Fatty Acid Morpholides as Plasticizers for Vinyl Chloride Resins. III. Ternary Compatibility-Composition Diagrams for the Oleic-Linoleic-Stearic and Oleic-Linoleic-Palmitic Systems[1]

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A systematic investigation has been made of the effect of fatty acid composition on the compatibility of the corresponding mixed morpholides as plasticizers for vinyl chloride-vinyl acetate copolymer resins. Plasticizer evaluation data were obtained for the morpholides of lauric, palmitic, elaidic, and epoxyoleic acids and compared with the literature values for other fatty acid morpholides and morpholide mixtures.

Ternary compatibility-composition diagrams have been constructed for the oleic-linoleic-stearic and the oleic-linoleic-palmitic morpholide systems. These diagrams make it possible to predict what adjustment, if any, must be made in the composition of any mixture of these fatty acids so that the corresponding morpholide mixture will be compatible. The diagrams will be useful in selecting the most appropriate and economical fatty acid sources from which to make compatible morpholide mixtures.

THE MORPHOLIDE of oleic acid is a good primary plasticizer for vinyl chloride-vinyl acetate copolymer resins (1). The morpholides of stearic and palmitic acids and of the mixed fatty acids from cottonseed oil, though otherwise satisfactory, proved to be incompatible. Preliminary tests with binary and ternary mixtures of oleoylmorpholine (OM), with linoleoylmorpholine (LM), and stearoylmorpholine (SM), and with LM and palmitoylmorpholine (PM) revealed that much larger proportions of PM than of SM can be present in such mixtures without causing incompatibility. The present communication deals with the construction of the ternary compatibility-composition diagrams for the systems OM-LM-SM and OM-LM-PM, and with the plasticizer evaluation of a number of long-chain fatty acid morpholides and morpholide mixtures.

Materials and Procedures

Commercial fatty acids of known purity and composition were used. The lauric, palmitic, and stearic acids, 93 to 96% purity, were Armour Neofats Nos. 12, 16, and 18, respectively. The oleic and linoleic acids were obtained from Emery Industries; the former, 233 LL Elaine, was 93% pure, and the latter, Emersol 305, contained 41% of oleic and 6% of stearic acid. The approximate composition of "animal-type acids," Armour Neofat No. 47, was 10% myristic, 43% palmitic, 9% stearic, 30% oleic, and 8% linoleic acids, and that of the "animal acids," Neofat No. 65, was 2% myristic, 26% palmitic, 16% stearic, 48% oleic, and 8% linoleic acids. Elaidic acid was prepared by elaidinization of the oleic acid, followed by two solvent crystallizations.

The procedure for preparing the acid-free morpholides is described elsewhere (2). The "morpholide of epoxyoleic acid" (oxirane oxygen, 4.71%) was prepared by epoxidation of the morpholide of a 93%-pure linoleic acid. The epoxidation of the morpholide of cottonseed fatty acids was approximately sufficient to convert all of the linoleic to epoxyoleic acyls.

The various morpholides and morpholide mixtures were screened as plasticizers for 95% poly(vinyl chloride)-5% poly(vinyl acetate) copolymer (Vinylite VYDR) in the following compounding formulation: Vinylite VYDR, 63.5%; plasticizer, 35.0%; stearic acid, 0.5%; basic lead carbonate, 1.0%. This formulation was milled, molded, and tested as previously described (1,3). Compositions which showed evidence of exudation or smearing during a shelf-life of 90 days were rated as incompatible. The mixtures used for constructing the ternary diagram were tested only for compatibility since the other plasticizing characteristics can be roughly predicted from the complete evaluation data for the individual components and specific mixtures.

