Reactive polyamides from cycloaliphatic C_{21} dicarboxylic acid and their evaluation as epoxy curing agents*

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Reactive polyamides with amine values ranging from 310 to 389 were prepared by reacting C_{21} cycloaliphatic dicarboxylic acid, prepared from acrylic acid and dehydrated castor oil fatty acids, with various polyamines, namely diethylenetriamine, triethylenetetramine and tetraethylenepentamine. Some reactive polyamides of matching amine values were also prepared by using C_{36} dimer acids and tetraethylenepentamine for comparison. The polyamides were then reacted with an epoxy resin (epoxy resin of equivalent weight 450) in different equivalent weight ratios. The cured product obtained by using an equivalent weight ratio of 1.00:1.00 of epoxy resin and reactive polyamide had better binding properties in comparison to other binders. The binders derived from C_{21} dicarboxylic acid were better than those derived from C_{36} dimer acids in both adhesion and hardness, and were superior in tensile strength.

(Keywords: C_{21} di-acid; C_{36} diacid; reactive polyamides; polyamines; epoxy-curing)

INTRODUCTION

Long-chain dicarboxylic acids are widely used in the preparation of polyamide resins[1–4]. Reactive polyamides of long-chain dicarboxylic acids are versatile products used as epoxy curing agents in the preparation of adhesives and surface coatings[1,5]. These resins have high corrosion and weather resistance, so they are presently gaining importance in place of synthetic binders used in surface coatings[6]. The reactive polyamines derived from C_{36} dimer acids (C_{36} diacids) are commercially employed as curing agents for epoxy resins[5,7]. The utilization of C_{19} diacid-based polyamides as epoxy curing agents has been reported[3]. Reactive polyamides are reported to have been made from C_{21} diacid, prepared from tall oil fatty acids and acrylic acid, but details about their preparation and use as epoxy curing agents are scanty[8].

In the present work reactive polyamides having amine values ranging from 310 to 389 were prepared by using C_{21} diacid and various polyamides, namely diethylenetriamine (DETA), triethylenetetramine (TETA) and tetraethylenepentamine (TEPA). The C_{21} diacid was prepared by reacting acrylic acid with dehydrated castor oil (DCO) fatty acids[9–11]. Some reactive polyamides of matching amine values were also prepared from C_{36} diacid and TEPA for comparison. The reactive polyamides derived from C_{21} and C_{36} diacids were used for curing an epoxy resin (epoxy resin of equivalent weight 450). The equivalent weight ratio of the epoxy resin and reactive polyamide was varied from 1.00:0.75 to 1.00:1.50. The cured products were evaluated for various physicochemical properties and compared.

EXPERIMENTAL

Materials

C_{21} cycloaliphatic dicarboxylic acid (C_{21} diacid) was prepared by Diels–Alder reaction of DCO fatty acids with acrylic acid[9] (acid value, 312 mg KOH g^{-1}; purity, 98%). C_{36} dimer acids (Empol 1010) were purchased from Emery Industries, USA (acid value, 198 mg KOH g^{-1}; purity, 97%). DETA, TETA, TEPA and other chemicals and solvents used were of reagent grade. The epoxy resin (molecular weight of 900 and equivalent weight of 450) used was Epikote 1001 grade supplied by Cibatul, Baroda, India, which was based on bisphenol A.

A typical procedure for the preparation of C_{21} diacid-based reactive polyamide is described. C_{21} dicarboxylic acid (*ca.* 100 g) was charged to a 0.5 l, five-necked round-bottom flask equipped with a stirrer, nitrogen inlet tube, dropping funnel, thermowell and Dean–Stark apparatus. After heating the contents to 140°C in 0.5 h, the required quantity of the polyamine was added dropwise over a period of 1.5 h. After adding the amine, the temperature was gradually raised to 200°C over a period of 1.5 h and the reaction was continued at this temperature for a further 3 h. The water liberated during the reaction was collected in the Dean–Stark apparatus. The reaction was monitored by determining the acid and amine values. When the acid value of the product fell below one, nitrogen supply was discontinued and the volatiles were removed under vacuum (5–10 mmHg) for 1 h. The vacuum was broken using nitrogen, and the product was cooled and stored. The steps involved in the preparation are shown in *Figure 1*.

