Epoxy Resins from Fatty Esters Derived from Cyclohexane and Epoxycyclohexane[1]

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Abstract

The magnitude of the physical properties of resins obtained by the phthalic anhydride cure of non-terminal epoxy monomers, prepared from fatty derivatives, was shown to be dependent on the distribution of the epoxy groups in the monomer.

The monomers were prepared by epoxidizing a series of unsaturated esters, selected to test the effect of the addition of a single symmetrically disposed epoxide group. Oleoyl and linoleoyl esters of tetrahydrophthalyl alcohol, as well as dioleyl and dilinoleyl tetrahydrophthalate, were epoxidized and cured with phthalic anhydride (Group A). For comparison, epoxy monomers were prepared from oleoyl and linoleoyl esters of hexahydrophthalyl alcohol, as well as dioleyl and dilinoleyl hexahydrophthalate (Group B). When these epoxides were cured with phthalic anhydride, it was found that the resins derived from Group A had heat distortion temperatures which were approximately 55–65C higher than those from Group B.

Introduction

In the development of epoxy resins, considerable research has been centered on glycidyl ethers of bifunctional phenols such as bisphenol A. Dearborn et al. (1) and Wynstra (2) have reported on the effect of varying the structure of the glycidyl ether on the physical properties of the resins.

In contrast with glycidyl resins, much less has been reported on the preparation of epoxy resins from non-terminal epoxides. However, during recent years, investigations concerning the preparation of epoxy resins from animal fat derivatives have been carried out at this laboratory and elsewhere. As a result of this work, it has been shown that resins can be prepared from epoxidized fatty glycerides, and that fat-based epoxy monomers can be used to modify or even replace commercially available epoxy monomers, such as the diglycidyl ether of bisphenol A (3,4).

It has been further demonstrated that variation of the chemical structure of the monomers prepared from fat-derived chemicals, leads to changes in the physical properties of the epoxy resins prepared from them. Correlations have been made between the chemical structure of epoxidized fatty esters and the properties of resins derived therefrom by curing with phthalic anhydride (5,6). It has been shown that linoleic acid derivatives produced epoxy resins exhibiting higher heat distortion temperatures than those of resins prepared from corresponding oleic acid intermediates. This was believed caused by the increased number of epoxide groups obtainable from linoleic acid derivatives, as well as by a more favorable distribution of these linkages within the monomer molecule.

The purpose of the present research was to study the effects of epoxide distribution in fatty ester monomers upon the properties of resins prepared from them. In this way, new correlations between monomer structure and resin performance could be derived. It was believed that the introduction of an additional epoxide group into the monomer in a position symmetrically disposed between the other epoxide groups present would impart increased cross-linking density with resulting higher heat distortion temperature in the resin prepared.

The monomers were synthesized by epoxidizing a series of unsaturated esters selected to test the effect of the addition of a single symmetrically disposed epoxide group. Thus, the dioleoyl ester of tetrahydrophthalyl alcohol and the dilinoleoyl ester of tetrahydrophthalyl alcohol, as well as dioleyl tetrahydrophthalate and dilinoleyl tetrahydrophthalate were prepared. Epoxidation with peracetic acid gave the corresponding polyepoxides: 4,5-epoxycyclohexane-1, 2-dimethanol bis-(9,10-epoxystearate) (IA), 4,5-epoxycyclohexane-1, 2-dimethanol bis-(9,10; 12,13-diepoxystearate) (IIA), bis-(9,10-epoxyoctadecyl) 4,5-epoxycyclohexane-1, 2-dicarboxylate (IIIA), and bis-(9,10; 12,13-diepoxyoctadecyl) 4,5-epoxycyclohexane-1, 2-dicarboxylate (IVA).

For comparison, the dioleoyl and dilinoleoyl esters of hexahydrophthalyl alcohol, as well as dioleyl and dilinoleyl hexahydrophthalate were prepared. Epoxidation of these esters with peracetic acid furnished cyclohexane-1, 2-dimethanol bis-(9,10-epoxystearate) (IB), cyclohexane-1, 2-dimethanol bis-(9,10; 12,13-diepoxystearate) (IIB), bis-(9,10-epoxyoctadecyl) cyclohexane-1,2-dicarboxylate (IIIB), and bis-(9,10; 12,13-diepoxyoctadecyl) cyclohexane-1, 2-dicarboxylate (IVB). It is evident that the monomers of the A group differ from those of the B group in having an additional symmetrically disposed epoxide linkage. All the epoxides were cured with phthalic anhydride. The heat distortion temperatures and tensile strengths of the resulting resins were determined.

An additional pair of resins was prepared from epoxides of 2-butene-1, 4-dioleate (VA) and butane-1, 4-dioleate (VB) as a further illustration of the effect of the presence of a symmetrically disposed epoxide group.

