The Plasticizing Characteristics of Some Fatty Acid Morpholides and Morpholide-Hydrocarbon Extender Blends

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Abstract

The preparation and plasticizing characteristics in poly(vinyl chloride-vinyl acetate) copolymer resin of 14 morpholides of unsubstituted and substituted C_{18} fatty acids are reported, as well as the plasticizing performance of blends of the morpholide of hydrogenated cottonseed acids with such hydrocarbon extenders as Conoco H-35, Amoco BN-1, and Monsanto HB-20 and 40.

Up to 50% of some of these extenders can be blended with the morpholide of hydrogenated cottonseed acids without loss of compatibility. Economics excepted, such blends are of questionable merit with respect to performance. Although substituent groups such as oxirane, benzyl, and carbonyl improve the compatibility, volatility, and soapy water extractability characteristics of the fatty acid morpholide plasticizers, they are almost invariably detrimental to low-temperature performance and efficiency.

The dimorpholides of the dimer acids exhibit no measurable volatility loss in plasticized stock and mixtures with a monomeric morpholide exhibit unusually low volatility losses.

Ternary composition-compatibility diagrams are described for two systems involving the morpholides of linoleic, epoxyoctadecenoic, and palmitic acid in one instance and oleic, dimer, and palmitic acid in the other. These diagrams delineate the fatty acyl compositional limitations consonant with compatibility of these two systems in poly(vinyl chloride-vinyl acetate) copolymer.

Introduction

PREVIOUS WORK ON FATTY ACID amide plasticizers has shown that the morpholides of oleic acid, lauric acid, and certain mixtures of oleic, linoleic, and palmitic or stearic acids were compatible and efficient plasticizers for homo- and copolymers of vinyl chloride (1,2).

It can now be reported that an even broader spectrum of fatty acids or modified fatty acids yields compatible morpholides. Among the morpholides investigated, those of the dimer acids are of particular interest because of their low-volatility and extraction-loss characteristics and their unique ability to disproportionately suppress the volatility of other morpholides in admixture with them.

Experimental

Materials

The following commercial products were used as received: oleic acid (Elaine 233LL) and dimer acids (Empol 1014 low in trimer acid, and Empol 1022) from Emery Industries;[2] palmitic acid (NF-16) from Armour Chemical Division; *meta*-chloroperbenzoic acid from F. M. C. Corporation; 9(10)-phenyloctadecanoic acid, erucic acid, and morpholine from Distillation Products Industries; 3,5-dimethylmorpholine from Jefferson Chemical Co.; and the hydrocarbon extenders Conoco H-35 from Continental Oil Co., HB-20 and 40 from Monsanto Chemical Co., and BN-1 from American Oil Co. The linoleic acid was a 93% pure product obtained from the Northern Utilization Research and Development Division. The hydrogenated cottonseed fatty acids were derived from a cottonseed oil hydrogenated selectively to an I.V. of 63.1 and T.C. of 62.9, as previously reported (1). Rapeseed and parsley seed fatty acids were prepared from the natural oils by the usual saponification and acidulation operation. Petroselinic acid was obtained from parsley seed acids as reported by Holmes (2a). The morpholides, except those of 9(10)-carboxyoctadecanoic acid, were prepared from the free fatty acid and morpholine as previously described (1). The epoxymorpholides were prepared by epoxidation of N-linoleoylmorpholine by the conventional procedure using the appropriate amount of *m*-chloroperbenzoic acid to achieve the desired level of epoxidation in the final product.

Dimorpholide of 9(10)-carboxyoctadecanoic acid (I): 9(10)-Carboxyoctadecanoic acid (II) was prepared by the interaction of oleic and formic acid (90%) according to the procedure reported by Roe and Swern (3). The crude II, neutralization equivalent (n.e.) 186–206, was upgraded to a n.e. of 172.9 (theory 163.5) by the following clathration operation. One to one proportions of the crude acid and urea were dissolved in sufficient methanol for complete solution at the boiling point. The solution was allowed to cool and stand for 24 hr to permit formation of the crystalline clathrate of the contaminating oleic acid which was subsequently removed by filtration. The upgraded acid II was freed of methyl esters by the usual saponification-acidulation procedure. On the basis of its n.e., its purity was 92% assuming that oleic acid was the contaminant.

