9,9(10,10)-Bis(acetoxymethyl)octadecanoate Esters as Plasticizers for Poly(vinyl chloride)

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ABSTRACT

Four alkyl 9,9(10,10)-bis(acetoxymethyl)octadecanoates were evaluated as plasticizers for poly(vinyl chloride). They were all compatible and imparted properties generally equal or superior to those obtained with a dioctyl phthalate (DOP) control. Permanence properties were also generally equal or superior to those reported for analogous acetoxy and acetoxymethyl plasticizers. Volatility was half that for DOP. On heating, the experimental samples remained flexible to failure, whereas the control samples with DOP became stiff and rigid. Acetone acetals of alkyl 9,9(10,10)-bis(hydroxymethyl)octadecanoates were incompatible with poly(vinyl chloride).

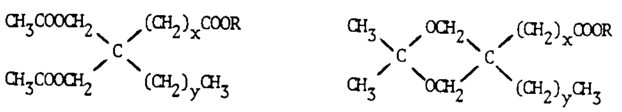
INTRODUCTION

Decreased supplies and increased costs of petroleum and natural gas, together with the need to use available supplies for energy production, make attractive the substitution of these irreplaceable resources by renewable agricultural raw materials. The transformation of agricultural raw materials into useful products by processes that have commercial potential will help ease the effect of petroleum shortages. Plasticizers represent a large market for petrochemicals. The 1.4 billion pound annual consumption is dominated by petroleum-derived di(2-ethylhexyl) phthalate, usually called dioctyl phthalate (DOP) (1). Because phthalate plasticizers may volatilize or be leached from plastics, they have been suspect as ubiquitous environmental contaminants. Thus, DOP is "sanctioned" by the Food and Drug Administration for use in food packaging films, but only with foods of low fat and high water content (2).

In a previous publication (3), we reported preparation and characterization of a series of high-boiling, low-melting liquids derived from 9,9(10,10)-bis(hydroxymethyl)octadecanoic acid, which in turn was derived from oleic acid through a series of simple reactions with inexpensive reagents (3,4). We now wish to report evaluation of some of these new compounds as plasticizers for poly(vinyl chloride) (PVC).

EXPERIMENTAL PROCEDURES

Compounds tested were described previously (3). Processing and testing were also previously reported (5,6) using the formulation Geon 102EP (a commercial PVC), 65%; plasticizer, 32%; G62 (epoxidized soybean oil stabilizer), 2%; and Vanstay RR (Ba-Cd complex), 1%.



1	R = CH_3	2	R = CH_3
3	C_2H_5	4	C_2H_5
5	1-C_4H_9		
6	$CH_2CH(C_2H_5)C_4H_9$		x = 7, y = 8; x = 8, y = 7

FIG. 1. Compounds evaluated as PVC plasticizers.

RESULTS AND DISCUSSION

Compounds evaluated are shown in Figure 1. Test results are shown in Table I, together with data for two other plasticizers containing two acetoxy or acetoxymethyl groups (7). Compatibility has been defined (6) as "the ability of the plasticizer and the plastic to mix and remain homogeneously dispersed in one another." The compatibility number (Δ, column 4, Table I) is the difference between T_f, the temperature at which the material passes from rigid to a nonrigid state (elastic modulus 135,000 psi), and T_4, the temperature at which change in stiffness of the sample is most temperature sensitive (elastic modulus 10,000 psi). The smaller the number, the more compatible is the plasticizer. Compatiblilities are shown graphically in Figure 2. The straight line plot of plasticizers with good compatiblility is taken as a standard. Plasticizers to the left of the line are more compatible than the standards. Those to be right of the line are less compatible. A full discussion of the compatiblility number and its derivation is given in Reference 6.

