Euphorbia and *Vernonia* Seed Oil Products as Plasticizer-Stabilizers for Polyvinyl Chloride

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Abstract

Seed oils of *Euphorbia lagascae* Spreng. and *Vernonia anthelmintica* (L.) Willd. were prepared, refined and epoxidized; trivernolin was prepared from *V. anthelmintica* and also epoxidized. These products were each comparatively evaluated as plasticizer-stabilizers for polyvinyl chloride against commercial controls. Epoxidized *Euphorbia* and *Vernonia* oils and epoxidized trivernolin have potential value as primary plasticizers with the added advantage of increased heat and light stability; they could also be used in combination with other plasticizers utilizing the latter properties. Crude and refined *Euphorbia* and *Vernonia* oils are not considered suitable primary plasticizers because of poor compatibility and permanence; at low levels they probably could be used as stabilizers.

Introduction

EVALUATION OF *E. lagascae* and *V. anthelmintica* products as stabilizers against heat and light for polyvinyl chloride (PVC) is a part of an extensive USDA project which seeks new cash crops particularly to relieve or replace those in surplus. The seeds of these two species of different genera, *Euphorbia* from the Euphorbiacae (Spurge) Family, and *Vernonia* from Compositae, both contain oils rich in 12,13-epoxyoleic (vernolic) acid. The amount of this acid in good quality seed oil is about 60% in the *E. lagascae* where is is randomly distributed (3) in glycerides; the quantity in *V. anthelmintica* seed oil is about 70% where it exists almost entirely as the triglyceride, trivernolin (4). The quantities of oils in these seeds are about 40–50% (7) and 25–30% (6), respectively.

Several previous reports (9,10) from this laboratory evaluated *Vernonia* products, particularly the seed oil and salts of vernolic acid as stabilizers. Since the oils of both *E. lagascae* and *V. anthelmintica* seeds are unusual in having a high content of vernolic glycerides and appear to have exceptionally good commercial potentials the object of this investigation is to comparatively evaluate them as plasticizer-stabilizer materials in the crude, refined and refined epoxidized forms; also, to compare these with the chief component of *Vernonia* oil, trivernolin, in its refined and refined epoxidized forms; trivernolin is readily obtainable from *Vernonia* oil miscella at temperatures below about −12C (4–6).

Experimental

Materials

The materials used in this investigation were prepared: a) from *Euphorbia lagascae* Spreng. seed, a Spanish import which has been collected from wild plants under Public Law 480 funds; b) from Indian *Vernonia anthelmintica* (L.) Willd. seed purchased from Herbst Brothers Seedmen, Inc., New York City; and c) from trivernolin obtained from a mixture of upgraded (5) domestic seed extracted in a soybean pilot plant at Angola, Indiana (5). Table I lists the materails and the three commercial controls used and presents pertinent analytical data related to their properties. Oxirane oxygen determination was by the modified (4) Durbetaki (2) method.

Preparation of Materials

Crude and refined *E. lagascae* oils were obtained by procedures described in a recent publication (7), crude and refined *V. anthelmintica* oils and trivernolin by methods previously described (6).

Epoxidations of refined *Euphorbia* oil, refined *Vernonia* oil and trivernolin were performed with solutions of 40% peracetic acid purchased from Becco Chemical Division of Food Machinery and Chemical Company, Buffalo, New York; the epoxidation procedure used for refined *Euphorbia* oil as described is illustrative: A 100.0-g sample of oil was continuously stirred at approximately 22–25C; control of temperature was by rate of addition of peracetic acid solution and by use of an ice bath. The peracetic acid was used in 40% excess over the calculated quantity based upon the iodine value of the oil. For the *Euphorbia* oil 96 g of peracetic acid solution containing 12 g of crystalline sodium acetate dissolved in the peracetic acid were added dropwise, requiring about 40 min for the addition. Intermittent cooling was needed thereafter until epoxidation was completed which required an additional 80–120 min; completion was judged by the fact that no elevation above that of room temperature occurred following the removal of the ice bath. After completion of the reaction an equal volume of cold water was added. To

TABLE I

Analytical Data *Euphorbia* and *Vernonia* Samples [a] Used in PVC Evaluation Studies

