Preparation and Plasticizing Characteristics of a Series of Symmetrical and Unsymmetrical N,N-Disubstituted Oleamides[1]

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Abstract

Thirty-five N,N-disubstituted oleamides, mostly dialkyl oleamides, have been prepared and evaluated as plasticizers for vinyl chloride-vinyl acetate copolymer to investigate the relative effect upon plasticizer performance of N,N-symmetrical and unsymmetrical substitution; groups such as alkyl, cycloalkyl, benzyl, 2-alkoxyethyl, 2-acetoxyethyl, 2-(3-carbobutoxy-propionlyoxy)ethyl, 2-(3-carbohexanoxypropionyloxy)ethyl, and cyanoethyl have been investigated in systematic combinations. The compatibility of symmetrical or unsymmetrical N,N-dialkyl oleamides, involving normal, branched, or cyclic alkyls, is controlled by the total carbon count of the combined substituent groups rather than that of the larger group. For retention of compatibility the total carbon count must not exceed about 13 atoms. Symmetrical and unsymmetrical dialkyl oleamides of the same total alkyl carbon count do not differ significantly in their plasticizing characteristics. Acyclic N,N-dialkyl oleamides are, with few exceptions, highly efficient plasticizers, which impart good, sebacate-like, low-temperature impact performance to the plastic composition. A substituent attached to the nitrogen through a secondary carbon severely impairs plasticizer efficiency and cyclic or cycloalkyl substituents are detrimental to low-temperature performance. Substitution of an alkyl group for one of the N,N-disymmetrical substituents has little or no effect upon low-temperature impact performance. Many of the disubstituted oleamides impart antistatic properties to the plastic composition.

Introduction

INVESTIGATIONS in this laboratory have shown that many symmetrical N,N-disubstituted amides of long-chain fatty acids are good plasticizers for vinyl chloride polymer and copolymer (PVC) resins. The N-substituents of these symmetrical amides, for which plasticizer evaluation data have already been reported, include the following radicals: various homologous n-alkyls, branched alkyls, cycloalkyls, 2-acyloxyethyl, 2-alkoxyethyl, and benzyl (1–6). The purpose of the present investigation was to determine the effect on plasticizer performance when the N-substituents on the amide are two different radicals. Plasticizer performance evaluation data were therefore obtained for a series of unsymmetrical N,N-disubstituted oleamides, mostly N,N-dialkyl and N-alkyl-N-cycloalkyl oleamides. A few unreported symmetrical N,N-disubstituted oleamides were included for a more complete correlation.

Experimental

The oleic acid (Emersol 233LL) and the oleoyl chloride were commercial products obtained from Emery Industries and Trubek Chemical Company respectively. The secondary amines, except those cited in Table II, were catalog items available from Aldrich Chemicals, Eastman Kodak Company, K&K Laboratories, Matheson, or Sapon Laboratories. The esteramides, Samples 30 to 35 of Table II, were prepared by the aminolysis of methyl oleate with the appropriate N-substituted alkanolamine, followed by acylation with the desired anhydride or acid chloride (3).

N,N-Bis[2-(3-carbobutoxypropionyloxy)ethyl]oleamide, Sample 37, was prepared by the interaction of 3-carbobutoxypropionyl chloride (I) with N,N-bis-(2-hydroxyethyl)oleamide (II). The former (I) was prepared by the interaction of thionyl chloride with the butyl half-ester of succinic acid. The latter (II) was prepared by the aminolysis of methyl oleate with diethanolamine (3). Forty-six g (0.22 moles) of I was added to a vigorously stirred benzene solution, containing 37 g (0.1 moles) of II and 17.4 g (0.22 moles) of pyridine. Stirring was continued for an additional hour. The pyridine hydrochloride was then removed by filtration, and the filtrate was washed with aqueous hydrochloric acid and water and dried over anhydrous Na_2SO_4. N,N-Bis 2-(3-carbohexanoxypropionyloxy)ethyloleamide, Sample 38, was prepared by the same procedure, substituting 3-carbohexanoxypropionyl chloride for I.

The other amides were prepared by the interaction of equimolar proportions of acid chloride and amine in the presence of a slight excess of pyridine, using benzene as a solvent. All the amide samples were finally dissolved in commercial hexane, percolated through activated alumina to remove residual free fatty acid, then stripped.

The amides were screened as plasticizers for vinyl chloride-vinyl acetate copolymer 95-5 (Vinylite VYNW-5) and compared with a number of controls including dioctyl phthalate (DOP), dioctyl adipate (DOA), and dioctyl sebacate (DOS). The formulation employed was as follows: resin 63.5%, plasticizer 35.0%, basic lead carbonate stabilizer 1.0%, stearic acid 0.5%. Milling, molding, and testing procedures were the same as previously described (1,7) except that 10–15 mil sheets were employed in the volatility, thermal stability, and extractability tests. Any composition which developed exudation of any kind during a 90-day test storage period was rated incompatible; those passing this test were rated compatible.