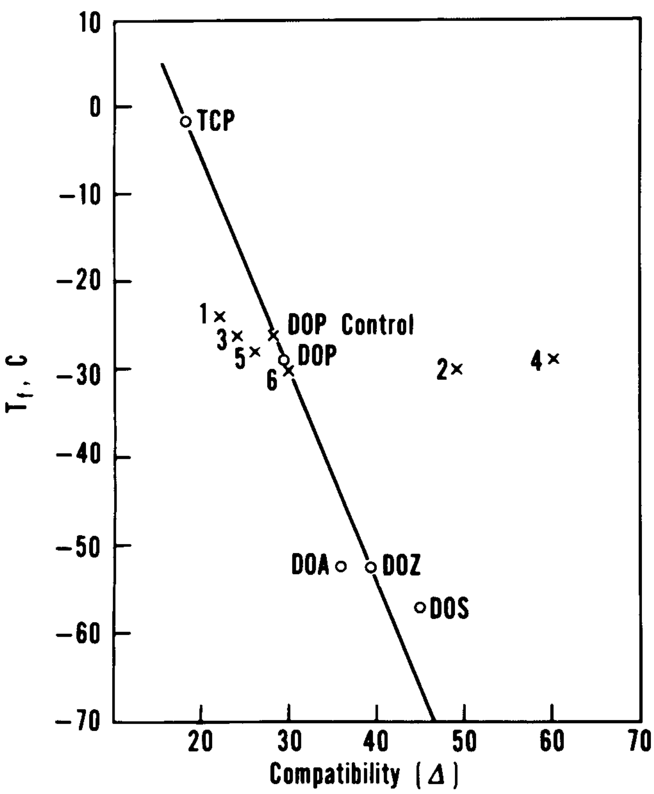


FIG. 2. Compatibility of experimental plasticizers with poly(vinyl chloride) compared to standard line (6). Numbers refer to compounds in Figure 1 and Table I. TCP = tricresyl phosphate; DOP = dioctyl phthalate; DOA = dioctyl adipate; DOZ = dioctyl azelate; DOS = dioctyl sebacate.

TABLE I

Properties of Plasticized Poly(vinyl chloride)[a]

Cpd.[b]	R	Torsional stiffness, temp. (C) T_f	T_4	Compatibility no. (Δ)	Tensile strength (psi)	Elongation (%)	100% Modulus (psi)	Migration wt loss (%)	Volatility wt loss (%)	Heat stability (hr)
1	CH_3	-24	-2	22	2760	335	1135	5.1	0.6	10
A1		-25	-1	24	2840	335	975	4.5	1.1	11.5
B1		-33	-8	25	2610	335	835	8.1	0.8	7.0
2		-30	19	49	2710	250	1580	---	---	---
3	C_2H_5	-26	-2	24	2805	300	1135	5.2	0.5	9
4		-29	31	60	2615	140	1910	---	---	---
5	C_4H_9	-28	-2	26	2705	330	1090	6.4	0.6	11
A5		-33	2	35	2785	450	1295	8.0	1.7	14
B5		-33	-7	26	2820	345	935	8.0	0.5	9.5
6	C_8H_{17}	-30	0	30	2815	290	1290	5.8	0.6	11
DOP		-26	2	28	2805	320	1170	4.3	1.2	9.5

[a]Data for compounds A and B from Reference 7.
[b]Compounds 1-6, R, see Figure 1. A-$CH_3(CH_2)_7CH(OCOCH_3)CH(OCOCH_3)(CH_2)_7COOR$,B-$CH_3(CH_2)_{5(4)}CH(CH_2OCOCH_3)CH_2$-$CH_2CH(CH_2OCOCH_3)(CH_2)_{7(8)}COOR$.DOP-Dioctyl phthalate control.

All four alkyl 9,9(10,10)-bis(acetoxymethyl)octadecanoates (**1**, **3**, **5**, **6**) were compatible with PVC. They had good compatibility numbers. All but the 2-ethylhexyl ester (**6**) were better than the DOP control and equal to or better than the 9(10)-acetoxyoctadecaoates (**A1**, **A5**) and 9,12(10,13)-bis(acetoxymethyl)octadecanoates (**B1**, **B5**). Tensile strength, elongation, and 100% modulus were generally comparable to or better than with DOP. Weight loss due to migration was greater than for DOP but less than three of the four others. Volatility was half that of DOP and the diacetoxy esters and about the same as the bis-(acetoxymethyl) compounds. Except for the ester (**3**), heat stability was better than with DOP, **B1** and **B5**, though not as good as with **A1** and **A5**. More significant, the test samples remained flexible at failure (9-11 hr). The DOP control was stiff after 3 hr and rigid after 4.5 hr.

Similar comparisons with three other esters (7), 9(10)-acetoxyoctadecanoates, 12-acetoxy-9-octadecenoates (acetylated ricinoleates) and 9(10)-acetoxymethyloctadecanoates, showed the 9,9(10,10)-bis(acetoxymethyl)octadecanoates to have better compatibility (smaller Δ), generally higher tensile strength, much lower migration and volatility losses, and intermediate heat stability.

Acetal esters **2** and **4** were incompatible with PVC. Fusion was obtained with these esters but not with 1-butyl and 2-ethylhexyl homologs. The molded sheets showed heavy surface exudate on standing overnight. Only tensile and flexibility tests were run with these two samples. They showed poor compatibility numbers (high), low elongation, and high modulus, indicating stiffness.

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