	Oxirane oxygen %	FFA as epoxy-oleic %	Iodine value (Wija)	Gardner No.
Euphorbia oil (crude)	3.34	0.97	91.7	8–9
Euphorbia oil (refined)	3.40	0.18	90.9	0–1
Euphorbia oil epoxidized (crude)	6.88	0.10	......	0–1
Euphorbia oil epoxidized (refined)	7.38	0.13	5.6	0–1
Vernonia oil (crude)	3.71	1.4	109	8–9
Vernonia oil (refined)	4.26	0.30	91.0	1–2
Vernonia oil epoxidized (crude)	7.13	0.52	......	0–1
Vernonia oil epoxidized (refined)	7.35	0.11	8.2	0–1
Trivernolin (97.8% pure)	5.06	0.13	88.7	0–1
Trivernolin epoxidized (crude)	8.30	0.19	6.4	0–1
Trivernolin epoxidized (refined)	8.35	0.13	5.3	0–1
Epoxidized linseed oil (control A)	6.60[b]	0.22	2.7[b]	1
Epoxidized soybean oil (control B)	9.00[b]	0.11	5.0[b]	0–1
Di-2-ethylhexylphthalate (control DOP)	0[b]	0.05	0[b]	0–1

[a] Unsaponifiable matter before and after refining *Euphorbia* oil 0.71 to 0.35%, *Vernonia* oil 6.7 to 1.2%, trivernolin negligible.
[b] Value supplied by manufacturer.

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[1] E. Utiliz. Res. Dev. Div., ARS, USDA.

completely remove the acetic acid from the product it was necessary to use a nonpolar solvent, and an ideal one was found to be a solution containing 80% petroleum naphtha (p.n.) bp 35–59C, which had been twice redistilled, and 20% benzene. In general to extract the product 500 this solution was used except that in the case of epoxidized *Euphorbia* oil an additional 50 ml of benzene was required. The water layer was further treated with two 150-ml portions of p.n.-benzene solution and these were added to the initial extract. Six 200-ml portions of water were used to wash the product mixture which was then dried over anhydrous sodium sulfate, filtered and allowed to stand overnight at 4C. In the case of the two epoxidized oils a small quantity of resinous impurity appeared and this was discarded. The solvent was removed by a rotating evaporator at room temperatures. Analytical data on each of the epoxidized products before and after purification are presented in Table I. In the case of *Euphorbia* 100.0 g of the refined oil gave 108.3 g of epoxidized product. To purify it 100 g of the refined oil was dissolved in 1250 ml of hot methanol and the solution was allowed to stand overnight at −20C. The precipitate which formed was removed by filtration at −20C, placed in 350 ml of cold methanol and slurried at −20C; the slurry was filtered and the precipitate washed three times on the plate with 100-ml portions of methanol; final weight of refined epoxidized *Euphorbia*, a white waxy solid, was 83.7 g.

The yield of epoxidized *Vernonia* oil from 100.0 g of refined *Vernonia* oil was 105.7 g; it was purified as described above for *Euphorbia*; 99.4 g was used which gave 77.5 g of the refined epoxidized *Vernonia* oil, also a waxy solid.

When the epoxidized trivernolin was allowed to stand overnight in p.n.-benzene solution a considerable quantity (15.0 g) of white precipitate appeared instead of the resinous material produced in the case of *Euphorbia* and *Vernonia*. Because of its low oxirane oxygen value of 5.67% it was discarded. The epoxidized trivernolin from the filtrate after removal of the p.n.-benzene solvent weighed 86.9 g, the quantity prepared from 100.0 g of trivernolin. Eighty grams of this crude epoxidized trivernolin gave 67.2 g of refined white crystalline product after recrystallization from methanol; its analytical properties are given in Table I.

Plasticizer Evaluation

A three-component formulation of resin, plasticizer and stabilizer was used. The formulation was Geon 101, PVC resin 65% by weight, of the total mix, plasticizer 34%, and Mark M 1%, a 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 160C for 7 min. Samples were molded from the milled sheets at 160C in the manner previously reported (10). The molded samples were stored and conditioned at 23C and 50% relative humidity.

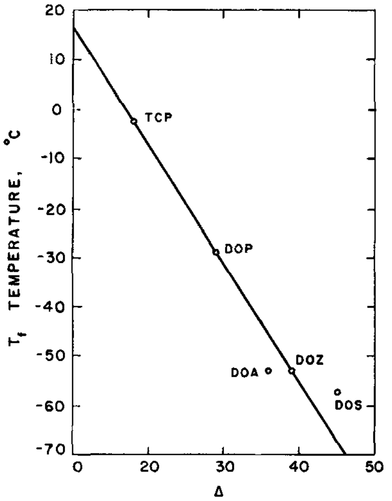

FIG. 1. Torsional stiffness T_f temperature versus compatability number Δ.

