



Surface Coating Studies of Polyurethane Derived from [(Alkyd)-(Epoxy Resin Treated Castor Oil)] Using Isophorene Diisocyanate - II

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ABSTRACT

Castor oil (C) was reacted with profitable epoxy resin (E) (diglycidylether of bisphenol-A, DGEBA) at a range of mole ratios. The consequential products (Castor oil- Epoxy resin) were nominated as CEs. Isocyanate terminated castor oil Polyurethane (ICOPU) was prepared by reaction of castor oil and various proportion of Isophoren diisocyanate. A commercial alkyd resin was blended with various proportions of CEs and ICOPU. A unique solvent system, which shows a one – phase clear solution and a clear coat of binder system, was used. All the blends were applied on mild steel panels and characterized for drying time, adhesion, flexibility, hardness, impact resistance and chemical resistance properties.

KEYWORDS

Alkyd Resin, Blends, Coating, Castor Oil, Castor Oil, Polyurethane, Epoxy Resin (DGEBA), Isocyanated Terminated Castor Oil Polyurethane.

INTRODUCTION

Alkyd resins¹⁻¹⁰, epoxy resins¹¹⁻¹⁸ and polyurethanes resins¹⁹⁻²² are the flexible materials for the construction of surface coating materials. Castor oil (C) is an agricultural important stuff for number of applications like raw materials for manufacturing of number of industrial utility products, coatings, urethane derivatives, surfactants, dispersant, cosmetics, fungicides, textile, nylon-type plastics and lubricants²³⁻²⁶. The presence of three functional groups such as double bonds, hydroxyl groups and esters are responsible for the attaining these applications²³⁻²⁶.

One of the polyurethane resins based on castor oil also play role for interpenetrating network polymer (IPNs).

The clubbing of alkyd resin, epoxy resin treated castor oil (CEs) and isocyanated terminated castor oil polyurethane (ICOPU) may meet the expense of good surface coating material. Hence it was thought to embark on such study. Thus the present communication comprises the studies on surface coating material based on alkyd, resin and CEs and ICOPU resin.

MATERIAL AND METHOD

Dehydrated castor oil (DCO) rosinated alkyd resin was procured from local market. Specifications of DCO alkyd resin, viscosity at 30°C 130 ±10 s, % of non volatile materials 50% and acid value (max) 10 mg/ gm resin. Castor oil was purchased from the local market. Specifications of castor oil: Viscosity at 30°C 130s, density at 28°C 0.95 g/ml, number of hydroxyl value 2.45 ≈ 3 / mole castor oil, number of unsaturation 2 /mole castor oil. Epoxy resin i.e (Diglycidylether ether of bisphenols A (DGEBA) was obtained from

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Synpole Product Pvt. Ltd., Ahmadabad, India, epoxy equivalent weight 190 g/mole, viscosity 400- 1000 cp at 25 °C. All other chemicals used were obtained from local market and were of laboratory pure grade.

Preparation of Castor Oil-Epoxy Resin Condensate Products (CEs)

Castor oil resin was prepared by the method reported from our laboratory, this method is described below. Castor oil (0.268 mole) was taken in three necked round bottomed flask equipped with a mechanical stirrer and placed in a water bath where temperature was maintained at 70-80°C. Under continuous stirring, the desired amount of epoxy resin (as shown in Table 1) was added gradually. Triethyl amine (0.05 % based on epoxy resin weight) was added as a base catalyst. At a regular interval of time, a sample was withdrawn from the reaction mixture using a siphoning device and a test was performed for the negative epoxy group [28, 29]. When the sample showed the negative test for the epoxy group, reaction was stopped and the product was allowed to cool at room temperature. The resultant products were designated as castor oil –epoxy resin (CEs) products. The varying type of mole ratios of castor oil(C): epoxy resin (E) used for the preparation of (CEs) and physical properties of the resulting products (CEs) are given in Table 1. Chemical properties of the products (CEs) are given in Table 2.

Table 2: Chemical properties of CEs

| Type of CEs | Hydroxyl Number | Hydroxyl value mg KOH/ gm | % Hydroxyl | Number of unsaturation Per molecule |
|-------------|-----------------|---------------------------------|------------|--|
| CE -1 | 3 | 145 | 4.56 | 2 |
| CE -2 | 3 | 130 | 3.89 | 2 |
| CE -3 | 3 | 113 | 3.37 | 2 |

Preparation of Isocyanated Terminal Caster Oil Polyurethane (ICOPU)

This was prepared by method reported in literature³⁰. To well stirred castor oil (1 mole) the hexamethyldaediisocyanate (3-5 mole) was added gradually. The resultant syrup was immediately used for next step.

