should turn out to be the case, it might serve to explain some heretofore obscure experimental facts, but, on the other hand, it would probably require a radical reformulation of some of our ideas about emulsion stability.

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Evaluation of Butyl Stearate, Butyl Oleate, Butyl Ricinoleate, and Methyl Linoleate as Poly(vinyl Chloride) Plasticizers[1]

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Abstract

An investigation of butyl stearate, butyl oleate, butyl ricinoleate, and methyl linoleate was made to determine the extent of their compatibility with poly(vinyl chloride) and their plasticizing effects on the physical properties of the resulting molded sheets. These monoesters were evaluated as the sole plasticizer and in combination with DOP. The results showed the materials to have limited compatibility in general, being less than 10% of the total mix. In combination with DOP these compounds were found to improve the plasticizer efficiency, color, low temperature flexibility, and heat stability of the molded poly(vinyl chloride) sheets over those containing DOP as the sole plasticizer. Tensile strength, per cent elongation, and light stability properties were essentially comparable to those found for pure DOP.

Introduction

THE PLASTICIZER literature contains numerous references to the limited compatibility of monoesters such as butyl stearate and butyl oleate with poly(vinyl chloride) resins. Doolittle (1) states that the quantity of butyl stearate that can be added to vinyl chloride compositions is very small since the resulting material tends to exude and develop an oil film on the surface and that butyl oleate is slightly more compatible, owing to its double bond; however, the extent of compatibility and the resulting properties are not discussed in the literature. Therefore, several monoesters of fatty acids were studied in order to determine the extent of compatibility and the effect on physical properties of poly(vinyl chloride). In addition, it has been stated that compounds containing free hydroxy groups have limited compatibility (2); an exception to this is the citrate esters. One of the compounds studied contains in addition to unsaturation a free hydroxyl group.

Experimental

Materials. The materials used in this investigation are all commercial.

Material	Source	Iodine number		% FFA
		Theory	Experimental	
Butyl Stearate	Ohio Apex	0	1.46	0.44
Butyl Oleate	Wilson-Martin	74.98	75.98	0.80
Butyl Ricinoleate	Baker Castor	71.59	74.95	1.75
Methyl Linoleate	Pacific Vegetable Oil	172.40	138.86	0.71

Plasticizer Evaluation. A three-component formulation of resin, plasticizer and stabilizer was used. The resin was Geon 101 poly(vinyl chloride). Two plasticizer formulations were employed, one (A) in which the plasticizer was varied from 4–34% with respect to the resin, and the other (B) using a total of 34% plasticizer of which the amount of the monoester varied from 4½–29½% combined with the necessary amount of DOP (di-2-ethylhexylphthalate) to bring the total plasticizer to 34% of the total mix.

A barium-cadmium liquid phenate stabilizer system (Mark M) was used at 1% of the total mix for all the formulations. Since the primary purpose of the study was to determine compatibility and effect on mechanical properties no attempt was made to attain maximum heat and light stability. The formulations were milled at 160C for 7 min except where low compatibility prevented fusion, thereby requiring a longer time on the mill. Samples requiring more than 5 min to fuse and form a complete band were milled an additional 3 min after forming a complete band. Compatibility was determined by observation of the time of fusion during milling and the time for exudation to appear after molding. Samples were

TABLE I
Fusion Time (Min)

%	Butyl stearate	Butyl oleate	Butyl ricinoleate	Methyl linoleate	DOP
Formulation A					
4	3	2	2	2	1½
9	5	3	2½	1½	1½
14	..	7	2½	2	½
19	..	..	5	2	½
24	..	..	5½	2	½
29	..	..	..	2½	½
34	..	..	..	3	½
Formulation B (Total plasticizer 34%)					
4½	½	½	½	½	..
9½	½	½	½	½	..
14½	½	½	½	½	..
19½	2	1½	1	½	..
24½	3½[a]	12	3	1	..
29½	..	..	7	2	..

[a] 22% butyl stearate.

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[1] Presented at the AOCS Meeting, Minneapolis, 1963.

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TABLE II

Characteristics of Molded Sheets

%	Butyl stearate	Butyl oleate	Butyl ricinoleate	Methyl linoleate	DOP
Formulation A					
4	No exudate; transparent, amber	No exudate; transparent, yellow	No exudate; transparent, yellow	No exudate; transparent, amber	No exudate; transparent amber
9	No exudate; opaque, amber	No exudate; hazy, yellow	No exudate; slight haze, yellow tint	No exudate; transparent, amber	No exudate; transparent pale amber
14	....	Slight exudate; opaque, ivory	Slight exudate; opaque, yellow tint	No exudate; transparent, pale amber	No exudate; transparent, light amber
Formulation B (Total plasticizer 34%)					
4½	No exudate; transparent, colorless	No exudate; transparent, colorless	No exudate; transparent, colorless	No exudate; transparent, crystal white	
9½	No exudate; transparent, colorless	No exudate; transparent, colorless	No exudate; transparent, colorless	Slight exudate; transparent crystal white	

inspected periodically for signs of exudation, up to 14 months.