It has become common practice to measure the stiffness in torsion as a function of temperature. This method was introduced by Clash and Berg (1) who arbitrarily 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 designed as Δ is a measure of the compatibility of the plasticizer. The compatibility number Δ is a value which constantly increases with decreasing T_f temperature (11).

Figure 1 shows a plot of T_f veruses 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 (to the left of) and 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 (8). Volatility values were obtained at 70C

TABLE II

Mechanical Properties of Molded PVC Sheets Containing 34% *Euphorbia* or *Vernonia* Product as Plasticizer

Material	Torsional stiffness Temp. °C		Compatibility Δ	Tensile strength PSI	Elongation %	100% Modulus PSI	Migration wt. loss %	Volatility, wt. loss	Stability Hours to failure	
	T_f	T_4							Heat	Light
Crude *Euphorbia* oil	−45	10	55	2200	220	1300	12.6	6.0	[a]	24
Refined *Euphorbia* oil	−40	10	50	2100	220	1250	13.4	5.7	5	192
Expoxidized *Euphorbia* oil	−15	6	21	2400	310	1350	1.2	.3	23	336
Crude *Vernonia* oil	−33	6	39	2400	210	1350	6.3	.3	5	120
Refined *Vernonia* oil	−34	0	34	2500	270	1275	6.5	.4	10	192
Epoxidized *Vernonia* oil	− 9	13	22	2200	320	1600	.6	.3	10	288
Trivernolin	−31	1	30	2450	330	1200	5.6	.4	11	192
Epoxidized trivernolin	− 9	10	19	2500	290	1400	.7	.3	18	552
Controls, commercial										
Epoxidized linseed oil (A)	− 5	12	17	2660	300	1300	.5	.3	17	552
Epoxidized soybean oil (B)	−16	6	22	2525	340	1200	3.7	4.1	28	456
Di-2-ethylehexylphthalate (DOP)	−28	0	28	2600	275	1225	3.4	1.3	2	264

[a] Opaque; therefore transmitatnce could not be measured. Visually, sample failed at about 7 hr.

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

All the materials investigated were found to be compatible at the 34% level during processing. No exudation was observed after molding and conditioning the samples overnight.

The values for torsional stiffness and compatibility are given in Table II. The values obtained for crude and refined *Euphorbia* and *Vernonia* oils are too high for these to be considered as having good compatibility. Observation of surface exudate after two days at constant room conditions on the molded samples of crude and refined *Vernonia* oil confirmed this interpretation as did the appearance of exudate on the crude and refined *Euphorbia* oil samples after six days. The epoxidized *Euphorbia* and *Vernonia* oils, trivernolin and epoxidized trivernolin all had values indicative of good compatibility. These samples have not shown signs of exudate after two months.

The tensile strengths (Table II) of all the *Euphorbia* and *Vernonia* products were lower than the controls, A (epoxidized linseed oil), B (epoxidized soybean oil) and DOP. The tensile strengths of refined *Vernonia* oil and epoxidized trivernolin were about equal to that of control B.

The elongation percentages (Table II) for the epoxidized products, *Euphorbia* and *Vernonia* oils and for trivernolin were of the same order as those obtained for controls A and B, also higher than that for control DOP. The percentages for the crude and refined *Euphorbia* and *Vernonia* oils were lower than for DOP.

The 100% modulus values (Table II) for crude *Euphorbia* and *Vernonia* oils and all the epoxidized products were either equal to or higher than those of the controls; the values for the other products fell in between those of the controls. The migration values (Table II) for the epoxidized *Euphorbia* and *Vernonia* oils and for epoxidized trivernolin were good, less than those for controls B and DOP; the epoxidized *Vernonia* products compared favorably with control A in this respect; the refined *Euphorbia* oil showed the highest migration.

The volatility (Table II) of each of the *Euphorbia* and *Vernonia* products was low (with the exceptions of crude and refined *Euphorbia* oil), lower than controls B and DOP, comparing favorably with control A. Heat stability of all the experimental products was of much longer duration than that of control DOP; epoxidized *Euphorbia* oil had excellent heat stability and compared favorably with controls A and B in this respect. Stability to light was exceptionally good for epoxidized trivernolin, much higher than DOP and better than controls A and B. Control A showed slight exudation and some stiffening at the 336th hr; the epoxidized trivernolin showed no signs of exudation or stiffening after the 552nd hr. The stabilities for epoxidized *Euphorbia* and *Vernonia* oils were also good with values higher than DOP but lower than A and B.

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