Preparation of Alkyd – CEs –ICOPU Blends

To achieve the desired results of solvency, evaporation, several combinations of solvents were tried. The solvent system that produced a one – phase clear solution and a clear coat of the binder system was as follows: 50 % THF, 40 % cyclohexanone, and 10 % toluene by volume).

Table 1: Mole ratios of C: E and physical properties of CEs

| Mole of reactant | | Designation | Appearance | *Viscosity seconds | Specific gravity gm/ml |
|------------------|----------------|-------------|-----------------------|--------------------|------------------------|
| Castor oil (C) | Epoxy resin(E) | | | | |
| 0.268 | 0.134 | CE-1 | Pale yellow and clear | 135 | 0.98 |
| 0.268 | 0.268 | CE -2 | Pale yellow and clear | 240 | 1.01 |
| 0.268 | 0.402 | CE- 3 | Pale yellow and clear | N/A** | 1.05 |

*Viscosity time was measured using ford cup type B – IV at 30°C

** N/A not analyzed

So the prepared ICOPU resin was dissolved in the above solvent system to prepare 50 % solutions of resin which was then utilized to prepare alkyd - CEs – ICOPU. In a three necked round-bottom flask equipped with a mechanical stirrer, alkyd resin was charged and stirred for 5 min. Under continuous stirring, the desired amount of specific CEs was added, and mixing allowed for 15 min. Solution of ICOPU resin thus prepared, was then slowly added to CE-alkyd mixture with continuous stirring. Upon completion of the addition of ICOPU resin solution, the final alkyd- CE - ICOPU mixture was stirred for 30 min to have a homogeneous mixture. After stirring, the mixture was kept in a cylindrical glass container overnight to check for any tendency of separation of layers. In neither case separation of distinct layers was observed. The proportions of alkyd- CEs - ICOPU blends along with designations are given in Table 3.

Preparation of Coating Composition Based on Alkyd- CEs – ICOPU Blends

To study the film properties of alkyd- CEs- ICOPU blends, the coating compositions of various blends were prepared in the following manner: 50.0 g of the desired blend was taken in a 250 ml glass beaker. The driers lead octoate (18% Pb), cobalt octoate (6% Co) and manganese octoate (6% Mn) were added to it in the proportions of 0.5, 0.05, and 0.05 %, respectively. The resultant blends of alkyd-CEs- ICOPU resins were diluted with the above solvent mixture to obtain a viscosity appropriate for application with a brush on clean mild steel panels.

Panel Preparation

The mild steel panels were first degreased in alkali solution and subsequently swabbed with xylene to remove any type of oily material or

Table 3: Proportion of alkyd – CEs-ICOPUs blends

| Type of CE | Weight of alkyd resin (gm) | Weight of CE (gm) | Weight of ICOPU (gm) | Designation |
|------------|----------------------------|-------------------|----------------------|-------------|
| CE-1 | 100 | 10 | 10 | B-a1 |
| | 100 | 10 | 10 | B-a2 |
| | 100 | 10 | 20 | B-a3 |
| | 100 | 10 | 20 | B-a4 |
| | 100 | 10 | 30 | B-a5 |
| | 100 | 10 | 30 | B-a6 |
| CE-2 | 100 | 10 | 10 | B-b1 |
| | 100 | 10 | 10 | B-b2 |
| | 100 | 10 | 20 | B-b3 |
| | 100 | 10 | 20 | B-b4 |
| | 100 | 10 | 30 | B-b5 |
| | 100 | 10 | 30 | B-b6 |
| CE-3 | 100 | 10 | 10 | B-c1 |
| | 100 | 10 | 10 | B-c2 |
| | 100 | 10 | 20 | B-c3 |
| | 100 | 10 | 20 | B-c4 |
| | 100 | 10 | 30 | B-c5 |
| | 100 | 10 | 30 | B-c6 |

contaminant. After the xylene has evaporated, panels were burnished with emery paper as per Indian Standards³⁰. Panels were again washed with xylene after burnishing to remove any trace of emery paper particles or metal particles. As soon as the panels were dry, coatings were applied on them without any delay.

Film Characterization

The coated panels were examined for drying time, adhesion test, flexibility test, scratch hardness, pencil hardness, impact resistance and chemical resistance by standard methods. The results are given in Tables 4-6 respectively.

Determination of Drying Time

Mild steel panels were used to determine the air-drying time of films of various coats³¹. 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”. The results are given in Table 4.

Determination 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. Cross-hatch 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 ensured 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. The results of cross-hatch adhesion test are given in Table 4.