Antistatic ratings were determined under controlled conditions of temperature and humidity (75 ± 3F, 35 ± 5% R.H.). The surface of the plastic composition was stroked ten times in one direction with a clean piece of nylon fabric tautly draped over the bristles of a ½- × 3-in. brush, after which the surface was immediately placed ½ in. above a layer of dry cigar ashes in a Petri dish. If no pickup of ashes occurred, the composition was highly antistatic and given a rating of "+." A heavy pickup, indicative of no antistatic effect, was given a rating of "0."

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Results and Discussion

The densities, refractive indices, and elemental analyses of the various amides investigated are reported in Table I. The plasticizing characteristics of the amides are given in Table II.

All the symmetrical dialkyloleamides are highly compatible plasticizers up to the N,N-diheptyl (a total alkyl carbon count of 14), which exhibits borderline compatibility and a sharp regression in low-temperature performance (6). N,N-Dioctyloleamide was found to be incompatible. The data in Table II shows

TABLE I

Analyses and Physical Properties of N,N-Disubstituted Oleamides

Compound	Density 30C	n^{30}_D	%C		%H		%N	
			Exp.	Theory	Exp.	Theory	Exp.	Theory
N,N-Dimethyloleamide	0.8806	1.4645	77.00	77.53	11.96	12.70	4.43	4.53
N,N-Diethyloleamide	0.8662	1.4611	78.08	78.26	11.88	12.84	4.26	4.15
N,N-Dipropyloleamide	0.8649	1.4622	78.82	78.86	12.98	12.98	3.64	3.83
N,N-Di-2-butyloleamide	0.8562	1.4560	79.04	79.27	13.38	13.06	2.94	3.56
N,N-Diisoamyloleamide	0.8597	1.4621	78.90	79.78	13.14	13.15	3.25	3.32
N,N-Di-2-amyloleamide	0.8670	1.4621	79.34	79.69	12.84	13.14	3.46	3.32
N,-Methyl-N-allyloleamide	0.8785	1.4684	77.68	78.70	12.13	12.22	4.21	4.18
N-Methyl-N-propyloleamide	0.8681	1.4632	77.64	78.23	12.91	12.85	3.97	4.15
N-Methyl-N-butyloleamide	0.8669	1.4625	77.67	78.56	12.88	12.90	3.88	4.00
N-Methyl-N-amyloleamide	0.8673	1.4641	78.76	78.80	12.84	12.86	3.86	3.83
N-Methyl-N-hexyloleamide	0.8598	1.4601	78.99	79.06	13.33	12.91	3.52	3.69
N-Methyl-N-octyloleamide	0.8646	1.4635	78.86	79.52	13.03	13.01	3.35	3.44
N-Methyl-N-dodecyloleamide	0.8608	1.4638	80.32	80.44	13.38	13.19	2.95	3.03
N-Methyl-N-cyclopentyloleamide	0.9058	1.4767	77.77	79.54	12.29	12.48	3.84	3.86
N-Ethyl-N-cyclohexyloleamide	0.8986	1.4767	79.26	79.73	12.35	12.61	3.58	3.58
N-Methyl-N-cyclooctyloleamide	0.9093	1.4818	79.93	80.00	12.60	12.67	3.42	3.45
N-Methyl-N-cyclododecyloleamide	0.9047	1.4833	80.81	80.69	12.91	12.91	3.03	3.04
N-Methyl-N-tetrahydrofurfuryloleamide	0.9218	1.4744	75.81	75.87	11.78	12.22	3.59	3.69
N-Methyl-N-furfuryloleamide	0.9314	1.4813	76.55	76.68	11.17	10.92	3.81	3.73
N-Ethyl-N-3-ethoxypropyloleamide	0.8864	1.4607	75.96	75.83	12.67	12.48	3.56	3.54
N-Propyl-N-butyloleamide	0.8635	1.4623	78.59	79.16	13.20	13.03	3.69	3.69
N-Isopropyl-N-cyclohexyloleamide	0.8909	1.4747	79.98	79.86	12.70	12.57	3.60	3.35
N-Isopropyl-N-benzyloleamide	0.9139	1.4930	81.27	81.22	11.61	11.36	3.39	3.39
N-Butyl-N-amyloleamide	0.8583	1.4615	79.68	79.54	12.96	13.10	3.39	3.44
N-Butyl-N-dodecyloleamide	0.8548	1.4614	80.55	80.71	13.53	13.35	2.88	2.77
N-Methyl-N(2-acetoxyethyl)oleamide	0.9308	1.4647	71.25	72.33	11.45	11.36	3.71	3.67
N-Ethyl-N-(2-acetoxyethyl)oleamide	0.9232	1.4616	73.04	72.83	11.69	11.38	3.35	3.54
N-Isopropyl-N-(2-acetoxyethyl)oleamide	0.9141	1.4606	73.91	73.34	11.92	11.65	2.93	3.47
N-Butyl-N-(2-acetoxyethyl)oleamide	0.9176	1.4628	73.47	73.66	11.63	11.66	3.44	3.31
N-Cyclohexyl-N-(2-acetoxyethyl)oleamide	0.9377	1.4730	74.65	74.73	11.45	11.43	2.92	3.12
N-Benzyl-N-(2-acetoxyethyl)oleamide	0.9625	1.4902	75.67	76.15	10.27	10.28	2.88	3.06
N-Cyclohexyl-N-(2-cyanoethyl)oleamide	0.9516	1.4825	78.08	77.00	11.77	11.29	6.90	7.19
N,N-Bis[2-(3-carbobutoxy-propionyloxy)ethyl]oleamide			67.90	66.90	10.24	9.90	2.08	2.06
N,N-Bis[2-(3-carbohexanoxy-propionyloxy)ethyl]oleamide	0.9800	1.4646	69.05	68.40	10.43	10.19	2.09	1.91
N,N-Bis(2-cyanoethyl)oleamide	0.9582	1.4772	73.69	74.36	10.63	10.66	10.80	10.85