Complete conversion of II to the dimorpholide, I, could not be achieved by direct interaction with morpholine at reflux temperatures. It was necessary to convert the unreacted carboxyls to acid chlorides with thionyl chloride, and then react with morpholine.

Butyl 9(10)-morpholinocarbonyloctadecanoate (III). Utilizing the differences in reactivity of the carboxyl groups of II (4) the terminal carboxyl group was esterified by refluxing 40 g of II with 200 ml of n-butanol for 19 min in the presence of 8 g of naphthalene-2-sulfonic acid.

The reaction mixture was dissolved in commercial hexane, washed with water until acid-free and stripped. The product was then dissolved in 150 ml of 50% aqueous ethanol, the solution made basic by the addition of Na_2CO_3 and extracted with successive portions of a 1/1 chloroform-diethyl ether mixture to remove the minor amount of diester present. The aqueous phase was then acidified and the liberated butyl 9(10)-carboxyoctadecanoate (IV) was separated as a hexane extract which was then washed, dried, and stripped. The product, IV, had a n.e. of 391.2 (theory 385.6). The yield was 15 g.

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

[2] Use of a company and/or product named by the Department does not imply approval or recommendation of the product to the exclusion of others which may also be suitable.

TABLE I
Elemental Analyses of Various Morpholides

Compound	% Carbon		% Hydrogen		% Nitrogen	
	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
N-Myristoylmorpholine	72.77	72.74	11.89	11.78	4.57	4.71
N-Petroselinoylmorpholine	74.85	75.09	11.63	11.75	3.94	3.98
N-Erucoylmorpholine	76.32	76.55	12.05	12.12	3.43	3.43
N-(9,10-Epoxyoctadecanoyl)morpholine[a]	....	....	....	....	3.82	3.83
N-(9,10–12,13-Diepoxyoctadecanoyl)morpholine[b]	....	....	....	....	3.73	3.73
N-[9,(10)-Phenyloctadecanoyl]morpholine	....	....	....	....	3.25	3.62
Dimorpholide of 9(10)-carboxyoctadecanoic acid	68.22	69.16	10.39	10.52	5.44	5.43
Butyl 9(10)-carbonylmorpholino-octadecanoate	71.48	71.46	11.15	11.35	2.87	3.09
N-[9(10)-carbobutoxyoctodecanoyl]morpholine	71.10	71.46	11.23	11.35	3.08	3.09
Dimorpholide of dimer acid (Empol 1014)	74.39	75.64	11.05	11.26	3.90	4.01
Dimorpholide of dimer acid (Empol 1022)	....	....	....	....	3.88	4.01
Morpholide of parsley seed fatty acids	....	....	....	....	3.44	3.66
Morpholide of rapeseed fatty acids	....	....	....	....	3.58	3.70
Morpholide of hydrogenated cottonseed acids[c]	....	....	....	....	3.90	4.09
N-Oleoyl-3,5-dimethylmorpholine	75.45	75.86	12.12	11.95	3.56	3.69

[a] Per cent oxirane 3.64 found, 4.35 calculated.
[b] Per cent oxirane 6.54 found, 8.40 calculated.
[c] Acids derived from a selectively hydrogenated oil, see text.

An additional 20 g of IV was obtained from the chloroform-ether phase, as follows: The material recovered from the organic phase (n.e. 475) was dissolved in hexane and the solution percolated through a 25-mm-diameter column containing 400 g of activated alumina. This was followed by 500 ml of a 5/1 hexane-ethanol mixture to wash out any diester on the column after which the adsorbed monoester was eluted with 500 ml of a 5/1 hexane-acetic acid solution. The product, IV, recovered after washing and stripping this eluate, had a n.e. of 398.2. The combined yield of IV was 35 g.