Table 4: Properties of films prepared from alkyd –CEs - ICOPUs blends

| Designation | Drying time in minutes | | Adhesion | Flexibility |
|-------------|------------------------|---------------|----------|-------------|
| | Surface dry | Tack-free dry | | |
| B-a1 | 89 | 268 | P | P |
| B-a2 | 90 | 269 | P | P |
| B-a3 | 87 | 237 | P | P |
| B-a4 | 78 | 243 | P | P |
| B-a5 | 71 | 216 | P | P |
| B-a6 | 81 | 207 | P | P |
| B-b1 | 78 | 239 | P | P |
| B-b2 | 70 | 233 | P | P |
| B-b3 | 61 | 227 | P | P |
| B-b4 | 64 | 214 | P | P |
| B-b5 | 56 | 196 | P | P |
| B-b6 | 63 | 203 | P | P |
| B-c1 | 69 | 229 | P | P |
| B-c2 | 71 | 223 | P | P |
| B-c3 | 56 | 204 | P | P |
| B-c4 | 61 | 203 | P | P |
| B-c5 | 55 | 206 | P | P |
| B-c6 | 58 | 202 | P | P |

Determination of Flexibility

For the determination of flexibility³², tinned mild steel panels were used. The coating compositions were applied and cured in the manner mentioned above. Flexibility test were carried out using mandrels having specific rod diameter. 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 mandrill. 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. The results of flexibility test are given in Table 4.

Determination of Hardness

Hardness of films of various alkyd- CEs – ICOPU Blends were determined using tinned mild steel panels after 168 hours of coating application . Two different methods were used to determine the hardness.

➤ Scratch Hardness

In first method³³, 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

In this method³⁴, 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° 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. The results of hardness determination are given in Table 5.

Determination of Impact Resistance

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. The results are generally expressed in (in. Ib) i.e. the number of inches the weight falls times its weight³⁵. The results of impact tests are reported in Table 5.

Table 5: Mechanical properties of films prepared from alkyd-CEs- ICOPUs blends

| Designation | Scratch hardness Kg | Pencil hardness | Impact resistance Direct in.lb |
|-------------|---------------------|-----------------|--------------------------------|
| B-a1 | 2.16 | 3H | 140 |
| B-a2 | 2.19 | 3H | 145 |
| B-a3 | 2.40 | 3H | 153 |
| B-a4 | 2.36 | 4H | 157 |
| B-a5 | 2.45 | 4H | 164 |
| B-a6 | 2.39 | 3H | 167 |
| B-b1 | 2.41 | 4H | 152 |
| B-b2 | 2.37 | 5H | 146 |
| B-b3 | 2.55 | 4H | 173 |
| B-b4 | 2.40 | 5H | 166 |
| B-b5 | 2.56 | 5H | 182 |
| B-b6 | 2.58 | 6H | 177 |
| B-c1 | 2.63 | 8H | 167 |
| B-c2 | 2.68 | 6H | 165 |
| B-c3 | 2.79 | 7H | 188 |
| B-c4 | 2.70 | 8H | 182 |
| B-c5 | 2.84 | 8H | 217 |
| B-c6 | 2.79 | 9H | 202 |

Determination of Chemical Resistance Properties

For the assessment of chemical resistance of the films to various chemicals³⁶, tinned mild steel panels were used which were prepared, coated and cured as mentioned above. Before subjecting the test panels to chemical resistance test, the backside of coated panel (i.e. the non

coated side) was coated with epoxy resin and cured at room temperature for 48 hours. Subsequently all the four edges of the panel were sealed with paraffin wax by dipping approximately 1 cm of each side in molten wax and cooling at room temperature to form a 1 cm thick impervious and continuous layer of wax.

When the panels were subjected to solvent resistance test particularly, the edges of the panel were sealed with 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

The results of chemical resistance test are furnished in Table 6.

RESULTS AND DISCUSSION

The results of evaluation of films properties of alkyd – CE – ICOPU blends are shown in Tables 4-6. For sake of the convenience, the amount of CEs was kept constant for all the blends (Table 3). The prime concern is to study the effect of ICOPU resins on properties of alkyd – CEs blends, so amount of ICOPU resins was varied keeping the amount of CEs constant.

Viscosity of various CEs was measured using Ford cup B IV at ambient room temperature (30 °C) and flow time was reported in seconds as a measure of viscosity. In case of CE -3, the sample was much viscous and so the viscosity could not be measured accurately with Ford cup B-IV.

