



Polyurethane Surfaces Coating Based on Alkyd-(Castor Oil-Epoxy resin Reaction Product) Blends

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ABSTRACT

Castor oil (CO) was reacted with commercial epoxy resin (ER) (Diglycidylether of Bisphenol-A i.e. DGEBA) at various mole ratios. Resultant condensate products of castor oil-epoxy resin was designated as COERs and characterized by physical, chemical and IR spectral study. Commercially available alkyd resin was blended with various proportions of castor oil-epoxy resin condensate products (alkyd-COERs blends) using different isocyanates namely toluene diisocyanate (TDI) and hexamethylene diisocyanate (HMDI). All blends were applied on mild steel panels and characterized for surface drying time, tack-free time, adhesion, flexibility, scratch hardness, pencil hardness, impact resistance and chemical resistance properties.

Keywords: Epoxy resin (DGEBA), Castor oil-Epoxy resin (COERs), Alkyd resin, Polyurethane (PU), Toluene diisocyanate (TDI), Hexamethylene diisocyanate (HMDI), Coating, Blend

INTRODUCTION

Alkyd resin is a prime candidate for the surface coating material because alkyds are relatively inexpensive in terms of raw materials and manufacturing costs. Alkyd resins are compatible with most substances used in surface coating industries and hence they can be easily modified for special applications. Other polymers may offer better properties in some specific area of application but alkyds have widest range of acceptable properties in terms of surface coating usage along with coat and versatility. It is generally manufactured from phthalic anhydride, polyol and drying oils. In order to improve properties of alkyd resins, modification with various other materials is the best method. These other materials, used for the modification may be present in physical or chemical combination. Modification of alkyd resin with cellulose nitrate gives fast-drying, modification of alkyd resin with chlorinated rubber gives good fire-resistance property. Alkyd resin is also used in number of applications [1-4].

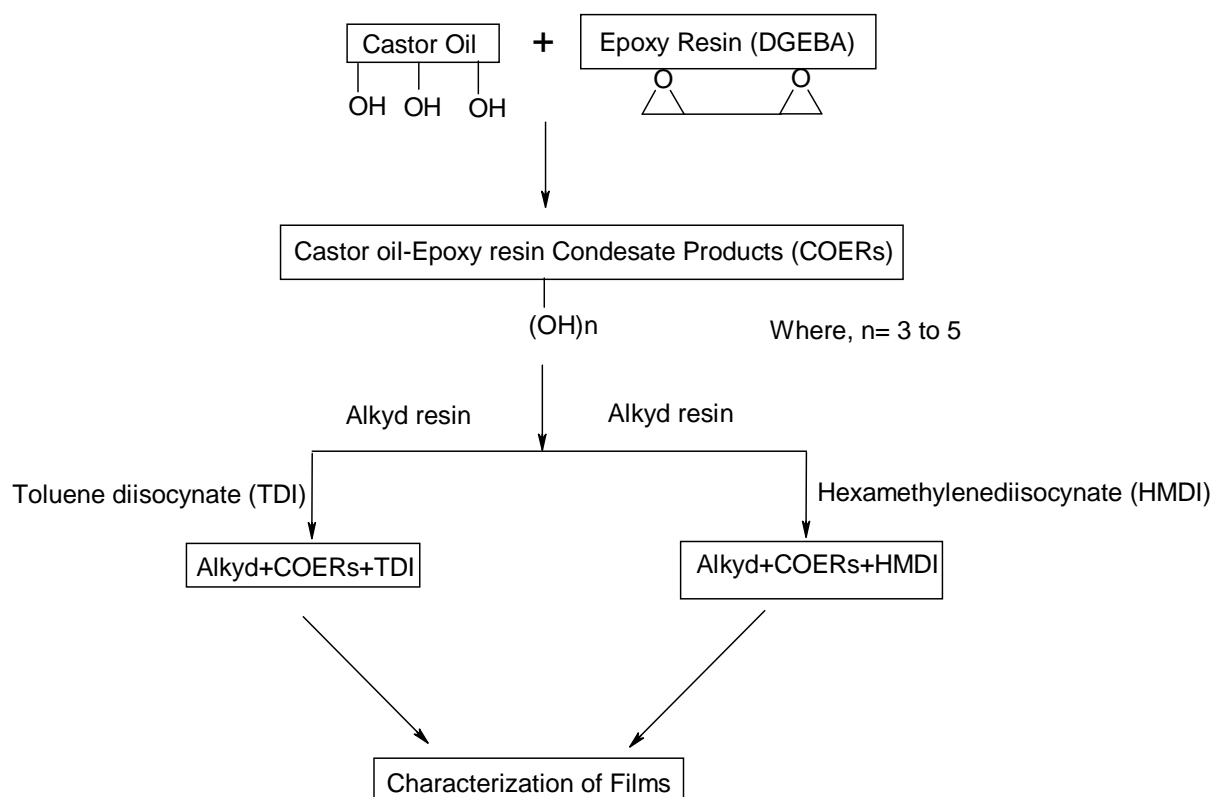
Castor oil (CO) sometimes described as a triglycerides of ricinoleic acid, is one of the naturally occurring glycerides that approaches being a pure compound. Castor oil (CO) serves as raw material for the manufacturing of number industrial utility products [5-7]. Castor oil known preliminary for its medicinal use as a cathartics, is now also used primarily as an industrial raw material for the manufacturing of industrial products used in coatings, urethane derivatives, surfactants, dispersant, cosmetics, textile and lubricants [8, 9].

