Plasticizer Properties of Methyl Vinyl Ketone-Methyl *alpha*-Eleostearate Adduct and Derivatives

LIDA L. PLACEK, FRANK C. MAGNE, and W. G. BICKFORD,
Southern Regional Research Laboratory,[1] New Orleans, Louisiana

IN PURSUING further the possibility of producing from tung oil new and improved plasticizers (1, 2, 3, 4) for the vinyl chloride copolymers, it appeared of interest to evaluate the methyl vinyl ketone-methyl *alpha*-eleostearate adduct and certain of its derivatives as plasticizers. As shown in the preceding article (5), the methyl vinyl ketone-methyl *alpha*-eleostearate adduct is a ring compound containing keto and ester groups as well as cyclic and exocyclic ethylenic bonds. It might be expected that this compound would have exceptional plasticizing efficiency owing to the presence of a keto group in addition to an ester group. It might be expected also that saturation of the ethylenic linkages by hydrogenation and epoxidation as well as aromatization of the cyclohexene nucleus would result in compounds having additional desirable plasticizer properties. For example, it has been found previously (4) that hydrogenation of the ethylenic bonds of the acrylonitrile-eleostearate adducts resulted in greatly improved compatibility. It is also well known that epoxides improve the thermal and light stabilities of polyvinyl chloride plastics. In addition, it is probable that aromatization of the adduct would result in a material having a higher degree of stability toward oxidative deterioration and possibly an increased plasticizing efficiency.

It is the purpose of this communication to describe the preparation of the aforementioned derivatives and to present an intercomparison of the plasticizer properties of these derivatives and the parent compound with those of di-2-ethylhexyl phthalate.

Experimental

Methyl Vinyl Ketone-Methyl alpha-Eleostearate Adduct. Preparation of this adduct and its properties have been described in the preceding article (5).

Hydrogenation of the Adduct. A 36.2-g. sample of the adduct (0.10 mole) was dissolved in 150 ml. of absolute ethanol and hydrogenated at room temperature in a Parr hydrogenation apparatus, employing 3.0 g. of 10% palladium-carbon as catalyst. The hydrogenation was initiated at a pressure of 35 p.s.i. and continued for 40 min. The calculated amount of hydrogen (0.20 mole) required to saturate completely both the cyclic and the exocyclic ethylenic bonds was taken up during this time. The catalyst was removed by filtering the product through a bed of Hyflo Super Cell. The solvent was removed by vacuum-stripping on a steam bath that employed nitrogen as a sweep gas. Results of spectral and chemical analyses conducted on this material indicated that the ethylenic bonds were hydrogenated without the attendant attack on the carbonyl group.

Anal. Calcd. for $C_{23}H_{42}O_3$: OCH_3, 8.5; carbonyl O, 4.4. Found: OCH_3, 8.3; carbonyl O, 3.9. Carbonyl absorptivity, (a) = 0.97 at 5.9 microns in CCl_4; $n^{20/D}$, 1.4690.

Epoxidation of the Adduct. A 56.2-g. sample of the adduct (0.15 mole) was treated with 580 ml. of a 0.59 molar solution of perbenzoic acid (0.34 mole) in chloroform. The method of H. Hibbert *et al.* (6) for the preparation of perbenzoic acid was modified by employing sodium methylate rather than sodium ethylate, and the aqueous solution of sodium perbenzoate was washed twice with 100-ml. portions of ice cold carbon tetrachloride for removal of traces of methyl benzoate. The reaction mixture was maintained at 5°C. for a period of 24 hrs. At this time, titration of an aliquot indicated that two moles of perbenzoic acid had been consumed per mole of adduct (0.04 mole of perbenzoic acid remained unreacted). The chloroform solution was diluted with 1,200 ml. of ether and washed with six 300-ml. portions of 3% potassium hydroxide solution and four 300-ml. portions of water. After the chloroform-ether solution was dried over anhydrous sodium sulfate for 3 hrs., the solvent was removed by vacuum stripping on a steam bath that employed a stream of nitrogen. On removal of residual solvent under high vacuum, there was obtained 54.8 g. of a colorless, viscous material. The low values found for the oxirane oxygen and carbonyl oxygen contents may indicate some attack of the perbenzoic acid on the acetyl group with the attendant formation of an acetoxy derivative.

Anal. Calcd. for $C_{23}H_{38}O_5$: OCH_3, 7.9; carbonyl O, 4.0; oxirane O, 8.1. Found: OCH_3, 8.0; carbonyl O, 2.4; oxirane O, 5.0; $n^{20/D}$, 1.4834.

Aromatization of the Adduct. Aromatization of 128.0 g. of the adduct (0.41 mole) was achieved by employing 350 ml. of freshly distilled nitrobenzene as a hydrogen acceptor and 40.0 g. of 10% palladium-carbon as a catalyst. The mixture was refluxed for 9 hrs. under a carbon dioxide atmosphere, after which the product was filtered through a bed of Hyflo Super Cell for removal of the catalyst. Excess nitrobenzene and the aniline produced during the reaction were removed from the crude aromatized product by means of vacuum distillation. Treatment of the distillate with anhydrous hydrogen chloride resulted in the formation of 18.2 g. of aniline hydrochloride, m.p. 195°C. High-vacuum distillation of the residue yielded 85.0 g. of aromatized product, b.p. 165–170°C./40 microns.