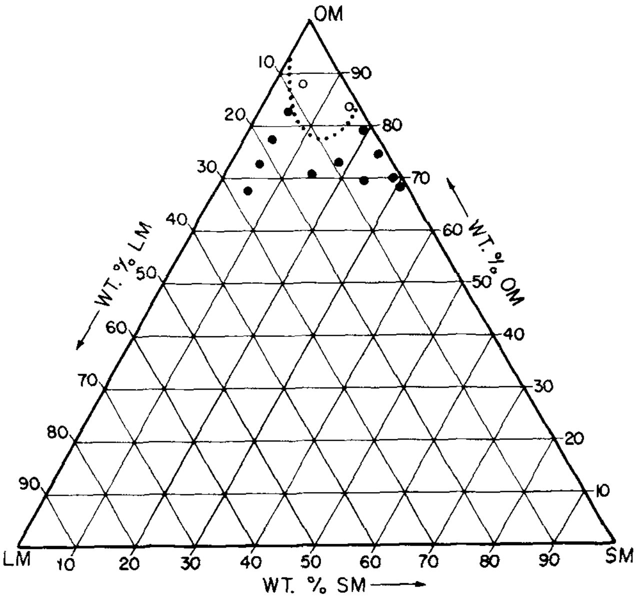

FIG. 1. Ternary compatibility-composition diagram for the system OM-LM-SM. ○ Compatible compositions; ● incompatible compositions.

Thermal stabilities were established in terms of the relative reflectances of the compositions (10–12 mil sheets) after subjection to increasing exposure periods in a forced draft oven maintained at 176°C. These

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[1] Presented at the 52nd Annual Meeting, American Oil Chemists' Society, St. Louis, Mo., May 1–3, 1961.

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values were determined by means of a "Hunter Multipurpose Reflectometer," using the amber 45°, 0° directional reflectance.

Results

Ternary compatibility-composition diagrams were constructed for the systems OM-LM-SM and OM-LM-PM. Various binary and ternary compositions were prepared by mixing stock samples of OM, LM, SM, and PM, taking into account the known proportion of saturated, monounsaturated, and diunsaturated morpholides present as impurities in each stock sample. The small amounts of saturated morpholides in the OM and LM were considered to be wholly SM or PM, depending upon the ternary system involved. Molded vinyl panels plasticized with the various binary and ternary mixtures were prepared and observed at regular intervals to detect the first signs of incompatibility.

The results of these tests are shown in Figures 1 and 2. The compositions represented by open circles were compatible, and those represented by the black circles showed signs of incompatibility within 30 days or less. The dotted curved line indicates the approximate boundary between the compatible and incompatible compositions.

Table I summarizes the more complete plasticizer evaluation results obtained for the morpholides of various fatty acids and fatty acid mixtures.

Discussion

Though SM and PM are both incompatible (Table I, Samples 2 and 3), much larger proportions of PM than of SM can be present in binary mixtures with OM or in ternary mixtures with OM and LM without causing incompatibility (Figures 1 and 2). For example, binary mixtures of OM and SM are incompatible when SM exceeds about 16% while almost 70% of PM can be tolerated in an OM-PM mixture. The presence of more than 10–12% of LM in either a binary OM-LM mixture or a ternary OM-LM-SM mixture results in incompatibility. In the OM-LM-PM system, on the other hand, larger percentages of LM can be tolerated, depending upon the proportion of PM present. For example, as shown by the dotted curve in Figure 2, a 40% OM-25% LM-35% PM mixture would be compatible.

These ternary diagrams make it possible to predict what adjustment, if any, must be made in the composition of any mixture of these fatty acids so that the corresponding morpholide mixture will be compatible.

The fatty acid mixture obtained from cottonseed oil consists almost entirely of oleic, linoleic, and palmitic acids, therefore the morpholide mixture obtained from cottonseed acids can be considered as belonging to the OM-LM-PM system. The composition of a typical morpholide mixture made from cottonseed fatty acids can be represented by point a in the incompatible region of Figure 2.

As previously reported (1,4), a compatible morpholide mixture can be prepared from cottonseed or peanut oil fatty acids by removing the saturated acids and converting the polyunsaturated to monounsaturated acyls by selective hydrogenation. This is consistent with Figures 1 and 2. Removal of the saturated fraction and subsequent conversion of the LM to the morpholide of epoxyoleic acid by epoxidation also resulted in a compatible mixture (1). This likewise would be expected from the diagrams since the morpholide of linoleic acid is compatible when epoxidized to this extent (Table I, Sample 7). Either of these procedures would obviously have been effective even if the saturated acid involved had been stearic or a longer-chain acid.