Thirty grams of IV in 40 ml of chloroform was added dropwise and with stirring to 10.7 g of thionyl chloride. Upon completion of the addition, the temperature of the reaction mixture was raised to 75C and maintained there for 1 hr, after which both chloroform and excess thionyl chloride were distilled off, leaving the product, butyl 9(10)-(chloroformyl) octadecanoate (V).

Compound III was prepared by the addition of 31.4 g of V dropwise with stirring to 14 g of morpholine in 150 ml of benzene at room temperature. After allowing 1 hr for completion of the reaction, the morpholine hydrochloride was filtered off and the filtrate was washed successively with portions of dilute HCl and subsequently with water until acid-free. After drying and stripping off the benzene the product was redissolved in hexane and percolated through a column of activated alumina to remove any residual acidity. The percolate after stripping yielded III.

N-[9(10)-Carbobutoxyoctadecanoyl]morpholine (VI). The intermediate, 9(10)-carbobutoxyoctadecanoic acid (VII), n.e. 375.9 theory 384, was prepared by partial saponification of the diester, butyl 9(10)-carbobutoxyoctadecanoate, following the procedure of Roe et al. (4) for the preparation of such mono esters.

9(10)-Carbobutoxyoctadecanoylchloride (VIII) was prepared by the dropwise addition of a chloroform solution containing 35 g of VII to 11 g of well-stirred thionyl chloride at 70C. Reaction conditions were maintained for 1 hr, after which both solvent and unreacted thionyl chloride were removed by distillation.

Compound VI was then prepared by the dropwise addition at room temperature of 36 g of VIII to a well-stirred solution of morpholine (17 g in 50 ml of benzene). After allowing the reaction to continue for ½ hr, the morpholine hydrochloride was filtered off and VI was recovered by the usual procedure.

The elemental analyses of all morpholide preparations are reported in Table I.

Plasticizer Evaluation

The formulation employed for all morpholides, morpholide mixtures and morpholide-extender blends was as follows: poly(vinyl chloride-vinyl acetate) copolymer 95:5 (Bakelite VYNW or VYDR) 63.5%, plasticizer 35%, basic lead carbonate stabilizer 1.0%, stearic acid 0.5%.

The milling, molding, and test procedures used were the same as previously reported (5,6) except for the use of 10–15 mil sheets in the volatility tests. Compositions which showed no signs of exudation during 90 days of shelf storage were rated compatible.

TABLE II
Plasticizing Characteristics of VYDR Vinyl Chloride Copolymer Compositions Plasticized with Various Fatty Acid Morpholides and Morpholide Mixtures. (35% Plasticizer)

Sample number	Plasticizer	Tensile strength psi	100% Modulus psi	Elongation %	Brittle point °C	Volatility loss %	Compatibility[a]	Extraction loss %
1	N-Myristoylmorpholine	2620	1210	390	−31	....	I	......
2	N-Petroselinoylmorpholine	2620	1180	280	−43	....	C	......
3	N-Erucoylmorpholine	3740	1580	280	−47	....	C	......
4	N-(9,10-Epoxyoctadecanoyl)morpholine	2850	1290	350	−28	0.5	C	......
5	N-(9,10-12,13-Diepoxyoctadecanoyl)morpholine	2950	1330	350	−16	0.4	C	......
6	N-[9(10)-Phenyloctadecanoyl]morpholine	3240	2060	250	−17	0.6	C	......
7	Dimorpholide of 9(10)-carboxyoctadecanoic acid	3290	3090	180	+15	....	C	......
8	N-[9(10)-Carbobutoxyoctadecanoyl]morpholine	2700	1540	240	−17	0.6	C	......
9	Butyl 9(10)-carbonylmorpholino-octadecanoate	2950	1860	220	−13	0.5	C	......
10	Morpholide of dimer acid (Empol 1014)	3420	2870	260	+ 3	0.0	C	......
11	Morpholide of dimer acid (Empol 1022)	3670	2870	300	+ 3	0.0	C	2.2
12	Morpholide of parsley seed fatty acids	2840	1200	350	−47	....	I	......
13	Morpholide of hydrogenated cottonseed acids[b]	2910	1390	360	−43	1.2	C	19.6
14	Morpholide of rapeseed fatty acids	3030	1470	400	−53	....	I	......
15	N-Oleoyl-3,5-dimethylmorpholine	2950	1670	280	−37	0.9	C	......
16	75% Sample 10 + 25% Sample 13	3490	2300	340	− 9	0.0	C	5.4
17	50% Sample 10 + 50% Sample 13	3220	1890	300	−21	0.1	C	9.0
18	25% Sample 10 + 75% Sample 13	3090	1570	330	−31	0.4	C	13.5
	Di-2-ethylhexyl phthalate (control)	3050	1610	330	−33	1.5	C	3.3