Epoxy resins contain hydroxyl and epoxy groups. They can be cured by cold curing or stoving with wide range of materials which includes amino and phenolic resin, AMINES, anhydrides, polyamides and isocyanates. The resulting films of epoxy resins are very abrasion resistant, resistant to chemical attack and show a high degree of adhesion to metal and other surfaces and thus widely used in industrial applications. Epoxy resins are versatile resins having wide range of properties such as adhesion to substrate, corrosion resistance and high tensile, flexural and

compressive strengths. Because of the versatile properties exhibited by epoxy resin it has found number of applications [10-16].

Term polyurethane (PU) originally referred to coating system that utilized high reactivity of isocyanates for chemical hardning. Polyurethane (PU) chemistry is based on reaction of a diisocyanate with compounds containing an active hydrogen atom to produce urethane linkages. There are many compounds that contain active hydrogen like water, alcohol, amines, hydroxyl group, acids etc. Such kind of reaction occurs at room temperature or at slightly elevated temperature. Due to such high reactivity of isocyanates with variety of compounds, it is possible to formulate urethane coating systems with different compositions and methods of applications. Polyurethanes are most widely used in coating industry as they exhibit excellent abrasion resistance, toughness, low temperature flexibility, chemical and corrosion resistance properties [17] and wide range of mechanical strength. The use of alkyd resin for modification with isocyanates in two component systems is well known [18].

Hence, the present article comprises synthesis, characterization and coating application of polyurethane composition based on alkyd-(castor oil-epoxy resin reaction product) blends with Toluene diisocyanate (TDI), Hexamethylene diisocyanate (HMDI).



Scheme 1 Synthetic Steps

MATERIALS AND METHODS

Materials

Castor oil was purchased from local market. Epoxy resin (i.e. DGEBA) was obtained from Atul Industries Limited (Valsad, India). Alkyd resin was procured from Pacific Paints (V. U. Nagar, India). All other chemicals used were of pure grade.

Preparation of Castor oil-Epoxy resin Condensate Products (COERs)

The Castor oil-Epoxy resin products (COERs) were prepared easily by using method reported in our earlier communication [19]. The method for preparation of Castor oil-Epoxy resin products (COERs) is given briefly as follows.

Castor oil (0.268 mole) was taken in to a three necked flask equipped with a mechanical stirrer and placed in a water bath where temperature was maintained at 70-80 °C. Under continuous stirring desired amount of epoxy resin (as shown in Table 1) was added with 0.05% of triethylamine (added as a base catalyst). At the regular interval of time, a sample was withdrawn from the reaction mixture using siphoning device and test was performed for the negative epoxy group [20]. When the sample showed the negative test for the epoxy group reaction was stopped and product was allowed to cool at room temperature. The resultant products were designated as castor oil-epoxy resin (COERs) products. The varying type of mole ratios of castor oil (CO): epoxy resin (ER) used for the preparation of COERs and physical properties of resultant products (COERs) are given in Table 1. Chemical properties of resultant products (COERs) are given in Table 2.