For cottonseed fatty acids the removal of the saturated fatty acids in the above procedures can be omitted. A completely compatible morpholide mixture should be obtainable by merely reducing the polyunsaturation to less than about 20%, *i.e.*, by changing the composition along ab (Figure 2). This has been confirmed (2) by plasticizer evaluation tests on the morpholide mixture, roughly of composition b, prepared directly from the fatty acids of selectively hydrogenated cottonseed oil (Table I, Sample 9) and on the morpholide of cottonseed fatty acids epoxidized to an oxirane oxygen content corresponding to the conversion of most of the LM to epoxyoleoylmorpholine (Sample 11). Compatibility could obviously have been attained with a lesser degree of hydrogenation or epoxidation.

An incompatible morpholide mixture can be made compatible by mixing it with a highly compatible morpholide mixture. For example, the morpholide of hydrogenated cottonseed acids (Sample 9, represented by point b, Figure 2) can be effectively employed, in predictable proportions, with the incompatible morpholide of cottonseed acids (Sample 8, point a) to produce a compatible blend, as illustrated by Sample 10, point c. Similarly blends of Sample 8 with the

TABLE I

Physical Characteristics of Vinyl Chloride-Vinyl Acetate Copolymer Stocks Plasticized with Morpholides of Fatty Acids (35% Plasticizer)

Sample	Morpholide of	Tensile strength	100% Modulus	Elongation	Brittle point	Volatility loss	Compatibility[e]
		p.s.i.	*p.s.i.*	%	°C.	%	
1	Lauric acid	2420	1070	350	–35	7.70	C
2	Palmitic acid	2530	1270	340	–27	......	I
3	Stearic acid[a]	2750	1780	280	–19	......	I
4	Oleic acid[a]	2680	1290	310	–45	......	C
5	Elaidic acid	......[b]	1300	......[b]	–42	1.46	C
6	Linoleic acid[a]	2680	1370	300	–45	......	I
7	Epoxyoleic acid	3030	1270	360	–16	0.63	C
8	Cottonseed acids[a]	2660	1200	330	–45	......	I
9	Hydrogenated cottonseed acids[c]	2910	1390	360	–43	1.26	C
10	30% Sample 8 + 70% Sample 9	......[b]	1330	......[b]	–40	......	C
11	Epoxidized cottonseed acids[d]	2940	1210	400	–26	0.73	C
12	"Animal type" acids	2940	1390	400	–30	0.84	I
13	"Animal" acids	2950	1370	390	–34	0.45	I
14	DOP (control)	3050	1690	330	–33	1.99	C

[a] Reference (1).
[b] Sample elongated without rupture beyond range of IP-4 tester.
[c] Selectively hydrogenated to convert all polyunsaturated to monosaturated acyls (2).
[d] Epoxidized sufficiently to convert all LM to epoxyoleoylmorpholine (2).
[e] C = *compatible*, I = *incompatible*.

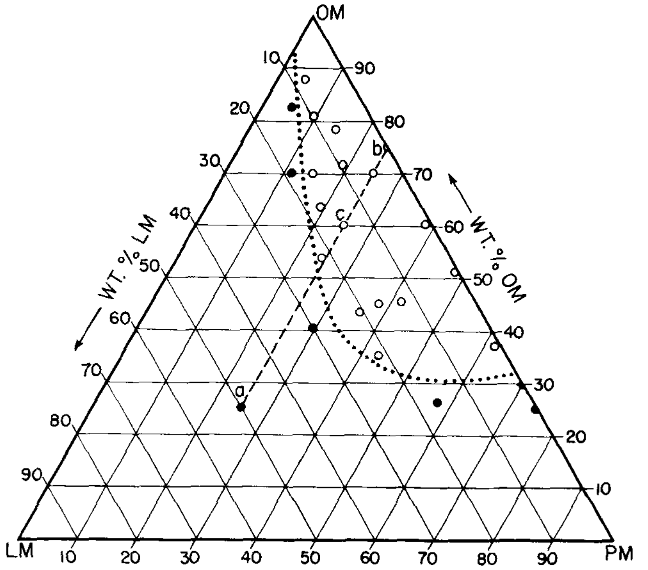

FIG. 2. Ternary compatibility-composition diagram for the system OM-LM-PM. ○ Compatible compositions; ● incompatible compositions.

morpholide of epoxidized cottonseed acids would also be expected to be compatible.