The experimental procedure used for the preparation of C_{36} diacid polyamide was similar to that described

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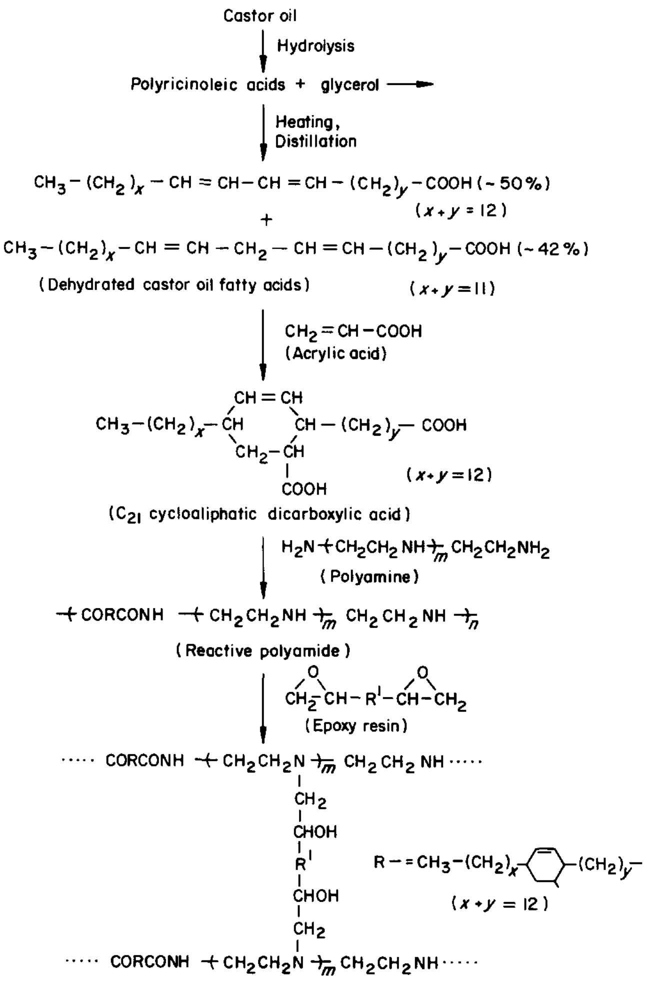

Figure 1 Reactive polyamide from C_{21} cycloaliphatic dicarboxylic acid for curing epoxy resin

for C_{21} diacid, except that after raising the temperature to 200°C, nitrogen sparging was discontinued and vacuum was applied. Acid and amine values of the polyamides were determined according to ASTM D 1980-61 and D 2074-62, respectively, by using a neutral mixture of ethanol and xylene (1:1 by volume) at 25°C for dissolving the polyamides. The viscosity of a 50% (by weight) solution of the polyamides in a mixture of isopropanol and toluene (1:1 by volume) was determined with an Emila viscometer and the colour of the solutions of the polyamides was determined in a 0.25 inch (0.64 cm) cell with a Lovibond Tintometer.

Methods

The solutions of the polyamide-cured epoxy resins were used for coating the following test materials. Mild steel discs (32 mm diameter) and steel panels (152 mm × 102 mm) were punched out of a 20 (0.9 mm) gauge plate, abraded with waterproof silicon-carbide emery paper in white spirit medium, swabbed with xylene and finally degreased for 2 h in methyl-isobutyl ketone. The residual solvent from the degreased specimens was removed in a vacuum desiccator. Tin panels (150 mm × 150 mm) cut out from electrolytically tinned mild steel plate (0.315 mm thick) were used. The tin panels were lightly abraded with a fine emery paper and subsequently swabbed with xylene. Tin foils (20 mm × 102 mm) of 0.025 mm thickness, clean glass strips (25 mm × 300 mm) and clean glass tubes (15 mm diameter × 150 mm length) were used.

