NOTE

Coatings from Epoxidized (Polyurethane-Polyester) Resin System

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ABSTRACT: Epoxidized polyurethane was synthesized from the reaction of the prepared epoxidized linseed oil with toluene diisocyanate (TDI) at a NCO-to-OH ratio equal to 5. The prepared epoxidized linseed oil was also reacted with phthalic anhydride at a molar ratio of 1 : 4 to give epoxidized polyester. Epoxidized polyurethane and epoxidized polyester were mixed in different weight ratio percentages to give three types of epoxidized (polyurethane-polyester) resin systems. These resin systems were tested physically and chemically and evaluated as coatings for both metal and glass panels. The data obtained indicate an exceptional combination of properties, such as adhesion, bending, and chemical resistance of the epoxidized (polyurethane-polyester) resin system of the weight ratio percentage of 15 : 85. Thus, these materials can be recommended to be used as coating materials. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci **67:** 577-581, 1998

Key words: epoxidized polyurethane; epoxidized polyester; coatings

INTRODUCTION

Polyurethane coatings are preferred for many applications because of a unique combination of performance and application properties.

These products provide excellent abrasion resistance, flexibility, hardness, and chemical and solvent resistance.¹ Raw materials include polyisocyanates and coreactants, e.g., polyester and polyether polyol. Generally, polyester-based materials are selected for high strength, tear, and chemical and heat resistance; and polyether-based materials are selected for low-temperature flexibility, high humidity conditions, and resistance to attack by fungi and bacteria.²

A series of polyesters were prepared for synthesizing polyurethane resins. The relation between the structures and properties of these prepared polyesters, and especially, the influence of polyester type on adhesion behavior of the corresponding polyurethane, are discussed.³ Polyester–polyurethane electrically insulating lacquer coating with high flexibility was also manufactured.⁴

Epoxy resins provide durable coatings of high mechanical strength with good adhesion to many substrates. Solvent and chemical resistant films are ob-

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Acid No (mg KOH/g oil)	Hydroxyl Value (mg KOH/g oil)	Epoxy Group Content (%)	Viscosity at 30°C (Cs)	Infrared absorption $bands^a$ (cm ⁻¹)
11.0	19.0	5.4	31.0	916, 1250, 2980 for epoxy groups 3560 for hydroxylic groups

Tahle I	Characteristics	of Enoxidized	Linseed O	i
rable r	Unaracteristics	of Epoxialized	Linseed U	1

^a Bellamy.¹²

tained by curing at ambient and elevated temperatures. $^{\scriptscriptstyle 5}$

Carboxylic or hydroxylic terminated polyesters were modified with epoxy resin as glycidyl ester terminated polyesters and used in the preparation of powder coating. When they were applied to steal panels, a coated panel with good impact, flex, and solvent resistance was obtained.^{6–8} The prepared epoxy– polyether⁹ resins were mixed with polyurethane and are also useful as coating material. It was found that incorporation of a crosslinking component containing epoxy group improves the coating properties.¹⁰ Throughout the present work, different types of epox-

Table II Curing Time for Different Ratios of EU-EP Resin Systems Spread on Metal and Glass Panels at 170°C

m (D);	Weight Percen Resin	t Ratio tage of as (%)	a : m :
Type of Resin System	EU	EP	Curing Time (h)
A	85	15	1.0
В	50	50	1.5
С	15	85	2.0

idized (polyurethane-polyester) resin systems were evaluated and applied as coating materials.

EXPERIMENTAL

Materials

Linseed oil, produced by Cairo Co. for Oils, as used, with the following specifications: an average molecular weight of 876.0; density at 23°C of 0.9271 g/cm³; viscosity at 25°C of 27.4 Cs; an iodine value of 178.0 Cgl₂/g; and an acid value of 0.75 mg KOH/g oil. Pure grade peracetic acid with a concentration of 60% was also used. In addition, a toluene diisocyanate (TDI) mixture of 80% 2,4 and 20% 2,6 toluene diisocyanate was used. All other chemicals were of pure grade.

Methods

Preparation of Epoxidized Linseed Oil

Peracetic acid (2 mol) was added dropwise in period of 20 h to linseed oil (1 mol) at 30°C to give epoxidized linseed oil (EL) according to the method described in Motawie et al.¹¹ The specifications of the prepared EL are shown in Table I.

Table III	Physical	Tests of	Coated	Metal	Panels	with	Three	Types	of EU-	-EP	Resin \$	Systems
												- ,

				Physical Tests	
Type of Resin System	Coated Film Thickness (μ)	Adhesion	Stripping	Bending	Water Resistance (After 4 h)
A B C	170 190 130	Pass Pass Pass	Pass Pass Pass	Cracking occurs Cracking occurs No cracking	No change No change No change

NOTE .