[a] C = Compatible; I = Incompatible.
[b] see footnote "c" of Table I.

TABLE III

Physical Characteristics of Vinyl Chloride Copolymer Compositions Plasticized with Various Hydrocarbon Extender-Selectively Hydrogenated Cottonseed Fatty Acid Blends. (35% Plasticizer)

Plasticizer composition			Tensile strength psi	100% Modulus psi	Elongation %	Brittle point °C	Volatility loss %	Compatibility[d]
Morpholide %	Extender[a]	%						
100	....	0[b]	2910	1390	360	—43	1.2	C
70	A	30[c]	3130	1720	280	—43	7.3	C
60	A	40			millable but incompatible			I
50	A	50			unmillable and incompatible			I
90	B	10	3080	1470	380	—37	3.3	C
80	B	20	3050	1540	370	—37	4.6	C
70	B	30	3150	1530	370	—33	5.3	C
60	B	40	3360	1910	410	—35	9.8	C
50	B	50	3370	1980	367	—33	9.6	C
90	C	10	3110	1435	400	—33	4.7	C
80	C	20	3020	1560	375	—35	5.5	C
70	C	30	3240	1560	380	—29	6.8	C
60	C	40	3260	1790	390	—25	12.0	C
50	C	50	3340	1930	330	—25	11.8	C
90	D	10	3040	1370	420	—35	4.1	C
80	D	20	3090	1520	380	—33	6.2	C
70	D	30	3230	1580	390	—29	7.7	C
60	D	40	3430	2300	330	—21	11.0	C
50	D	50	3440	2450	320	—17	10.9	C

[a] A = Conoco H-35, B = Monsanto HB-20, C = Monsanto HB-40, C = Amoco BN-1.
[b] Soapy water extraction loss 19.6%.
[c] Soapy water extraction loss 11.5%.
[d] C = Compatible, I = Incompatible.

Results and Discussion

Only two of the morpholides listed in Table II, those of the parsley seed and the rapeseed fatty acids, were incompatible with the copolymer at the 35% level. That these two proved to be incompatible was not altogether unexpected in view of the fatty acid composition and distribution in these two samples and the established compatibility tolerances of polyvinyl chloride for binary and ternary mixtures involving morpholides of oleic and linoleic, with stearic or palmitic acids (2). It was surprising, however, to find that the dimorpholides of the dimer acids, despite their polyunsaturation, present no compatibility problem in view of the known incompatibility of the morpholide of linoleic acid (2). This performance may be attributed to either the cyclic structure or the reduction of unsaturation to the level of one double bond per 18 carbon atoms in the dimerization reaction, more likely a combined effect.

The unsubstituted fatty acid morpholides of Table II, excluding the morpholides of erucic and rapeseed fatty acids, exhibit low-temperature characteristics in the temperature range expected from past experience with morpholides (2,5). The practically identical plasticizing characteristics imparted by the N-oleoyl, N-elaidoyl (2) and N-petroselinoyl morpholines show that no significant plasticizing differences result from a difference in geometric or positional double bond isomerism involving the 6 to 9 carbon atoms of a C_{18} monoolefinic acid. The morpholides of erucic and rapeseed fatty acid give somewhat better low-temperature performance than the —41 to —45C range observed for the morpholides of oleic, linoleic, or hydrogenated cottonseed fatty acids previously investigated (2,5).