TABLE 1 Mole Ratios of CO: ER and Physical Properties of COERs

Mole of reactants taken		Designation	Appearance	*Viscosity in sec.	Sp. gravity in gm/cc
Castor oil	Epoxy resin				
0.268	0.134	COER-1	Pale yellow and clear	135	0.98
0.268	0.268	COER-2	Dark yellow and clear	240	1.01
0.268	0.402	COER-3	Brownish yellow and clear	290	1.05

*Viscosity time was measured using ford cup type "B" IV. (at 30°C)

TABLE 2 Chemical Properties of COERs

Type of COER	Hydroxyl Number	Hydroxyl value in mg of KOH/gm	% Hydroxyl	Number of unsaturation per molecule
COER-1	3	145	4.56	3
COER-2	3	130	3.89	3
COER-3	3	113	3.37	3

TABLE 3 PU Compositions Based on Alkyd-COERs Blends for TDI and HMDI

Type of COERs taken	Weight of alkyd resin taken in gms.	Weight of COER taken in gms.	Designation For TDI	Weight of alkyd resin taken in gms.	Weight of COER taken in gms.	Designation For HMDI
COER-1	100	10	ACT-101	100	10	ACH-201
	100	20	ACT-102	100	20	ACH-202
	100	30	ACT-103	100	30	ACH-203
COER-2	100	10	ACT-104	100	10	ACH-204
	100	20	ACT-105	100	20	ACH-205
	100	30	ACT-106	100	30	ACH-206
COER-3	100	10	ACT-107	100	10	ACH-207
	100	20	ACT-108	100	20	ACH-208
	100	30	ACT-109	100	30	ACH-209

TABLE 4 Properties of Films Prepared from PU Compositions Based on Alkyd-COERs Blends with TDI and HMDI

Designation	Drying time in minutes		Adhesion	Flexibility
	Surface dry	Tack-free dry		
ACT-101	55	145	F	F
ACT-102	50	135	P	P
ACT-103	40	110	P	P
ACT-104	45	120	P	F
ACT-105	35	105	F	P
ACT-106	30	95	P	P
ACT-107	25	75	P	P
ACT-108	20	65	P	P
ACT-109	10	50	P	P
ACH-201	70	160	F	F
ACH-202	60	140	F	P
ACH-203	55	125	P	P
ACH-204	50	150	F	P
ACH-205	45	135	P	P
ACH-206	40	120	P	P
ACH-207	30	110	P	P
ACH-208	25	95	P	P
ACH-209	20	80	P	P

P=Pass, F=Fail

Preparation of COERs-Alkyd Blends

To prepare COERs-alkyd blends, a simple method involving physical mixing was employed, both can be prepared by same method as described below:

Three necked flask equipped with a mechanical stirrer, alkyd resin was charged and under continuous stirring desired amount of specific COERs (as shown in Table 3) were added gradually over the period of half an hour. Upon the completion of addition the reaction mixture was stirred for an hour after which it was kept aside in a cylindrical glass container for over night to check any tendency of separation of the two layers. In neither case separation of the two layers was observed.

TABLE 5 Mechanical Properties of Films Prepared from PU Compositions Based on Alkyd-COERs Blends with TDI and HMDI

Designation	Scratch hardness in gms.	Pencil hardness	Impact resistance in-lb
ACT-101	1800	1H	125
ACT-102	2200	1H	125
ACT-103	2200	2H	150
ACT-104	2400	3H	150
ACT-105	2400	4H	175
ACT-106	2600	4H	175
ACT-107	2800	4H	175
ACT-108	3000	5H	200
ACT-109	3000	5H	225
ACH-201	1000	1H	125
ACH-202	1200	1H	125
ACH-203	1200	2H	150
ACH-204	1400	1H	125
ACH-205	1600	2H	150
ACH-206	1800	3H	175
ACH-207	2100	3H	150
ACH-208	2100	4H	175
ACH-209	2200	4H	200

TABLE 6 Chemical Resistances Properties of Films Prepared from PU Compositions Based on Alkyd-COERs Blends with TDI and HMDI

Designation	Acid resistance 5% HCl 24 hrs.	Alkali resistance 3% NaOH 2 hrs.	Water resistance (Dist. Water) 168 hrs.	Solvent resistance Xylene 168 hrs.
ACT-101	3	2	4	3
ACT-102	4	3	5	3
ACT-103	4	4	5	4
ACT-104	4	3	4	3
ACT-105	5	4	5	4
ACT-106	5	4	5	4
ACT-107	5	4	5	4
ACT-108	5	5	5	5
ACT-109	5	5	5	5
ACH-201	3	2	4	3
ACH-202	4	3	5	3
ACH-203	4	4	5	4
ACH-204	4	3	4	3
ACH-205	5	4	4	4
ACH-206	5	4	5	4
ACH-207	5	4	5	4
ACH-208	5	5	5	5
ACH-209	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

Preparation of PU Coating Composition Based on Alkyd-COERs Blends

The PU compositions based on various alkyd-COERs blends were prepared using the following procedure:

Two isocyanates were used namely toluene diisocyanate (TDI) (i.e. aromatic) and other is hexamethylene diisocyanate (HMDI) (i.e. aliphatic). The hydroxyl values of alkyd-COERs blends were not determined satisfactorily. Thus prior to addition of isocyanates to alkyd-COERs blends was considered. Isocyanates were added to the blends till the resultant mixture showed turbidity. Over all experiments indicates that approximately 33-34 ml of TDI and 38-39 ml HMDI were appropriate amounts till which turbidity was not observed (i.e. clear material for instant coating application was obtained).