The tensile data were obtained using an Instron tensile tester. Two speeds of testing were necessary since the materials ranged from rigid (0–14½%) to flexible (above 14½%). These were tested in accordance with the appropriate ASTM test procedure (3,4).

It has become common practice to measure the stiffness in torsion as a function of temperature. This method was introduced by Clash and Berg (5) 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 approximate equivalence to the temperature of maximum slope. Heat stability tests were conducted on molded specimens in an air convection oven at 160C. Samples were removed periodically and examined using a visible range spectrophotometer to measure the % loss of transmittance at 600 $m\mu$ wavelength. Time of failure was arbitrarily chosen as the time at which 20% transmittance was recorded.

Light stability was determined by exposing 1-in squares under a UV lamp the samples being 7 in. from the source. The samples were necessarily heated during exposure; the temperature averaged ca. 60C. Complete details of the method of test sample preparation and testing have previously been published (6).

Results and Discussion

Compatibility. The first indication of the compatibility of a plasticizer is observed during the preparation of the test specimen upon milling. A completely incompatible material will not fuse with the resin, the rate of fusion varying with the efficiency. The more efficient the plasticizer the faster the rate of fusion. The rate of fusion for the materials investigated is shown in Table I.

All the experimental materials produced fused sheets on the mill; however, the extent to which they could be employed varied. In formulation A (Table I) butyl stearate and butyl oleate show the poorest miscibility, being completely incompatible above 9 and 14%, respectively (no fusion). Although the butyl ricinoleate showed miscibility at 24%, the fusion time was long. On the other hand, methyl linoleate could be incorporated to the greatest extent (34%), requiring a fusion time of 3 min.

The compositions listed in Table I were then molded into sheets and observed immediately after cooling for surface exudate. The results are shown in Table II. All samples show no immediate exudate up to 9%, and no exudate was observed even after 12 months. Butyl oleate and butyl ricinoleate first exhibit slight exudation at 14%, whereas methyl linoleate was exudate-free. With methyl linoleate, exudate appeared at 19% and became heavier at higher levels. The DOP control shows no exudate at any level investigated, the highest level in this case being 34%.

In formulation B, where these materials are used in combination with DOP (Table I), the tolerance is increased and the fusion times are greatly lowered, except where the incompatibility level is approached and the fusion time increases. With the exception of the methyl linoleate, the fusion time begins to increase above the 14½% level. All the molded sheets at 9½% and below (Table II), like those of formulation A, show no immediate exudation. The butyl stearate and butyl oleate at the 4½% level remain free of exudate after 14 months and at the 9½% level show exudate after 12 months. The butyl ricinoleate and methyl linoleate at the 9½% level showed surface exudation after 1 and 6 months, respectively, and at the 4½% level showed exudate after 12 months.

TABLE III

Tensile Data

%	Butyl stearate		Butyl oleate		Butyl ricinoleate		Methyl linoleate		DOP	
	Tensile strength (psi)	Elongation %	Tensile strength (psi)	Elongation %	Tensile strength (psi)	Elongation %	Tensile strength (psi)	Elongation %	Tensile strength (psi)	Elongation %
Formulation A										
0	7700	10	7700	10	7700	10	7700	10	7700	10
4	7100	10	6500	10	7200	10	7100	10	7100	10
9	6000	10	5700	10	5500	10	5500	10	6200	10
14			4700	10	5300	10	4600	10	5100	10
19					3000	150	3500	200	3300	150
24					2900	275	3200	250	3000	275
29							2900	300	2900	250
34							2800	325	2700	325
Formulation B (Total plasticizer 34%)										
0	2700	325	2700	325	2700	325	2700	325	(34% DOP)	
4½	2600	375	2600	350	2600	400	2600	375		
9½	2500	375	2600	375	2600	375	2500	375		
14½	2400	375	2500	375	2600	375	2600	375		
19½	2500	400	2500	350	2700	375	2500	400		
24½	2000[a]	250[a]	2400	250	2800	350	2500	350		
29½					2500	275	2900	375		

[a] 22% butyl stearate.