The morpholides of the substituted fatty acids of this series exhibit, as in previous series (7), less satisfactory low-temperature characteristics. Substitution in the acyl moiety has always been observed to have a deleterious effect on the low-temperature performance of morpholides, the degree varying with the substituent group (7). The poor performances of the dimorpholide and ester morpholides of 9(10)-carboxyoctadecanoic acid are consistent with both the concept of the substitution effect and the poor low-temperature performance pattern characteristics manifested by diamides or ester amides derived from dicarboxylic acids (8–10).

Volatility losses are, with one exception, of the order generally observed for morpholides of C_{18} fatty acids (2,5) and about one-third of that for di-2-ethylhexyl phthalate (DOP). The dimorpholides of the dimer acids on the other hand exhibit no measurable volatility loss and, furthermore, appear capable of transmitting this characteristic to blends with other morpholides wherein it accounts for at least 50% of the overall plasticizer concentration. Blending with the morpholide of dimer acid 1022

TABLE IV

Plasticizing Characteristics of Binary and Ternary Compositions of Oleic, Linoleic and Dimer Acid Morpholides in Vinyl Chloride Copolymer, VYDR. (35% Plasticizer)

	Plasticizer composition[a]			Tensile strength psi	100% Modulus psi	Elongation %	Brittle point, °C	Compatibility[b]
Sample No.	DM%	OM%	PM%					
1	100.0	0.0	0.0	3420	2870	260	+ 3	C
2	75.0	12.5	12.5	3400	2320	310	— 7	C
3	50.0	25.0	25.0	3240	1830	390	—19	C
4	25.0	37.5	37.5	3070	1590	380	—27	C
5	0.0	50.0	50.0	2880	1310	390	—33	C
6	0.0	100.0	0.0	2680	1290	310	—45	C
7	12.5	75.0	12.5	2970	1410	370	—37	C
8	25.0	50.0	25.0	2970	1450	400	—33	C
9	37.5	25.0	37.5	3120	1580	370	—29	C
10	50.0	0.0	50.0	3280	1930	360	—13	C
11	0.0	0.0	100.0	2530	1270	340	—27	I
12	12.5	12.5	75.0	2780	1350	340	—25	I
13	25.0	25.0	50.0	3190	1660	380	—25	C
14	37.5	37.5	25.0	3120	1640	400	—23	C
15	50.0	50.0	0.0	3310	1860	375	—19	C

[a] DM = Dimorpholide of dimer acid, OM = N-Oleoylmorpholine, PM = N-Palmitoylmorpholine.
[b] C = Compatible, I = Incompatible.

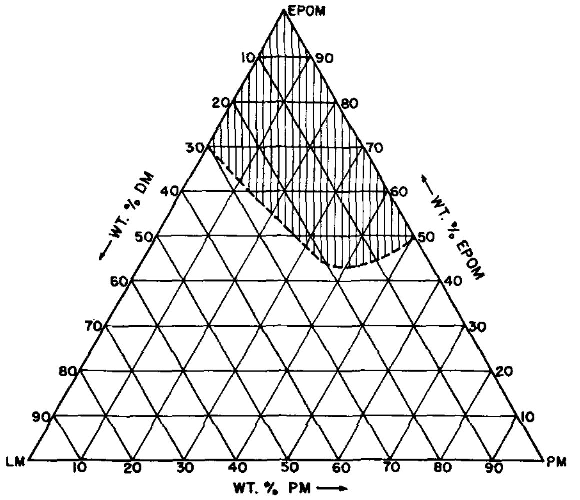

FIG. 1. Ternary composition-compatibility diagram for mixtures of N-epoxyoctadecenoylmorpholine (EPOM), N-linoleoylmorpholine (LM), and N-palmitoylmorpholine (PM). Shaded area represents composition compatible with PVC copolymer at 35% level of incorporation.

is also a means of effectively reducing the rather high soapy water extractability of the other morpholide component, Table II, without impairing the compatibility characteristics.

