

Vernolic Acid Esters as Plasticizers for Polyvinyl Chloride¹

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Abstract

The methyl, propyl, butyl, isobutyl, hexyl, cyclohexyl, octyl, and 2-ethylhexyl esters of vernolic (epoxyoleic) acid, a naturally-occurring epoxy acid, were prepared and evaluated as plasticizers of polyvinyl chloride. All the esters showed good compatibility. The data indicated that they are excellent low temperature plasticizers having T_f temperatures below -50°C . They also have the added advantage of greatly increasing the heat stability of the polyvinyl chloride and improving the light stability. The results are compared with DOP and other epoxy-containing plasticizers now being used commercially. These esters should not only be useful as primary plasticizers but also in combination with other plasticizers as plasticizer-stabilizers.

Introduction

ESTERS OF EPOXIDIZED oleic acid such as butyl epoxy-stearate and other alkyl epoxystearates have been employed commercially as plasticizers and plasticizer-stabilizers for polyvinyl chloride. Preparation of these materials requires epoxidation of the unsaturated fatty acid. Oil obtained from the seed of *Vernonia anthelmintica* from which trivernolin (tri-epoxyolein) can be readily obtained (1) contains about 76% of 12, 13 epoxyoleic (vernolic) acid. Therefore, several vernolic acid esters of the naturally-occurring epoxy acid were prepared for evaluation as plasticizers of polyvinyl chloride.

Experimental

Preparation of Alkyl Esters of Epoxyoleic Acid

The methyl, propyl, butyl, isobutyl, hexyl, cyclohexyl, octyl and 2-ethylhexyl esters of epoxyoleic acid were prepared by alcoholysis of trivernolin, catalyzed by the sodium alkoxide of the corresponding alcohol, except that in the preparation of cyclohexyl ester potassium methoxide was added as catalyst. The general procedure was as follows: To 300 ml of the pure dry alcohol, freshly cut small pieces of sodium were added in amounts calculated to make a 0.1 molar solution of the alkoxide. This solution was added to 200 g of triepoxyolein in a 1-liter glass-stoppered flask and the mixture shaken at 40°C for 3-4 hr. The reaction mixture was cooled and then neutralized by adding the calculated amount of 0.5 N HCl slowly and with stirring, then transferred to a separatory funnel with low boiling petroleum ether and washed thoroughly with water until neutral. The solution was dried over sodium sulfate and the product crystallized at low temperatures, usually from about -50 to 80°C depending on the particular ester. Several recrystallizations were required to yield substantially pure esters 98-99+ % as judged by oxirane oxygen determinations, iodine values, thin-layer and gas-liquid chromatography. Yields of the recrystallized esters will be discussed in a subsequent publication.

Plasticizer Evaluation

A three-component formulation of resin, plasticizer and stabilizer was used. The formulation was Geon 101, PVC (polyvinyl chloride) resin 65% by weight of the total mix, plasticizer 34%, and Mark M 1%, a

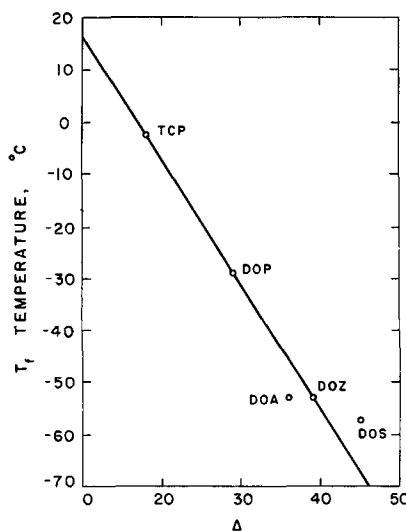


FIG. 1. Torsional stiffness T_f temperature versus compatibility number Δ .

barium-cadmium complex stabilizer. No attempt was made to determine the stabilizer system necessary to obtain maximum heat and light stability. The formulations were milled at 160°C for 7 min. Samples were molded from the milled sheets at 160°C in the manner previously reported (2). The molded samples were stored and conditioned at 23°C and 50% relative humidity.

It has become common practice to measure the stiffness in torsion as a function of temperature. This method was introduced by Clash and Berg (3) who empirically selected an apparent modulus of elasticity of 135,000 psi as the borderline between a rigid and nonrigid material. This is a value called the flex temperature T_f . The temperature at which the stiffness of 10,000 psi is observed is called T_4 and is significant because of its equivalence to the temperature of maximum slope. The difference between the T_f and T_4 values Δ is a measure of the compatibility of the plasticizer (4). The compatibility number Δ is a value which constantly increases with decreasing T_f temperature. Figure 1 shows a plot of T_f versus Δ values for TCP (tricresyl phosphate), DOP (di-2-ethylhexyl phthalate), DOZ (di-2-ethylhexyl azelate). The straight line plot defines the limits of compatibility at the T_f temperatures along the plot. A plasticizer with a compatibility number plotted above (to the right of) the line will be less compatible than the standards and, conversely, a plasticizer plotted below

TABLE I
Oxirane and Iodine Values of Alkyl Esters of Epoxyoleic Acid

Ester	Iodine value		% Oxirane oxygen	
	Found	Theory	Found	Theory
Methyl	81.4	81.7	5.14	5.15
Propyl	75.3	75.0	4.65	4.73
Butyl	72.1	72.0	4.53	4.54
Isobutyl	72.3	72.0	4.44	4.54
Hexyl	66.9	66.8	4.14	4.21
Octyl	62.0	62.2	3.84	3.92
2-Ethylhexyl	63.0	62.2	3.83	3.92
Cyclohexyl	66.7	67.1	4.11	4.23
Controls				
DOP	0	0
A	1.7	3.14
B	2.4	4.19
C	2.2	4.50

¹ Presented at the AOCs Meeting, Cincinnati, October 1965.