Table 3 represents the amount of alkyd-COERs blends and designation of resultant PU compositions. The driers Lead Octoate (18% Pb), Cobalt Octoate (6% Co) and Manganese Octoate (6% Mn) were added into it in the proportions of 0.5%, 0.05% and 0.05% respectively. Dry xylene was used to thin the coating compositions to obtained suitable viscosity for brush application.

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 contaminant from the surface. After xylene has been evaporated the panels were coated by the above prepared coating composition.

FILM CHARACTERIZATION

The coated panels were examined for drying time, adhesion test, flexibility test, scratch hardness, pencil hardness, impact resistance and chemical resistance properties by standard methods. The results are given in Tables 4, 5 and 6 respectively.

Determination of Drying Time

The mild steel panels were used to determine the air drying time of films of various blends. The panels were prepared in a similar manner written above and coating compositions were applied. The films were checked for 'surface dry' and 'tack-free dry' stages at regular interval of time. The results of drying time determination are given in Table 4.

Determination of Adhesion Test

Adhesion of films were determined by employing cross-hatch adhesion test and panels for the test were prepared exactly in a similar manner to that of drying time determination test. Cross-hatch adhesion test was carried out after 168 hour of coating application. Adhesion test was carried out using reported method [19]. The results are given in Table 4.

Determination of Flexibility

For the determination of flexibility, mild steel panels were used. The coating compositions were applied and cured in the same manner as mentioned above. Flexibility test were carried out using mandrels having specific rod diameter. Generally 1/8 inch rod diameter mandrel was used and if film passed through 1/8 inch mandrel then it was said to be passed for the flexibility test. The results are given in Table 4.

Determination of Scratch Hardness

In this 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 was scratched. The results are given in Table 5.

Determination of Pencil Hardness

In this method the use of pencil having different hardness are 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 and hardness off that pencil was reported as the pencil hardness test. The results are given in Table 5.

Determination of Impact Resistance

The coated test panels for impact resistance test were prepared in the same manner as described above. The test was carried out after 168 hour of coating application. The coated panel was kept on a platform (coated side upward). The panel was then indented with an object of specific weight from the 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 given in Table 5.

Determination of Chemical resistance properties

The assessment of chemical resistance of the films to various chemicals, mild steel panels were used which were prepared, coated and cured as mentioned above. 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 with 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 results of resistance against chemicals are given in Table 6.

RESULTS AND DISCUSSION

Results of Table 1 itself suggest that viscosity of COERs increases as the mole ratios of epoxy resin increases. Specific gravity of COERs increases as the amount of epoxy resin increases in COERs. Results given in Table 2

gives evident that the number of hydroxyl groups in all three COERs 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 COER is 3, which are same as in castor oil. It means that the reaction of epoxy resin has not occurred at double bond of castor oil. The IR spectra of castor oil and all three COERs were scanned neat on KBr pellets. The IR spectra of castor oil and all three COERs are found to be consistent with their predicted structures.

The drying time of films based on PU compositions is much lower than that of alkyd-COERs blends. This can be attributed to presence of urethane linkages which is known for the fast drying characteristic [21]. Comparison of drying time of PU films based on TDI and HMDI shows that the PU films based on HMDI have higher drying time than PU films based on TDI. This can be due to structural difference in both isocyanates; TDI is aromatic while HMDI is aliphatic. Also, results of adhesion test and flexibility suggest that, these films give good adhesion and flexibility. Flexibility of all the films was measured by using 1/8" mandrel as per ASTM D 622. Excellent scratch hardness was obtained from the films, prepared from these blends. The pencil hardness and impact resistance are also good for such kind of films. Chemical resistance properties of all the films give satisfactory results.

CONCLUSION

Room temperature curing composition can be prepared easily and give satisfactory results. Drying time of films based on TDI shows faster drying than compared to PU films based on HMDI. PU films based on TDI shows improved scratch hardness than PU films based on HMDI. Also results of scratch hardness, pencil hardness and resistance against chemicals are higher in case of PU films prepared from TDI as compared with PU films prepared from HMDI.

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