TABLE IV

Clash-Berg Flexibility

%	Butyl stearate		Butyl oleate		Butyl ricinoleate		Methyl linoleate		DOP	
	T_f	T_4	T_f	T_4	T_f	T_4	T_f	T_4	T_f	T_4
Formulation A										
0	79	82	79	82	79	82	79	82	79	82
4	59	68	60	68	59	69	62	71	60	70
9	53	62	50	58	48	60	51	59	50	58
14			48	57	47	56	40	53	40	47
19					43	54	16	44	16	40
24					24	53	0	41	−1	26
29							−5	40	−18	12
34							−9	40	−28	1
Formulation B (Total plasticizer 34%)										
0	−28	1	−28	1	−28	1	−28	1	(34% DOP)	
4½	−35	−1	−36	−4	−35	−2	−38	−6		
9½	−34	2	−42	−4	−38	−2	−35	−2		
14½	−30	11	−51	0	−38	8	−35	−3		
19½	−22	36	−54	20	−30	23	−33	3		
24½	−15[a]	46[a]	−37	46	−20	41	−30	12		
29½					−30	46	−19	32		

[a] 22% butyl stearate.

The butyl oleate and methyl linoleate did not produce immediate exudate at 14½%; however, exudate appeared after 1 month. In general it can be seen from the results obtained for the two formulations that 9½% is the highest percentage of these compounds which can be employed without exudation occurring immediately after molding, although the resin will tolerate larger amounts, e.g., butyl ricinoleate and methyl linoleate.

Physical Properties. The data obtained on the tensile strength and per cent elongation at break are summarized in Table III. In general for formulation A the effect of the various materials on these properties is seen to be comparable to those obtained for equivalent amounts of DOP. It should be noted that in formulation B a small amount (4½%) causes a slight decrease in the tensile strength and an increase in the per cent elongation, compared to the DOP control indicating increased plasticizer efficiency. This is also generally the effect obtained for the higher levels, and there is little change in these properties as the ratio of DOP is decreased.

In Table IV are given the Clash-Berg T_f and T_4 values observed for the PVC specimens plasticized with the monoesters. It can be seen that for the low concentrations of 4 and 9% that these materials produce the same effect on flexibility as DOP, but that at the higher concentrations none of the experimental materials in formulation A develop the low temperature flexibility obtainable with DOP. It can also be seen that at 29 and 34% the methyl linoleate which exhibits poor compatibility as demonstrated by heavy exudation, produces a material whose flexibility changes more slowly over a wider temperature range than the DOP control as seen by the 45 and 49° temperature difference between T_f and T_4 as compared to 30 and 29° for the DOP.

TABLE V

Heat Stability at 160C (hr)

%	Butyl stearate	Butyl oleate	Butyl ricinoleate	Methyl linoleate	DOP
Formulation A					
0	1¼	1¼	1¼	1¼	1¼
4	¼	¾	1¼	¼	¼
9	[a]	1	2	½	½
14		[a]	2	½	1
19			[a]	1	1
24			[a]	1	1
29				1¼	1¼
34				1½	1½
Formulation B (Total plasticizer 34%)					
0	1½	1½	1½	1½	(34% DOP)
4½	2½	1¾	3	2	
9½	2½	1¾	3¾	2	
14½	2¼	1¾	4½	2¼	
19½	2¼	1¾	4¾	2¼	
24½	2¼[b]	1¾	3¾	2¼	
29½			4¾	2¼	

[a] Opaque.
[b] 22% butyl stearate.

The effect of the combination with DOP (formulation B) shows that in all cases addition of as little as 4½% of the experimental materials improves the low temperature properties by lowering the flex temperatures as much as 10°. The butyl oleate at 19½%, although not highly compatible, greatly decreases the low temperature flexibility (−54°).

In addition, as the DOP content is decreased the over-all flexibility decreases, as noted by the T_4 temperatures which increase as the DOP content is decreased.

Heat Stability. The first indication of heat stability was observed after molding (Table II). The colors of the formulation B sheets were all improved over both the formulation A materials and the DOP control. The combination of 4½% methyl linoleate with DOP produced the best color, being nearly crystal clear.

The effect on heat stability at 160C of the various materials is shown in Table V. Butyl stearate, methyl linoleate and DOP are comparable. Butyl oleate and butyl ricinoleate greatly improve heat stability compared to DOP. In combination with DOP (formulation B) all the materials have increased stability over the control, with the butyl ricinoleate producing the greatest stability.

Light Stability. Under severe UV exposure the light stability, with regard to color change, for all samples tested (formulation A) including the DOP control improved as the plasticizer level increased. At the 4% level the experimental materials had greater stability toward initial color change than the control; all were black after 20 hr.

The greatest light stability was observed for the plasticizer content of 34%. The test specimens (formulation B) containing 4½% of the monoester showed essentially the same stability as the control; all became tacky after 15 min and all showed the same degree of failure after 100 hr (yellow with a large brown area). Above 4½% color change occurred earlier and exudation became a second factor.

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