Extender-Morpholide Blends

The use of incompatible hydrocarbon extenders such as Conoco H-35, Monsanto HB-20 or 40, and Amoco BN-1 in conjunction with a compatible plasticizer to lower the overall cost or to achieve a desired physical characteristic in the plastic composition is a common practice. The data of Table III show that up to 50% of the morpholides of selectively hydrogenated cottonseed fatty acids can be replaced in a plastic composition by some of these extenders with retention of compatibility. The results show that incorporation of these extenders with an efficient morpholide such as that of the hydrogenated cottonseed acids is, however, of questionable merit. Although benefit does accrue to one performance area, soapy water extractability (e.g. footnotes *b* and *c* Table III), by such blending, in all other areas the effect is distinctly adverse. This development might have been anticipated since the morpholide already exhibits, with this one exception, plasticizing characteristics superior to those of the extenders. Less efficient plasticizers such as the dimorpholide of dimer acid are more promising candidates for these extenders since performance areas subject to improvement would outnumber or outweigh those subject to impairment.

Ternary Compatibility Diagrams

The two ternary-composition-compatibility diagrams, Fig. 1 and 2, were developed to establish approximately what proportions of the respective fatty acid moieties could be tolerated as morpholides at an overall concentration of 35% in a PVC-copolymer composition with retention of compatibility for at least 30 days. The experimental procedure followed in establishing the diagrams was the same as that previously described (2). Comparison of Fig. 1 with the published diagram for the ternary system N-(oleoyl-linoleoyl-palmitoyl) morpholine (2) shows that though N-(9,10-epoxyoctadecenoyl)morpholine is comparatively less effective than N-oleoylmorpholine as a compatibilizer for N-palmitoylmorpholine, it is more effective for N-linoleoylmorpholine. From a practical viewpoint, this suggests that epoxidation may be a more effective procedure than selective hydrogenation for compatibilizing fatty acid morpholide mixtures with a high linoleic content and a large proportion of linoleic to saturated acid.

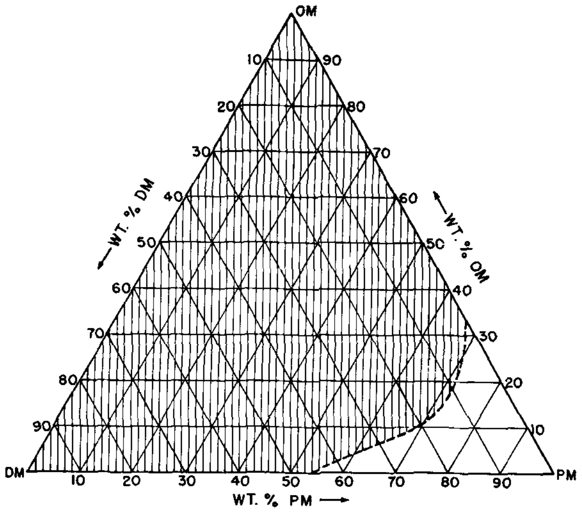

FIG. 2. Ternary composition-compatibility diagram for mixtures of N-oleoylmorpholine (OM), dimorpholide of dimer acid (DM), and N-palmitoylmorpholine (PM). Shaded area represents compositions compatible with PVC copolymer at 35% level of incorporation.

Comparison of Fig. 1 and 2 shows that the dimorpholide of dimer acid (DM) is a better compatibilizer of the palmitoyl moiety than is the N-(9,10-epoxyoctadecenoyl)morpholine (Fig. 1) and almost as effective in this respect as N-oleoylmorpholine.

The physical properties of the various compatibility test compositions of the DM-OM-PM ternary system are reported in Table IV. An analysis of the effect of compositional change upon plasticizing characteristics along the three medians of Fig. 2 show that modulus and low-temperature characteristics vary essentially linearly with composition while tensile strength varies nonlinearly. In this respect the greatest changes in modulus and low-temperature performance with composition occur along the DM median (Samples 1, 2, 3, and 4 of Table IV) while the greatest change in tensile strength occurs along the PM median (Samples 11, 12, 13 and 14). The least variation in low-temperature performance with composition is, as might be expected, along the PM median. Plasticizing characteristics vs. compositional changes on the binary axes (OM-PM, DM-PM, OM-DM) are essentially linear as to low-temperature performance and modulus and appear to be nonlinear as to tensile strength.

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