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TABLE II
 Mechanical Properties of Molded PVC Sheets Containing 34% Vernolic Acid Esters

Ester	Torsional stiffness Temp, C		Compati- bility Δ	Tensile strength PSI	Elonga- tion %	100% Modulus PSI	Migration wt. loss %	Volatility wt. loss	Stability Hours to Failure	
	T_f	T_4							Heat	Light
Methyl vernolate	-54	-24	30	2050	300	725	21.6	7.2	11	168
Propyl vernolate	-56	-25	31	2050	430	620	22.4	4.1	18	144
Isobutyl vernolate	-52	-20	32	2200	300	825	21.6	3.3	16	120
Butyl vernolate	-54	-23	31	2150	275	800	21.5	2.0	16	120
Hexyl vernolate	-58	-21	37	2100	355	740	22.1	1.7	22	120
2-Ethylhexyl vernolate	-55	-17	38	2400	350	975	20.7	1.4	20	96
n-Octyl vernolate	-58	-17	41	2250	275	950	23.5	1.3	17	96
Cyclohexyl vernolate	-42	-13	29	2300	345	750	12.0	.9	24	144
Controls (commercial)										
DOP	-28	0	28	2600	275	1225	3.4	1.3	2	264
A	-50	5	45	2450	300	950	16.4	2.9	16	120
B	-43	3	40	2230	300	1050	12.8	1.0	20	120
C	-44	6	38	2350	360	950	12.9	1.2	24	144

(to the left of) the line will be more compatible than these standards.

Determination of tensile strength, 100% modulus, percent elongation, volatility, migration, heat and light stability were obtained by previously reported methods (5). Volatility values were obtained at 70C and migration values were obtained with the samples in contact with silicic acid at 23C. Heat stability was determined from sample exposure at 160C.

Discussion

The iodine and oxirane oxygen values of the vernolic acid esters are shown in Table I. There is very little difference between the theoretical and experimental iodine and oxirane values. The iodine and oxirane values are found to decrease with increase in the length of the alkyl chain of the alcohol. The highest iodine value shown in Table I is 81.4 for the methyl vernolate and the lowest value is 62.0 for the octyl ester. The highest oxirane value is 5.14 and the lowest 3.83 for the methyl and 2-ethylhexyl esters, respectively.

Also included in the table are several commercial plasticizers as controls. These are epoxy plasticizers, with the exception of DOP (di-2-ethylhexyl phthalate) which is considered to be the standard PVC plasticizer. Samples A, B and C are commercial, mixed alkyl esters of epoxystearic acid having slightly different variations in the mixed alkyl portion. The highest iodine value for the controls is 2.4 for sample B. Control C has the highest oxirane value, 4.50. The lowest iodine and oxirane values of the epoxy plasticizers are 1.7 and 3.14, respectively, for sample A. The vernolic acid esters all have relatively high iodine values and are much higher than the controls. In general materials having high iodine numbers are regarded as poor plasticizers and are not highly compatible with PVC.

All the materials investigated were found to be compatible at the 34% level during processing. No exudation was observed after molding and conditioning the sample overnight. Surface exudate was noted after 2 weeks on the molded sample A, the mixed alkyl ester of epoxystearate. All of the other samples have not shown signs of exudation after 7 months at the constant room conditions.

Shown in Table II are the values found for torsional stiffness, T_f and T_4 with the compatibility number Δ . The vernolic acid esters all exhibit good low temperature flexibility as noted by the T_f temperatures all being below -50C with the exception of the cyclohexyl sample (-42C). All have suitable compatibility numbers. The control sample A has a value that is too high for good compatibility, corroborated by the above noted exudate after 2 weeks. A value greater than 38

at a T_f of -50 indicates a lessening of compatibility and the larger the difference the greater the incompatibility.

The tensile properties (tensile strength, percent elongation and 100% modulus) shown in the table indicate that these esters are more efficient than DOP and the commercial epoxy controls.

The epoxy esters all exhibit high migration, which is generally the case for low temperature plasticizers. The cyclohexyl ester has the lowest migration, being nearly half that of the other vernolate esters and is slightly lower than the epoxystearate controls. The volatility loss of the vernolic esters decreases as the alkyl chain length of the alcohol increases. The methyl, propyl and isobutyl esters have volatility values that are too great for good permanence. All the vernolic esters gave excellent heat stability to the PVC.

The light stability is noted to be about the same for all the epoxy compounds. The epoxy esters failed earlier than the DOP but the failure was because of exudation of the plasticizer. The DOP sample failure was due to discoloration of the molded specimen, owing in part to PVC degradation. Only slight discoloration of the molded specimen was noted for the epoxy esters at 264 hr at which time the DOP sample was amber-colored.

Two surprising results were shown from the evaluation data. The first was that the vernolic acid esters were found to have good compatibility even though they had high iodine values. This compatibility is believed to be because of the location of the epoxy group with respect to the unsaturation. The second surprising result was that the n-octyl ester was compatible. Normal octyl esters of C_{18} straight chain acids usually have been found to be incompatible or to have very limited compatibility.

The cyclohexyl vernolate produced properties that were equal to or better than the commercial controls. The other vernolate esters had better low temperature properties, T_f and T_4 temperatures, and in general were more efficient.

ACKNOWLEDGMENT

Help in the preparation of the vernolic acid esters given by Mrs. Tatiana Zell.

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[Received October 18, 1965]