any foreign material that can reduce substrate-coating interaction. Presence of any foreign materials reduces the wet ability of substrate by coating system followed by reduced interaction between substrate and coating system and finally resulting in poor adhesion.

Adhesion cannot be measured as such because it is defined as interfacial forces between coating and substrate and these forces cannot be measured directly by any mechanical means. Thus, adhesion is evaluated by determining the forces needed for the removal of coating from the substrate.

Wide range of methods and devices [153] for measurement of adhesion has been employed over the years but the most commonly method known as cross-hatch test is described below:

Using a sharp knife, a number of parallel cuts are made through the film to the substrate at 1 mm distance. These are crossed by another set of such lines at 90° angle to earlier ones so as to form 100 squares, a self-adhesive tape and coating. The tape is kept in contact with the coating for 10 seconds and then it is pulled off with a single
jerk. Some these squares are removed from substrate and a number of such squares on percentage basis is expressed as the result.

### 2.5.2 Flexibility as per BS 3900

According to Indian Standard Specifications [154], flexibility is defined as the degree to which a film after drying is able to confirm to movement or deformation of its supporting surface without cracking. Flexibility does not depend only on the elasticity of the film but it also involves adhesion of film to the substrate. Humidity, temperature and strain rate are the factors which affect the flexibility of the film. Methods used for assessing flexibility with adhesion include Bend Test (BS 3900 or ASTM E 855) and Erickson Test (BS 3900 or ASTM D 5894) [155].

In the bend test, coated panels are bent around mandrels of prescribed diameters embodied in a hinge. The panel is placed in such a way that coated side is remained outsideside. The panel is bent through $180^\circ$ in the second in a single stroke and without removing from the mandrel; the coated side is examined visually for crack or loss of adhesion.

Erichsen test uses a large hemispherical ended indenter. Coated panel is mounted against a rigid steel plate containing an orifice. The hemispherical indenter is placed against the back of the coated panel in line with the orifice. Pressure is applied to indenter so that a dome is gradually formed. It is continued till film cracks or for a specified distance. The coating on dome is then checked for cracks or loss of adhesion.

### 2.5.3 Hardness as per BS 3900

A material is considered to be hard when it can resist indentation and scratching. The hardness of coating material [156] cannot be expressed quantitatively or not even in absolute or intrinsic value. Thus, the measurement of hardness of coating material is done on practical basis.

Generally hardness testes are based on measuring the resistance of coating film to sharp edged instrument while cutting through the film or by determination of the resistance of the coating film to indentation. When resistance to indentation is used as a measure of hardness, it is related to rigidity of molecule or its elastic modulus. There most commonly used tests are:
I. **Pencil Hardness as per BS 3900**

In this test pencils having varying degree of hardness are used to scratch the film on test panels till one is found which cut through the film. Pencil is held at 45 °C angle and uniform pressure is applied to scratch film. Hardness of the pencils varies from 6H to 4B. The coatings are rated according to their resistance to be marked or scratched by pencil hardness [157].

![Pencil Hardness Tester](image1.png)

II. **Scratch Hardness as per BS 3900**

This test uses a mechanized or hand operated apparatus to scratch the dried film of coating material under specific load and resistance to scratching is measured and reported as hardness.

![Scratch Hardness Tester](image2.png)
III. Pendulum or Rocker type hardness as per BS 3900

In this method hardness is assessed by dampening effect with the help of a pendulum or rocker. The dampening effect i.e. dampening of oscillations is due to hysteresis losses of materials, rolling friction, shear modulus and hardness of the substrate, in case of thin coatings.

Pendulum Hardness Tester

2.5.4 Impact Resistance as per BS 3900

Impact tests evaluate the ability of coating films to withstand extension without cracking when deformation is applied rapidly [155].