Experimental

Preparation of Esters. The general procedure used to prepare the esters listed in Table I was to reflux a toluene solution of the required amounts of alcohols and acids with a catalytic amount of 2-naphthalenesulfonic acid monohydrate. A 5% molar excess of the monofunctional alcohol or acid was used. The amount of catalyst added was 1 mole per cent of the difunctional alcohol or acid. The reaction mixture was refluxed under nitrogen in a flask equipped with a water trapping device for azeotropic removal of water. After

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TABLE I

Yield and Analytical Data for Esters Prepared

Ester	Reactants		% Yield (crude)	Iodine No.	
	Acid	Alcohol		Calcd.	Found
4-Cyclohexene-1, 2-dimethanol dioleate	Oleic	4-Cyclohexene-1, 2-dimethanol	50.0	113.4	112.8
4-Cyclohexene-1, 2-dimethanol dilinoleate	Linoleic	4-Cyclohexene-1, 2-dimethanol	55.0	190.2	187.5
Dioleyl 4-cyclohexene-1, 2-dicarboxylate	Cis-4-cyclohexene-1, 2-dicarboxylic acid anhydride	Oleyl	99.1	113.5	106.9
Dilinoleyl 4-cyclohexene-1, 2-dicarboxylate	Cis-4-cyclohexene-1, 2-dicarboxylic acid anhydride	Linoleyl	100.0	190.3	179.9
2-Butene-1, 4 dioleate	Oleic	2-Butene-1, 4 diol	93.7	123.4	124.2
Cyclohexane-1, 2-dimethanol dioleate	Oleic	Cyclohexane-1, 2-dimethanol	60.0	75.4	73.5
Cyclohexane-1, 2-dimethanol dilinoleate	Linoleoyl chloride	Cyclohexane-1, 2-dimethanol	94.0	152.0	151.0
Dioleyl hexahydrophthalate	Hexahydrophthalic anhydride	Oleyl	86.5	75.4	76.4
Dilinoleyl hexahydrophthalate	Hexahydrophthalic anhydride	Linoleyl	100.0	151.7	145.6
Butane-1, 4-dioleate	Oleic	Butane-1, 4-diol	82.4	82.0	80.9

all the water of reaction had been removed, petroleum ether (B.P. 63–70C) was added, and the mixture was washed successively with water, 50% ethanol containing 5% potassium hydroxide, and with more water until neutral. The neutral solution was dried over anhydrous magnesium or calcium sulfate and the solvent removed under reduced pressure. The crude esters obtained were used in subsequent epoxidations without further purification.

TABLE II

Yield and Analytical Data for Epoxy Esters

		Yield %	% Oxirane	
			Calcd.	Found[a]
Polyepoxides of				
Group A	4-Cyclohexene-1, 2-dimethanol dioleate (IA)	89.6	6.68	6.55
	4-Cyclohexene-1, 2-dimethanol dilinoleate (IIA)	82.3	10.71	9.68
	Dioleyl 4-cyclohexene-1, 2-dicarboxylate (IIIA)	87.4	6.68	6.30
	Dilinoleyl 4-cyclohexene-1, 2-dicarboxylate (IVA)	83.0	10.71	9.64
	2-Butene-1, 4-dioleate (VA)	84.1	6.69	7.22
Group B	Cyclohexane-1, 2-dimethanol dioleate (IB)	80.0	4.54	4.36
	Cyclohexane-1, 2-dimethanol dilinoleate (IIB)	85.4	8.73	8.04
	Dioleyl hexahydrophthalate (IIIB)	88.1	4.54	4.47
	Dilinoleyl hexahydrophthalate (IVB)	81.8	8.73	7.85
	Butane-1, 4-dioleate (VB)	86.1	4.92	4.83

[a] Durbetaki method (11).

A different procedure was used for the preparation of cyclohexane-1, 2-dimethanol dilinoleate. In this case, a 1% molar excess of linoleoyl chloride was added dropwise to a solution of hexahydrophthalyl alcohol in pyridine, keeping the temperature below 25C. The mixture was stirred 1 hr at room temperature and 1 hr at 36–42C. The solution was cooled, poured into water and extracted with chloroform. The extracts were washed with 1% sodium hydroxide and then with water until neutral before removal of the solvent.

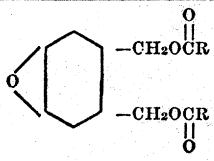
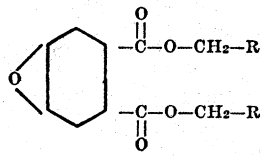
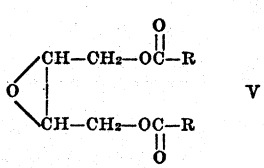
A summary of the esters prepared and the results obtained is given in Table I.

