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Resins from Phenolic Esters of Epoxidized Fatty Acids*

Attempts have been made by several workers to correlate the heat distortion temperature (HDT) of epoxy resins with their chemical structure. Among empiric correlations may be noted the work of Dearborn et al.[1] on epoxy resins from polyglycidyl ethers which showed that the resistance to deformation at elevated temperature was increased by the functionality of either the epoxide or the anhydride, by the "compactness" of the molecule involved, and by the presence of substituents (e.g., chlorine) which produce van der Waals forces of high energy density by dipole-dipole interaction. Wynstra[2] observed that HDT increased with the combined functionality of the amine hardener and the epoxy monomer, with the existence of a cyclic structure in the amine, and with symmetry; an inverse effect was produced by an increase in the alkylene chain separating the amine functions. In the bisphenol glycidyl ether used, the chemical nature of the structural link joining the aromatic rings also affected HDT. Aelony[3] found that the flexural deformation temperature increased with epoxide functionality, but decreased with nonfunctional ring substitution and replacement of glycidyl by 2,3-epoxybutyl.

In the initial study[4] of a series of controlled alterations of the chemical structure of epoxy monomers, esters of some polyols (ethylene glycol, glycerin, pentaerythritol, and dipentaerythritol) and, respectively, 9,10-epoxystearic acid and 9,10,12,13-di-epoxystearic acid were prepared, were cured with phthalic anhydride, and HDTs were compared. The polyols were selected with the objective of keeping the nominal distance (as represented by the number of atoms) between crosslinks approximately constant. This choice of monomers was expected to permit an estimate to be made of the effects of increasing functionality (number of acyl chains) and of adding a reactive site (epoxy group) at a specific location in the acyl chain. It was found that a linear relationship existed between HDT and the num-

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ber of acyl chains in the ester, that HDT increased 17.5°C. per acyl chain, and that HDT was 91°C. higher (on average, 108°C. at maxima) when the acyl chain was 9,10; 12,13-diepoxyoctadecanoyl than when it was 9,10-epoxyoctadecanoyl.

It was the object of the presently reported work to investigate the effect of altering the chemical constitution of the epoxy ester intermediate on HDT of the phthalic anhydride derived resin by substituting an aromatic structure, dioxyphenylene (OC_6H_4O), for the aliphatic structure dioxyethylene (OC_2H_4O). For this purpose, dioleoyl and dilinoleoyl esters of catechol, resorcinol, and hydroquinone were prepared and were epoxidized to the corresponding bis(9,10-epoxyoctadecanoyl) and bis(9,10,12,13-diepoxyoctadecanoyl) esters. The latter were then cured with phthalic anhydride and HDT of the resins were measured. Thus, the differential effect on HDT of substituting dioxyphenylene for dioxyethylene could be evaluated. It was of interest, also, to determine whether the difference in HDT of resins prepared from di- and monoepoxyoctadecanoyl derivatives would be the same as that found previously from the analogous glycol esters.

EXPERIMENTAL

1. Preparation of Unsaturated Phenolic Esters

These were prepared (Table I) by the addition of oleoyl chloride or linoleoyl chloride[5–7] to catechol, resorcinol, and hydroquinone, respectively, in pyridine. The preparation of resorcinol dilinoleate exemplifies the synthesis. Linoleoyl chloride (92.5 g., 0.303 mole) was added to 16.5 g. (0.15 mole) resorcinol in 90 cc. pyridine at ca. 10°C. After the addition had been completed, the reaction mixture was heated to 45–50°C. for 1 hr., cooled to room temperature, and diluted with 250 cc. of chloroform. The solution was washed successively with water, 1% sodium hydroxide solu-

TABLE I
Unsaturated Ester Intermediates, RCO Z COR
RCO = *cis*-$CH_3(CH_2)_7CH{=}CH(CH_2)_7CO$

Experiment No.	Z	Yield, %	n_D^{30}	Carbon Calc.	Carbon Found	Hydrogen Calc.	Hydrogen Found	Iodine value Calc.	Iodine value Found
1	1,2-OC_6H_4O	88	1.4795	78.94	78.82	11.04	11.18	79.45	79.2
2	1,3-OC_6H_4O	89	1.4805	78.94	77.98	11.04	11.29	79.45	81.6
3	1,4-OC_6H_4O	39	[a]	78.94	78.88	11.04	10.93	79.45	76.0
RCO = *cis,cis*-$CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_7CO$									
4	1,2-OC_6H_4O	42	1.4880	79.44	79.02	10.48	10.50	159.9	160.2
5	1,3-OC_6H_4O	87	1.4928	79.44	79.97	10.48	10.57	159.9	159.0
6	1,4-OC_6H_4O	64	1.4903	79.44	79.21	10.48	10.86	159.9	156.8

[a] M.p. 65–7°C.