Powdered epoxy resin was dissolved in a mixture of xylene, toluene and methyl-isobutyl ketone (85:10:5 by volume) to obtain a solution containing 50% solids. Polyamide solutions containing 50% solids were separately prepared by dissolving the polyamide in a mixture of isopropyl alcohol and toluene (1:1 by volume). Gel time of the polyamide and epoxy resin blend (10 g) was determined by mixing the solutions of the polyamide and the epoxy resin in the required ratios in a glass beaker (100 ml) at 30°C and intermittently stirring the mixture with a glass rod. The time when the glass rod could not be pulled out from the mixture was taken as the gel time. Appropriate quantities of the solutions of the polyamide and the epoxy resin were mixed at 30°C and the viscosity of the blend was adjusted to 70–80 s (Ford Cup No. 4) with xylene at 30°C and used for further work. The drying time of the solution of the polyamide–epoxy-resin blend coated on glass strips to a constant film thickness (72 μm) was measured with a B.K. drying time recorder. The properties mentioned below were measured after the 'hard dry' time.

The gloss of the cured-resin films obtained on mild steel panels was measured with a Gardner multiangle glossmeter at 45° with the standard panel adjusted to a 52 reading. The scratch hardness of the films obtained on tin panels was determined by using an automatic power-operated Erichsen scratch test unit, Model 601 (Instruction Manual, Erichsen GmbH COK G, D-5870, Hemersundwing, Germany). The results are expressed as force in terms of newtons needed to scratch through the film. The flexibility of the films obtained on tin panels was tested with a 0.25 inch (0.64 cm) mandrel as per IS:101 (1964). Direct and indirect impact resistance of the films on mild steel panels was measured with a falling-weight-type instrument in which a 10.5 lb (4.76 kg) weight dropped from a fixed height of 23 inches (0.58 m) according to DEF 1053: Impact resistance test. The bond strength (kg cm^{-2}) of the resin films obtained on mild steel discs was determined by the Sandwich pull-off technique with a Hounsfield Tensometer[12,13].

The test specimens were prepared by applying the binders to the mild steel discs with an ICI spin coater to a dry film thickness of about 27 ± 2 μm. The type of bond failure was estimated as percentage adhesive failure. The binders were coated on tin foils to a uniform film thickness and the films were dried at room temperature and matured for seven days. The free films were then obtained by amalgamating the tin foils with mercury. The tensile strength of the film was determined by using an Instron tensile strength tester[14]. The resin solution was coated on clean test tubes by a dip-coating method and the resistance of the cured and matured resin films to distilled water, xylene, white spirit, butanol and solutions of sulphuric acid, sodium hydroxide, sodium carbonate and sodium bicarbonate was determined according to IS:101(1964) and IS:2932(1974).

RESULTS AND DISCUSSION

In the present studies binders were prepared by curing an epoxy resin with various C_{21} diacid-based reactive polyamides to evaluate them for various physicochemical properties. Reactive polyamides having amine values ranging from 310 to 389 were prepared by reacting the

Table 1 Properties of reactive polyamides of C_{21} and C_{36} diacids

Sample no.	Diacid	Polyamine	Mole ratio of diacid:polyamine (used in the polyamide preparation)	Amine value (mg KOH g^{-1})	Viscosity of 50% (by weight) solution in isopropanol and toluene (1:1 by volume) (cP)	Colour of 50% (by weight solution in isopropanol and toluene (1:1 by volume) (Y + 5R)
1	C_{21}	Diethylenetriamine (DETA)	1.00:1.50	310	102	25.0
2	C_{21}	Triethylenetetramine (TETA)	1.00:1.50	339	80	17.5
3	C_{21}	Tetraethylenepentamine (TEPA)	1.00:1.25	381	85	20.0
4	C_{36}	TEPA	1.00:1.25	310	120	3.2
5	C_{36}	TEPA	1.00:1.50	349	90	5.0

Table 2 Drying and gel times of the epoxy resin cured with reactive polyamide derived from C_{21} diacid and TEPA in different equivalent weight ratios