In a broader sense the ternary compatibility-composition diagrams will be useful in selecting the most appropriate and economical fatty acid sources from which to make compatible morpholide mixtures. On the basis of fatty acid compositional data, for example, it would be expected that the morpholide mixtures prepared directly from the unmodified fatty acids of olive oil, palm oil, or of selected lard oils or white greases would be compatible. For other fatty acid mixtures obtainable from fats or oils, or as byproducts, the approximate degree of fractionation, hydrogenation, epoxidation, or mixing required can be estimated.

The morpholide of lauric acid (Sample 1) proved to be a compatible plasticizer. This fact along with the relative effects of SM and PM on compatibility in the binary and ternary mixtures of Figures 1 and 2 indicates that the compatibility of the saturated fatty acid morpholides increases as the chain length decreases. Thus the morpholide of myristic acid would probably have even less tendency than PM to cause incompatibility in ternary mixtures with OM and LM.

The behavior of the morpholide of elaidic acid (Sample 5), which would be expected to be a constituent of the selectively hydrogenated morpholide mixtures, differs little from that of OM.

Samples 12 and 13 were included to determine the possibility of using animal fatty acids, which contain larger proportions of stearic acid, for making compatible morpholide mixtures. Neither showed signs of incompatibility until 65 days after milling and molding, indicating that in each case the proportion of SM present was only slightly above the tolerance limit. They could undoubtedly be made compatible however by mixing with a small proportion of the morpholide either of oleic acid or of selectively hydrogenated or partially epoxidized cottonseed fatty acids.

Although the individual and mixed morpholides of Table I exhibit considerable divergence in many of their plasticizing characteristics, they have uniformly high plasticizing efficiency. In this respect their copolymer stocks are equal to and in most instances better than copolymer-DOP stocks at the same plasticizer level. This justifies the assumption that all the compatible compositions of Figures 1 and 2 would also be highly efficient plasticizers.

The low-temperature performance of the morpholides in Table I covers a rather wide range. While some are inferior to DOP, others are superior, approaching the performance of the adipates in this respect. Chain length of the fatty acid moiety, unsaturation, and epoxidation are controlling factors. The unsaturated morpholides and mixtures incorporating a substantial amount of the unsaturated morpholides give the most outstanding performances. Hydrogenation within those limits necessary to achieve compatibility does not appear to alter this characteristic. However a comparable degree of epoxidation has an immediate and adverse effect, even more severe than that induced by complete hydrogenation. It follows that better low-temperature properties may be expected for a saturated fatty acid morpholide than for the epoxidized next higher homologous morpholide. A comparison of the respective brittle points of Samples 2 and 7 is illustrative of this point. Indeed the presence of a lower saturated homolog in an epoxidized morpholide mixture is beneficial. For example, a morpholide mixture which had a composition corresponding to that of Sample 11, but with the PM removed, had a brittle point of −17°C. (1) as compared to −26°C. for Sample 11.

The unexpoxidized morpholide-vinyl compositions of the standard formulation exhibit thermal stabilities, as indicated by relative reflectances, which are about the same as a comparable DOP composition. Compositions plasticized with the epoxidized morpholides, on the other hand, have much better thermal stabilities than those of DOP, *i.e.*, a longer exposure period (120 min. as compared to 60 min.) to failure. The incorporation of 3.5% of epoxidized morpholide in the morpholide-plasticized composition improves its stability by an additional 10 to 30 min. to failure.

It has been observed that all these plasticized compositions have lower reflectance losses during the earlier stages of the test when 1.5 parts of a barium-cadmium laurate (Mark XI, Argus Chemical Corporation) stabilizer per 100 parts of resin were included in the formulation. The over-all thermal stability would be expected to be further improved by incorporating appropriate amounts of epoxymorpholide, barium-cadmium, and lead stabilizers in the standard formulation.

Acknowledgments

The authors are indebted to the Northern Utilization Research and Development Division for the pure linoleic acid; to Harold P. Pastor for some of the plasticizer evaluation determinations; and to George I. Pittman for drawing the figures.

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[Received October 24, 1960]