TABLE II

Epoxidized Ester Intermediates, RCO Z COR

RCO = *cis*-$CH_3(CH_2)_7CH—CH(CH_2)_7CO$ (O)

Experiment No.	Z	Yield, %	M.p., °C.	Carbon Calc.	Carbon Found	Hydrogen Calc.	Hydrogen Found	% Oxirane Calc.	% Oxirane Found	HDT, °C.	Tensile strength, psi	Modulus psi × 10^{-5}
1	1,2-OC_6H_4O	55	49–53	75.18	75.52	10.52	10.84	4.77	4.74	13	1100	1.05
2	1,3-OC_6H_4O	61	39–40	75.18	75.29	10.52	10.80	4.77	4.67	23	1500	0.88
3	1,4-OC_6H_4O	55	77–79	75.18	75.55	10.52	10.52	4.77	4.50	16	960	0.64
RCO = *cis,cis*-$CH_3(CH_2)_4CH—CHCH_2CH—CH(CH_2)_7CO$ (O) (O)												
4	1,2-OC_6H_4O	30	50–52	72.17	72.62	9.52	9.50	9.16	8.61	110	6000	2.85
5	1,3-OC_6H_4O	19	42–43	72.17	72.11	9.52	9.63	9.16	8.53	123	2000	1.31
6	1,4-OC_6H_4O	32	93–98	72.17	72.33	9.52	9.79	9.16	8.49	131	1400	0.95

tion, and water until neutral. After the solution had been dried over calcium sulfate, the solvent was distilled off to yield the ester with an acid number of 4.1 (2%, calculated as linoleic acid).

Hydroquinone dioleate (Table I), experiment No. 3, was prepared by heating hydroquinone and vinyl oleate (10% excess) in the presence of 1 mole-% β-naphthalenesulfonic acid at 150°C. in a stream of nitrogen for about 26 hr. The product was recrystallized from acetone.

2. Preparation of Epoxidized Amides and Esters

The method of Findley, Swern, and Scanlan[8] was used with the slight modification of the use of chloroform as a solvent. Characterizing and yield data for the epoxy monomers are listed in Table II. All the esters were recrystallized from acetone except experiment No. 6, for which a mixture of petroleum ether-acetone was used.

3. Preparation and Testing of Cured Resins

Resin mixtures were prepared from equivalent amounts of the epoxide and phthalic anhydride (1 mole epoxide equivalent: 1 mole anhydride) and were cured as previously described.[4] The test methods reported earlier for determining HDT and tensile properties were again used.[4,9]

RESULTS AND DISCUSSION

The physical properties of the resins prepared by curing the epoxidized ester intermediates with phthalic anhydride are listed in Table II. Previously,[4] it was found that HDT for a resin from phthalic anhydride and ethylene glycol bis(9,10-epoxystearate) was −29°. Although HDT of the resins derived from the isomeric dihydroxybenzene monoepoxystearates vary among themselves, the variation is small compared with the difference between HDT for the resins from the ethylene glycol ester and from the phenolic esters. If the values for HDT are averaged, an "average" HDT of 17° is obtained. If may be said, therefore, that, in the monoepoxystearate series, the effect of substituting dioxyphenylene for dioxyethylene is to increase HDT by 46°. Similarly, from Table II, an "average" value for the resins derived from bis(9,10; 12,13-diepoxystearate) esters is computed as 121°. Since HDT for the phthalic anhydride resins from the analogous ethylene glycol bis(9,10; 12,13-diepoxystearate) was found[4] to be 79°, the effect of the chemical substitution is to increase HDT by 42°. As a concomitant result, it was found that the effect of substituting a diepoxy acyl for a monoepoxy acyl group in the phenolic ester resins was to increase HDT by 104°. In the previous[4] work, the increase was 108°.

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Synopsis

Resins were prepared from the respective monoepoxystearoyl and diepoxystearoyl esters of the isomeric dihydroxybenzenes and phthalic anhydride. The average value of the heat distortion temperature of the resins derived from the monoepoxystearoyl esters was 17°C. and that from the diepoxystearoyl esters was 121°C. From results of previous work, it was concluded that the effect of substitution of dioxyphenylene for dioxyethylene was to increase the heat distortion temperature 42–46°C.

Résumé

On a préparé des résines au départ respectivement des esters monoépoxystearoylet diépoxystéaroyl- du dihydroxybenzène isomérique et de l'anhydride phtalique. La valeur moyenne de la température de distortion thermique des résines dérivées des esters de monoépoxystéaroyle était de 17° et celle des esters de diépoxystéaroyle de 121°. Des résultats de travaux antérieurs, on a conclu que l'effet de substitution de dioxyphénylène par du dioxyéthylène était d'augmenter la température de distortion thermique de 42 à 46°.

Zusammenfassung

Harze wurden aus den Monoepoxystearoyl- und Diepoxystearoylestern der isomeren Dihydroxybenzole und Phthalsäureanhydrid dargestellt. Der Mittelwert der Hitzeformbeständigkeits-Temperatur der von den Monoepoxystearoylestern abgeleiteten Harze betrug 17° und für die aus Diepoxystearoylestern 121°. Aus den Ergebnissen früherer Versuche kann man schliessen, dass der Einfluss einer Substitution von Dioxyphenylen für Dioxyäthylen in einer Erhöhung der Hitzeformbeständigkeits-Temperatur um 42–46° besteht.