The determination of impact resistance involves indentation by an object having specific weight, generally low, onto a panel from varying heights. The weight is dropped from grater and grater height until the film on panel cracks. The results are generally reported in in.lb i.e. number of inches the weight falls times its height. If the weight is directly dropped on coated side of the panel it is known as direct impact test, in which coating is compressed. If the weight falls on the back side of the coated panel then it is termed as reverse impact test. Reverse impact tests are more severe than direct one as in reverse impact test film is expected whereas in latter case it is compressed.
The nature of substrate i.e. its thickness, mechanical properties and surface largely effect the result of impact test [158].

2.5.5 Drying Time as per BS 3900

The drying time of coating system is the time required for the film to change from liquid condition as applied to a solid film. Several stages of drying process are recognized among which important stages of drying time determinations are:

a) Surface Dry
b) Tack free Dry
c) Hard Dry
“Surface dry” stage also known as “a Dry to touch stage” is the stage where the paint film on the surface is dry but soft and tacky underneath.

“Tack Free Dry” stage is the stage where film is free from thickness even under pressure.

“Hard Dry” stage is condition when drying has reached such a stage that a further coat can be satisfactorily applied if desired.

In different standard specification [159,160], various methods for determination for drying times have been reported. The drying time of coating systems are affected by humidity, air circulation, light intensity, film thickness and temperature.

2.5.6 Water and Moisture resistance

The primary function a coating is to act as barrier between substrate and environment. Many workers have studied the effect of water on film and substrate and reported it in literature [161].

To measure the water resistance of coating, three basic test employed are:

1) Measurement of water vapor permeability of the film.
2) Measurement of effect of water that condense or is slashed on to the film
3) Determination of the effect of water vapor transmitted to a permeable substrate as in case of porous substrate.

In case of non-porous substrate, measurement of water resistance is carried out using water that has been condensed on substrate, mechanically spared on substrate or using water as immersion media (i.e. Coated substrate is insured in water). The coating must be able to repelled or resist the determinate effect of water.

2.5.7 Chemical Resistance

A coating should possess resistance to various chemicals [162,163]. Chemical resistance test range from simple spots test to complicate test involving used of more sophistic instruments. Various chemicals adversely affect the film properties like gloss, color or cause swelling or sifting of a film. In extreme cases, film can be detached from research plate or vanished by solvent action.

2.5.7.1 Resistance to acids and alkies

A film should have sufficient resistance to acids and alkies [164] as they also have deleterious effect on substrate on which film is applied. The test is carried out by immersing the coated panels at ambient temperature into acids and alkalies solution of appropriate concentration. After the specified time period of immersion, the panels are examined by visually for parameters like belistring, bloom etc. and peel off in extreme cases.

Chemical nature of polymer back bone and in case of thermosetting resin the degree of cross linking play important role in resistance to acid and alkali. Presence of certain groups likes esters in polymer backbone or free functional group like –COOH, -NH₂ etc Have determinal effect on resistance.

2.5.7.1 Resistance to Solvents

Solvent resistance [165,166] of a coating system is related to certain mechanical properties of system so it is needed to have balance between these two properties keeping the end application in mind.

In general thermosetting resins have batter solvent resistance than thermoplastic resins. In case of thermoplastic resin, film formed by solvent evaporation, is always sensitive to parent solvent.

Solvent resistance tests can be carried to by two methods. The most commonly performed method to assess solvent resistance is immersion test [167]. After the
specific period of time, panels are removed from the bath and assessed for blistering, hardness, adhesion and discoloration etc.

In another method known as solvent rub test, coated test panel is rubbed with a piece of soft cloth or cotton moistened with the solvent till the film is removed from panel and number of rubs needed for this is reported as solvent resistance. Alternatively a specified.

**Determinations of Drying Time**

Mild steel panels were used to determine the air-drying time of films of various coats. The panels were prepared in the above manner and coating compositions were applied. The films were checked for “surface dry” and “tack-free dry” stages at regular intervals of time. While moving the finger on the film without applying any pressure if impression of fingerprint is not observed on the film, it was said to be “surface dry”. If the thumb is pressed on the film and twisted with applying some pressure and yet no thumb impression or detachment of film is observed then it was said to be “tack – free dry”.