Sample no.	Epoxy resin:reactive polyamide (equivalent weight ratio)	Drying time		Gel time (h-min)
		Surface dry (h-min)	Hard dry (h-min)	
1	1.00:0.75	2 00	5 00	6 00
2	1.00:1.00	1 15	2 50	4 45
3	1.00:1.10	1 30	3 05	5 00
4	1.00:1.25	1 45	3 30	5 00
5	1.00:1.50	1 45	4 15	5 00

Table 3 Physicochemical properties of the films of epoxy resin cured with reactive polyamide derived from C_{21} diacid and TEPA in different equivalent weight ratios

Sample no.	Epoxy resin:reactive polyamide (equivalent weight ratio)	Gloss at 45° (Std 52)	Scratch hardness (N)	Flexibility (0.25" mandrel)	Impact resistance		Practical adhesion (kg cm^{-2})	Adhesive failure (%)	Tensile strength (kg cm^{-2})
					Direct	Indirect			
1	1.00:0.75	75.0	16.8	P	P	P	182.4	45.0	228
2	1.00:1.00	75.6	20.0	P	P	P	234.6	30.0	860
3	1.00:1.10	75.9	17.3	P	P	P	229.8	50.0	794
4	1.00:1.25	79.8	16.9	P	P	P	225.1	75.0	367
5	1.00:1.50	80.0	16.0	P	P	P	196.5	100.0	194

P for pass

C_{21} diacid with different polyamines such as DETA, TETA and TEPA in two different molar ratios (1.00:1.25 and 1.00-1.50). Polyamides of matching amine values were prepared from C_{36} dimer acid and TEPA (in the mole ratio 1.00:1.25 and 1.00:1.50) for comparison. The properties of these polyamides are given in *Table 1*. The data in *Table 1* show that the solutions of reactive polyamides of either C_{21} or C_{36} diacids with lower amine value of 310 had higher viscosities (102 and 120 cP) than those of the polyamides with higher amine values of 349 to 389 (80 to 90 cP) because of their lower molecular weights. The solutions of the polyamides derived from C_{36} dimer acid are lighter in colour than those derived from C_{21} diacid (*Table 1*).

To study the effect of the variation of equivalent weight ratio of the epoxy resin and the reactive polyamide on the properties of the films of cured materials, a reactive polyamide derived from C_{21} diacid and TEPA having an amine value of 381 was chosen (*Table 1*). The equivalent weight ratio of the epoxy resin and the polyamide were varied from 1.00:0.75 to 1.00:1.50. An increase in the equivalent weight ratio of the epoxy resin to reactive polyamide had no significant effect on the gel time, while the drying time of the films had been affected (*Table 2*). The binder prepared by using a 1.00:1.00 ratio had the lowest surface-drying, hard-drying and gel time. Physicochemical properties of the cured films (*Table 3*) indicate that variation in the equivalent weight ratio of the epoxy resin to the polyamide from 1.00:0.75 to 1.00:1.50 has practically no effect on gloss and all the films pass the flexibility and impact resistance tests. However, scratch hardness, adhesion and tensile strength of the films are found to increase with the increase in the equivalent weight ratio from 1.00:0.75 to 1.00:1.00, but above this ratio the properties are found to decrease. The films in general are found to be resistant to various solvents and chemicals. However, the films obtained by using higher epoxy resin to polyamide ratios (1.00:1.25 and 1.00:1.50) are found to fail in 2% sulphuric acid and in butanol.

Table 4 Drying and gel times of the epoxy resin cured with different reactive polyamides

						Drying time		
Sample no.	Diacid	Polyamine	Reactive polyamide (diacid:polyamine mole ratio)	Viscosity of polyamide solution (cP)	Epoxy-resin: reactive-polyamide (equivalent weight ratio)	Surface dry (h min)	Hard dry (h min)	Gel time (h min)
1	C_{21}	DETA	1.00:1.50	102	1:1	2 00	2 30	5 15
2	C_{21}	TETA	1.00:1.50	80	1:1	2 15	3 05	6 15
3	C_{21}	TEPA	1.00:1.25	85	1:1	1 15	2 50	4 45
4	C_{36}	TEPA	1.00:1.25	120	1:1	1 15	1 45	3 05
5	C_{36}	TEPA	1.00:1.50	90	1:1	2 00	3 05	3 28