Preparation of Epoxy Esters. Conventional epoxidation procedures (7) with peracetic acid were used for epoxidation of all but one of the esters given in Table I. The epoxy esters were purified by recrystallization to remove unreacted ester as well as compounds containing acetoxy-hydroxy groups formed by ring opening (8). Results are summarized in Table II.

Use of peracetic acid with 2-butene-1, 4-dioleate (VA) led to incomplete epoxidation, probably because

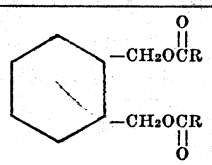
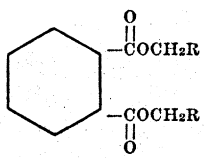
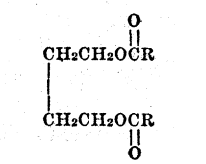
TABLE III

Physical Properties of Resins from Epoxy Esters

Group A	Monomer	Gel time (min)	H.D.T. (C)	Tensile strength (psi)
	I	40	52–56	2400–2800
	II	3	132	3400
	III	31	69	4500–4900
	IV	3	133	4500
	V	20	52	2300

I, III, V R = $-(CH_2)_7-\underset{\diagdown O \diagup}{CH-CH}-(CH_2)_7CH_3$

II, IV R = $-(CH_2)_7-\underset{\diagdown O \diagup}{CH-CH}-CH_2-\underset{\diagdown O \diagup}{CH-CH}-(CH_2)_4-CH_3$

Group B	Monomer	Gel time (min)	H.D.T. (C)	Tensile strength (psi)
	I	115	−7	450
	II	8	78–79	4600–6100
	III	49	9–13	400
	IV	5	67	1600
	V	240	−12	30

of the deactivation of the central olefinic group (9). However, p-nitroperoxybenzoic acid was found to be of sufficient activity to effect complete peroxidation of this ester. This reagent was prepared by addition of 94% hydrogen peroxide to a slurry of p-nitrobenzoic acid in methanesulfonic acid, as described by Silbert, Siegel, and Swern (10). The ester was epoxidized by adding it dropwise at room temperature to a slurry of excess p-nitroperoxybenzoic acid in chloroform. The mixture was stirred for 24 hr at room temperature, then cooled to 0C. The chloroform solution was washed with 2% sodium bicarbonate until neutral and then with water before drying over anhydrous magnesium sulfate. Removal of solvent and recrystallization from 10 parts of acetone resulted in recovery of the epoxidized ester.

General Procedure for Preparation of Resins. Resins were prepared by reaction of equivalent amounts of polyepoxide with phthalic anhydride (one epoxide equivalent requires one mole of phthalic anhydride). The reaction was catalyzed with 2.5 wt % of benzyldimethylamine and the resin cured as described previously (5) by heating at 150C for 3 hr after gelation and at 120C for 24 hr. Test-specimens were machined from the resins and their physical properties determined using the methods given earlier (5,12).

The results obtained are listed in Table III.

Results and Discussion

The physical properties of the resins prepared by curing the epoxidized ester intermediates with phthalic anhydride are listed in Table III. Comparison of the heat distortion temperatures of resins prepared from monomers IA-VA with those resins prepared from monomers IB–VB, shows that in each case the A group monomers furnished resins having significantly higher heat distortion temperatures than those prepared from the corresponding B group monomers. These differences varied from 59–72C (for IA vs IB), 53–54C (for IIA vs IIB), 56–60C (for IIIA vs IIIB), 66C (for IVA vs IVB) and 64C (for VA vs VB). The increase in heat distortion temperature in resins prepared from group A monomers is ascribed to the incorporation of the additional, symmetrically disposed epoxide group, into the monomer unit with resulting increased cross-linking density.

Resins prepared from monomers of linoleic acid derivatives had higher heat distortion temperatures than those from corresponding oleic acid derivatives, as would be expected. These increases varied from 67–80C (for IA vs IIA), 85–86C (for IB vs IIB), 64C (for IIIA vs IVA) and 54–58C (for IIIB vs IVB).

The presence of the substituted cyclohexane ring apparently has no great effect on the heat distortion temperature, since the magnitude of the HDT of resins from monomers IA, IIIA, and VA (all prepared from epoxidized oleic acid or oleyl alcohol derivatives) is about the same. Similar HDT are obtained from resins of monomers IB, IIIB and VB. Also the arrangement of the atoms in the ester function seems to have little effect on HDT. For example, the HDT remains approximately the same regardless of whether the carboxyl function is attached directly to the cyclohexane ring as in monomer III or to the fatty acid chain as in monomer I.

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