From Table 1, we can predict that the viscosity of CEs increases as the mole ratios of epoxy resin increases. Specific gravity of CEs increases as the amount of epoxy resin increases in CEs. From Table 2, it is evident that the number of hydroxyl groups in all three CEs is 3, but hydroxyl value and % hydroxyl decreases as the mole of epoxy resin increases. From the unsaturation test it is clear that the number of unsaturation per molecule in each CE is 2, as in castor oil. It means that the reaction of epoxy resin has not occurred at the double bonds of castor oil.

From the results given in Tables 4-6 it suggests that these films give good surface dry and good tack-free dry properties as well as good adhesion and flexibility. The drying time reduces on increasing the amount of ICOPU resin added. The good drying time can be attributed to the presence of carbonyl groups in the polymer backbone, which activate the methylene groups in the ICOPU resin. Therefore in the presence of suitable driers, the oxygen activation of the methylene group is further accelerated, which results in faster drying time. The drying time is further improved as the concentration of epoxy resin increases.

Excellent scratch hardness was obtained from the films prepared from these blends. As the concentration of ICOPU resin increases, gradual increase in hardness is observed. Also the films show significant improvement in hardness in blends with higher epoxy content in CEs and higher concentration of ICOPU resin in alkyd – CE – ICOPU blends. This improvement can be attributed to excellent structural compatibility of components in the blend which form a crosslinked polymer. Pencil hardness and impact resistance were also good. Chemical resistance tests of the films gave satisfactory results as shown in Table 9 and 10, due to combination of individual properties of components. Each individual components of the blend shows good acid, alkali, solvent and water resistance and so the resistance of resultant blend is also improved.

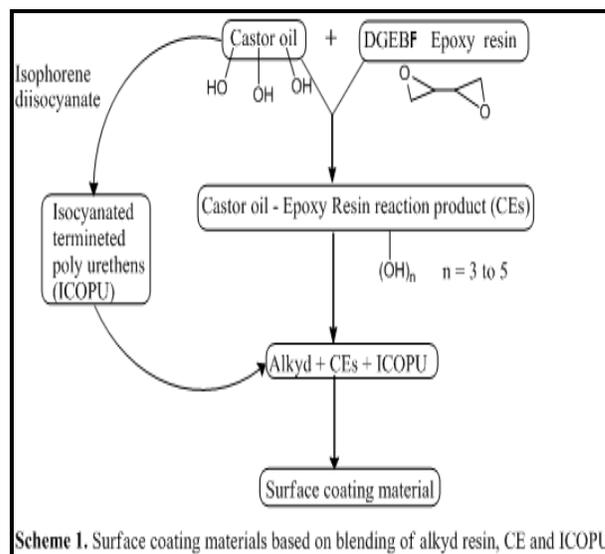
Table 6: Chemical resistances properties of films prepared from alkyd-CEs- ICOPU blends

| Designation | Acid resistance 5% HCl 24 h | Alkali resistance 3% NaOH 2h | Water resistance (Dist. Water) 168 h | Solvent resistance Xylene 168 h |
|-------------|--------------------------------|---------------------------------|--|------------------------------------|
| B-a1 | 2 | 3 | 1 | 2 |
| B-a2 | 2 | 3 | 1 | 2 |
| B-a3 | 3 | 4 | 2 | 2 |
| B-a4 | 3 | 4 | 2 | 2 |
| B-a5 | 4 | 4 | 3 | 3 |
| B-a6 | 4 | 4 | 3 | 3 |
| B-b1 | 3 | 4 | 3 | 3 |
| B-b2 | 3 | 4 | 3 | 3 |
| B-b3 | 4 | 4 | 3 | 4 |
| B-b4 | 4 | 4 | 3 | 4 |
| B-b5 | 4 | 5 | 4 | 4 |
| B-b6 | 4 | 5 | 4 | 4 |
| B-c1 | 4 | 4 | 4 | 4 |
| B-c2 | 4 | 4 | 4 | 4 |
| B-c3 | 5 | 5 | 4 | 5 |
| B-c4 | 5 | 5 | 4 | 5 |
| B-c5 | 5 | 5 | 5 | 5 |
| B-c6 | 5 | 5 | 5 | 5 |

*0 = film completely removed. *1 = film removed and particularly cracked.
 *2 = film partially cracked. *3 = loss in gloss.
 *4 = slight loss in gloss. *5 = film largely unaffected.

CONCLUSION

Room temperature curing composition can be prepared easily and give satisfactory results. Castor oil and epoxy resin reaction products upon blending with resins like alkyd and ICOPU resin (based on maleated / tetrahydrophthalated cyclohexanone formaldehyde resin) give good mechanical and chemical properties. All films based on CHF resin of 300 OHV exhibited better performance than those based on CHF resin of 235 OHV. Films based on tetrahydrophthalated CHF resins showed better performance than those based on maleated CHF resins.



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