Table IV	Chemical]	Resistanc	es of C	oated Gla	ss and M	etal Panels w	vith Thre	e Types of	EU-EP R	esin Syst	ems at 28°C	for Six Mo	nths
	Coated												
Type of	Film	NaOH	HCI	${ m H}_2{ m SO}_4$	HNO ₃		NaCl	Na_2CO_3					
Resin	Thickness	1%	10%	3%	10%	CH ₃ COOH	10%	20%		Crude			Gas
System	(η)	Soln	Soln	Soln	Soln	5% Soln	Soln	Soln	Acetone	Oil	Gasoline	Kerosine	Oil
A	160	Ċ	ы	E	Ċ	E	E	E	Ŀ	E	E	E	ы
В	130	Ċ	되	ы	E	E	ഥ	E	Ċ	ഥ	E	E	뙤
C	120	G	ы	ы	E	Э	ы	E	G	E	E	E	ы
G = Goo	od: E = Excelle	nt: F = Fai	L										

Preparation of Epoxidized Polyurethane Resin

Reaction of the prepared epoxidized linseed oil (29.3 g) with TDI (10 g) at a NCO-to-OH ratio equal to 5 gives epoxidized polyurethane resin (EU), as described in Motawie et al.¹¹

Preparation of Epoxidized Polyester Resin

The prepared epoxidized linseed oil was reacted with phthalic anhydride at ratio of 1:4 to give epoxidized polyester (EP), as described Motawie et al.¹¹

Preparation of coated films. EU and EP were mixed in different weight ratio percentages to give three types of EU-EP resin systems, as shown in Table II and described in Motawie et al.¹¹

The resin blend were spread on clean metal and glass plate specimens $(2.5 \times 7.5 \text{ cm})$. The plates were put in a vertical position by suitable supports for a half an hour to slowly remove the solvent. Finally, complete curing was carried out at 170°C. The film thickness was measured according to the British Standards method of test for paint, BS 3900, Part E2, 1983.

Evaluation of coated films. Stripping, adhesion, bending, and water resistance tests were carried out according to API RP 5L2, March 1981. The chemical resistance test was carried out according to ASTM D 543-67 (reaproved 1987) and ASTM G 20-72 (1987).

RESULTS AND DISCUSSION

Although diisocyanates are the intermediates responsible for chain extension and the formation of urethane links or a variety of crosslinks by further reaction, much of the ultimate polymer structure is dependent on the nature of the components carrying the groups with which the isocyanates react initially. Linear polymers carrying OH groups would react with TDI, through a chain lengthening process, to form tough elastomeric or plastic materials, which crosslinked by additional diisocyanate.¹³

The rate at which these reactions occur is dependent on temperature since a diisocyanate only becomes effectively active at the curing temperature. Hot air oven cure improves physical properties of the polymer network.¹³

In the present work, it was found that the curing time of EU-EP resin system is dependent upon the weight ratio percentages between EU and EP in the system, as shown in Table II.

Table II indicates that the curing time of the resin

system increases with an increase in the weight ratio percentage of EP in the system.

Throughout this work, three different types of resin systems, A, B, and C, were tested physically and chemically and evaluated as coatings for both metal and glass panels.

Physical tests, such as stripping, adhesion, bending, and water resistance tests were carried out for cured coated metal panels; the results are shown in Table III. Both glass and metal cured coated panels were subjected to chemical tests by direct immersion in acidic or alkaline media, dilute solutions of inorganic materials, and organic solvent, as well as crude petroleum oil and its products. The chemical resistance of the coated panels is shown in Table IV.

The results in Table III indicate that type C of the resin system has a high level of physical properties, while types B and C have high chemical resistances, as indicated in Table IV.

Hence, one can conclude that type C of resin system has good physical properties and also has high chemical resistances. This can be attributed to the high degrees of crosslinking attainable by the reaction between the free hydroxyl group in the epoxidized polyester and the free isocyanate groups in the epoxidized polyurethane.

The mechanism of the crosslinking may proceed as follows:

$$\begin{array}{ll} \text{HO-}R_1 & -\text{OH} + \text{OCN-}R_2 & -\text{NCO} & \longrightarrow \\ \text{Linear} & \text{Difunctional} \\ \text{polymeric glycol} & \text{diisocyanate} \\ \text{(polyester)} \end{array}$$

HO-
$$R_1$$
-O-C-NH- R_2 -NCO
Prepolymer

This prepolymer is hydroxyl-end-tipped to make it stable in storage, but by itself, it is too weak in physical properties to be a useful industrial material; hence, it must be either further chain-extended or crosslinked to increase its strength to a useful range.¹³

Then,

$$HO-R_1-O-C-NH-R_2-NCO + OCN-R_2-NCO \longrightarrow OCN-R_2-NH-C-O-R_1-O-C-NH-R_2-NCO$$

Prepolymer with unreacted isocyanate

Also, the isocyanate group (NCO) can be reacted with another molecule of polyester.

linking occurred due to the presence of free isocyanate groups in the polyurethane.

The data obtained indicate that the weight ratio percentage of 15 : 85 of EU to EP in the resin system has good physical properties and high chemical resistance to be used as materials in coating fields.

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$$HO-R_{1}-O-C-NH-R_{2}-NH-C-O-R_{1}$$

$$O-R_{1}-O-C-NH-R_{2}-NCO \xrightarrow{HO-R_{1}-OH} O$$

$$HO-R_{1}-O-C-NH-R_{2}-NH-C-O-R_{1}$$

$$OO-R_{1}-O-C-NH-R_{2}-NH-C-O-R_{1}$$

$$OO-R_{1}-O-R_{1}-OH$$

However, the role of isocyanate is to link the polyester molecules together, and so a higher degree of cross-

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