**Determinations of Adhesion**

Adhesion of films to substrate was determined by employing cross-hatch adhesion test according to ASTM D-3359 and panels for the test were prepared in the manner described above. Crosshatch adhesion test was carried out after 168 hours of coating application. By using a sharp - edged knife, 10 parallel lines 1mm apart from each other were drawn on the film. Another set of such lines at right angles of 90° to previous lines was superimposed to give a pattern of squares consisting of 100 squares with each square having 1 mm side length. A self – adhesive tape was stuck over the square pattern in such a way that no air is present between tape and film. Intimate contact between tape and film was assured by pressing the tape over the length with fingers. The tape was kept in contact for 10 seconds and then the tape was rapidly pulled off in a single stroke at an angle of 120° approximately. The test was rated “passed” if not more than 5% of squares were removed.
Determining Flexibility

For the determination of flexibility, tinned mild steel panels were used. The coating compositions were applied and cured in the manner mentioned above. Flexibility tests were carried out using mandrels having specific rod diameters. A test panel was inserted between the hinges and rod in such a way that the coated side was kept outside to the direction of bending. The hinge was closed at a single stretch without jerking in about a second causing the test panel to bend through an angle of 180°. The panel was examined for presence of cracks or loss of adhesion without removing the panel from the mandril. Generally, 1/4 inch rod diameter mandrel was used and if film passed through 1/4 inch mandrel then it was said to pass the flexibility test.
Flame Retardant Properties

The composites fabricated from brominated epoxy resin (BE) were analyzed for their flame retardant properties. The property was measured by the self-extinguishing time method according to ASTM D-635. In this test the major task is to measure the time elapsed between the removal of the sample from the burner and complete self-extinguishing of the sample. This was taken as the average time for 10 standard specimens of 150 mm X 20 mm each. Satisfactory results were considered when these times were below 60 s.

Their self-extinguishing time is well below 60 sec and, hence they have good resistance to fire.
Scratch Hardness as per BS 3900

In first method, a hand operated instrument was used in which test panel was kept on a sliding base with coated side upward and scratched under specific load with a needle which was in contact with film on test panel. The load was kept increasing till the film was scratched which was indicated by a light bulb that glows when film is scratched. The results were expressed in (Kg) corresponding to the load at which film is scratched.

Pencil Hardness as per BS 3900

In this method, pencils having different hardness were used. Sharp tipped pencils having hardness 4B (soft) and 6H (hard) were used to scratch the film. The pencil was held approximately at an angle of $45^\circ$ to the film and with uniform pressure pulled down over the length of the film. The test was repeated till a pencil with specific hardness was able to scratch the film. The hardness of that pencil was reported as the pencil hardness test.

Determination of Impact Resistance as per BS 3900

The coated test panels for the impact resistance test were prepared in the manner. The coated test panels for the impact resistance test were prepared in the manner described above. The test was carried out after 168 hours of coating application. The coated panel was kept on a platform with the coated side upward.

The panel was then indented with an object of specific weight from varying heights. The test was repeated by increasing the height from which the object falls till the film was cracked or detached.

Determination of Chemical Resistance Properties as per BS 3900

For the assessment of chemical resistance are the films to various chemicals, tinned mild steel panels were used which were prepared, coated and cured as mentioned above.

When the panels were subjected to solvent resistance test particularly, the edges of the panel were sealed with bromo epoxy resin cured at room temperature for (48 hrs.) instead of wax. The immersion method was utilized to assess the chemical resistance of
films in which the panels were immersed vertically in the baths containing solutions of different chemicals in specific concentration at room temperature for the specific time period. Upon completion of the specified time period the panels were removed from the baths and allowed to dry before visual examination. The following solutions with their respective concentrations were used for chemical resistance test:

1. For acid resistance: 5% HCl solution
2. For alkali resistance: 3% NaOH solution
3. For water resistance: Distilled water
4. For solvent resistance: Xylene

Coating

Steel substrate