Table 5 Physicochemical properties of films of epoxy resin cured with different reactive polyamides

								Impact resistance				
Sample no.	Diacid	Polyamine	Reactive polyamide (diacid: polyamine mole ratio)	Epoxy-resin: reactive-polyamide (equivalent weight ratio)	Gloss at 45° (52 standard)	Scratch hardness (N)	Flexibility (0.25" mandrel)	Direct	Indirect	Practical adhesion (kg cm^{-2})	Percentage adhesive failure	Tensile strength (kg cm^{-2})
1	C_{21}	DETA	1.00:1.50	1:1	79.1	20.0	P	P	P	315.8	97.0	398
2	C_{21}	TETA	1.00:1.50	1:1	86.3	20.8	P	P	P	283.0	87.5	930
3	C_{21}	TEPA	1.00:1.25	1:1	75.6	20.0	P	P	P	234.6	30.0	860
4	C_{36}	TEPA	1.00:1.25	1:1	71.9	16.0	P	P	P	267.0	100.0	300
5	C_{36}	TEPA	1.00:1.50	1:1	70.2	23.8	P	P	P	223.0	60.5	361

P for pass

The results indicate that the weight ratio of 1.00:1.00 of epoxy resin to polyamide gives better film properties (*Table 2*). Similar observations were made with C_{36} diacids. Further work was done by reacting the epoxy resin and various polyamides of different amine values derived from either C_{21} or C_{36} diacid in the equivalent weight ratio of 1.00:1.00 and the binding properties of the films were determined. The cured product prepared by using polyamide of C_{21} diacid and TETA had higher surface-dry, hard-dry and gel times than those of C_{21} diacid and DETA (*Table 4*), which is due to the lower molecular weight of the polyamide of C_{21} diacid and TETA (viscosity, 80 cP) when compared to that of C_{21} diacid and DETA (viscosity 102 cP). Similarly, the cured product obtained by using C_{21} diacid and TEPA (viscosity 85 cP) had slower drying and gel times compared to those based on C_{36} diacid and TEPA (viscosity 120 cP). The same is the case with the cured product obtained by using C_{36} diacid and TEPA (mole ratio 1.00:1.50; viscosity, 90 cP) when compared to that obtained by using C_{36} diacid and TEPA (mole ratio, 1.00:1.25; viscosity, 120 cP).

Table 5 shows that the cured product based on C_{21} diacid and higher molecular weight polyamine (TETA) had higher tensile strength (930 kg cm^{-2}) and higher scratch hardness (20.8 N) than that obtained by using C_{21} diacid and DETA (398 kg cm^{-2} and 20 N). It shows that the use of higher molecular weight polyamine gave a product of better tensile strength and scratch hardness than that obtained from using lower molecular weight polyamines.

The film properties of the cured product based on C_{21} diacid and TEPA had higher tensile strength (860 kg cm^{-2}), higher scratch hardness (20 N) and higher adhesion (234.6 kg cm^{-2}) with 30% adhesive failure than that derived from C_{36} dimer acid and TEPA (1:1.25), indicating the effect of the nature of the diacid used. The cured product obtained by using a higher ratio of C_{36} diacid to TEPA (1.00:1.50) had higher scratch hardness (23.8 N) and tensile strength (361 kg cm^{-2}) than that obtained by using a lower ratio of C_{36} diacid to TEPA (1.00:1.25).

All the cured products derived from either C_{21} or C_{36} diacid-based reactive polyamides were found to be resistant to various solvents and chemicals.

CONCLUSIONS

The cured products obtained by using an epoxy resin and the reactive polyamides derived from C_{21} or C_{36} diacid, in the equivalent weight ratio of 1:1, had better coating properties than those obtained by using other equivalent weight ratios. Epoxy-cured materials obtained by using C_{21} diacid and DETA, and TETA, showed that the TETA-based products had better tensile strength than those based on DETA. The coating properties of the epoxy-cured materials obtained from C_{21} diacid and TEPA were superior to those obtained from C_{36} dimer acid and TEPA in tensile strength and had better hardness and adhesion, indicating the effect of the structure of the diacid on the properties of the binders.

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