Anal. Calcd. for $C_{23}H_{34}O_3$: OCH_3, 8.4; carbonyl O, 4.4. Found: OCH_3, 8.0; carbonyl O, 4.0. Aromatic absorptivities, (a) = 0.42 at 6.25 and 6.75 microns in $CHCl_3$, and (a) = 28.58 at 242 millimicrons in C_2H_5OH; $n^{20/D}$, 1.4930.

Plasticizer Screening. Compositions employed in these tests were formulated as follows: Vinylite VYDR (vinyl chloride-vinyl acetate copolymer, 95:5), 63.5%; plasticizer, 35.0%; stabilizer (basic lead carbonate), 1.0%; and stearic acid, 0.5%.

In those instances where less than 35% plasticizer was used, the resin content was varied in accordance with the following formula, percentage of resin = (98 − x), where x is the percentage of plasticizer.

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[1] One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

TABLE I

Plasticizing Characteristics of the Methyl Vinyl Ketone-Methyl *alpha*-Eleostearate Adduct and Derivatives

Plasticizer	Plasticizer	Tensile strength	100% Modulus	Elongation	Brittle point	Volatility loss[a]
	(%)	(p.s.i.)	(p.s.i.)	(%)	(°C.)	(%)
Methyl vinyl ketone-methyl *alpha*-eleostearate adduct	30	3560	1960	290	—21	
	35	2930	1250	340	—31	1.5
Hydrogenated derivative	30	3350	1840	310	—21	
	35	3000	1310	410	—29	1.8
Epoxidized derivative	35	3400	2300	320	+1	0.5
Aromatized derivative	30	3750	2170	280	—23	
	35	[b]	1270	[b]	—33	2.9
Control (DOP)	30	3390	2290	240	—27	
	35	2940	1530	340	—33	1.6

[a] Activated carbon method A.S.T.M. D 1203-52T.
[b] Beyond limit measurable on IP-4 tester (6 in.) on 1-in. standard test length.

Milling, molding, and testing procedures were the same as those reported previously (7). Compositions were rated as compatible if no active bleeding, blooming, or contact smearing were observed during the 90 days of observation.

Discussion

The methyl vinyl ketone-methyl *alpha*-eleostearate adduct and its derivatives, listed in Table I, are all compatible primary plasticizers for the vinyl chloride-vinyl acetate copolymer. It is apparent from the data presented that this group of plasticizers, with the exception of the epoxidized adduct, has better plasticizing efficiency than DOP although in low-temperature performance and volatility they are in the same general class. However the stock plasticized with the epoxidized adduct has a very low volatility loss and excellent stability to deterioration induced by exposure to heat and ultraviolet radiation. It is noteworthy that this stock remained unaffected after receiving thermal exposure for a period twice that which produced complete failure in the stock plasticized with DOP. Similarly this composition showed no color change after 200 hrs. of exposure in the Atlas Weatherometer whereas the formulation containing DOP was heavily darkened during this time. The thermal stabilities of the various plasticized stocks fall into three main categories, namely, less stable than, equally stable as, and more stable than the control. The stocks plasticized with the original adduct and its aromatized derivative are the least thermally stable, that plasticized with the hydrogenated derivative has the same order of stability as the control, while the stock plasticized with the epoxidized derivative is superior as mentioned previously. Apparently the best balance between thermal stability and the other physical properties reported is achieved in the hydrogenated adduct. This is a compromise which gives reasonable stability without seriously sacrificing the other desirable properties of the plastic. It is of interest to note with regard to the methyl vinyl ketone derivatives that there is no impairment of the low-temperature characteristics of the plasticized stocks whereas it has been reported that polymers of methyl vinyl ketone are very brittle at subnormal temperatures (8). As a class, the methyl vinyl ketone-methyl *alpha*-eleostearate series appears to be superior to other eleostearate derivatives which were tested previously as plasticizers for vinyl chloride-vinyl acetate copolymer (1, 2, 4).

Summary

The Diels-Alder adduct of methyl vinyl ketone and methyl *alpha*-eleostearate was subjected to modification by hydrogenation and epoxidation of its unsaturated centers and by aromatization of its cyclohexene nucleus. These derivatives, as well as the original adduct, were intercompared with DOP as primary plasticizers for vinyl chloride-vinyl acetate copolymer. All of these materials were found to be highly compatible as primary plasticizers and generally more efficient than DOP. The stocks plasticized with the hydrogenated and epoxidized adducts exhibited very good thermal stability on long exposures to heat. The epoxidized adduct not only imparted excellent heat stability to the plastic but also prevented deterioration on exposure to ultraviolet irradiation.

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