TABLE II

Physical Characteristics of Vinyl Chloride-Vinyl Acetate Copolymer Stocks Plasticized with N,N-Disubstituted Oleamides (35% Plasticizer)

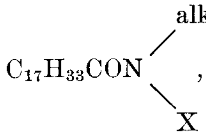
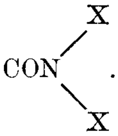
Sample number	Plasticizer[a]	Tensile strength psi	100% Modulus psi	Elongation %	Brittle point °C	Volatility loss %	Compatibility[b]	Anti-static rating[d]
1	N,N-Dimethyloleamide	2400	990	400	−57	2.7	C	+
2	N,N-Diethyloleamide	2520	1130	400	−57	2.2	C	+
3	N,N-Dipropyloleamide	2600	1270	370	−61	0.8	C	+
4	N,N-Di-2-propyloleamide[c]	2960	1660	330	−53	2.5	C	+
5	N,N-Dibutyloleamide[c]	2710	1470	330	−63	0.5	C	+
6	N,N-Diisobutyloleamide[c]	2730	1540	310	−55	2.6	C	+
7	N,N-Di-2-butyloleamide	2650	1720	320	−53	2.5	C	+
8	N,N-Diamyloleamide[c]	2680	1500	330	−61	0.7	C	+
9	N,N-Diisoamyloleamide	3180	1540	340	−59	1.1	C	+
10	N,N-Di-2-amyloleamide	1910	1780	160	−33	....	C	—
11	N,Methyl-N-allyloleamide	2380	1130	310	−61	....	C	—
12	N-Methyl-N-propyloleamide	2510	1140	380	−59	2.3	C	—
13	N-Methyl-N-butyloleamide	2620	1250	350	−61	1.4	C	+
14	N-Methyl-N-amyloleamide	2540	1150	370	−61	1.4	C	—
15	N-Methyl-N-hexyloleamide	2560	1290	370	−65	1.7	C	+
16	N-Methyl-N-octyloleamide	2700	1400	380	−63	1.1	C	—
17	N-Methyl-N-dodecyloleamide	2300	1590	260	−53	0.9	C	—
18	N-Methyl-N-cyclopentyloleamide	2810	1500	360	−41	0.7	C	+
19	N-Ethyl-N-cyclohexyloleamide (A)	2820	1460	350	−37	0.7	C	—
20	N-Methyl-N-cyclooctyloleamide	2700	1540	320	−39	0.2	C	+
21	N-Methyl-N-cyclododecyloleamide	3060	2090	340	−33	....	C	—
22	N-Methyl-N-tetrahydrofurfuryloleamide (M)	2900	1320	350	−41	0.7	C	—
23	N-Methyl-N-furfuryloleamide (M)	2700	1370	370	−51	1.0	I	—
24	N-Ethyl-N-3-ethoxypropyloleamide	2580	1250	360	−57	1.1	C	+
25	N-Propyl-N-butyloleamide	2650	1340	390	−61	0.7	C	+
26	N-Isopropyl-N-cyclohexyloleamide (A)	2960	1850	310	−39	0.7	C	0
27	N-Isopropyl-N-benzyloleamide (M)	3000	1690	340	−35	0.6	C	0
28	N-Butyl-N-amyloleamide	2710	1540	320	−61	0.6	C	+
29	N-Butyl-N-dodecyloleamide			Incompatible—will not mill			I	—
30	N-Methyl-N-(2-acetoxyethyl)oleamide	2830	1310	380	−43	....	C	—
31	N-Ethyl-N-(2-acetoxyethyl)oleamide	2610	1300	316	−45	1.5	C	+
32	N-Isopropyl-N-(2-acetoxyethyl)oleamide (P)	2560	1700	270	−37	1.5	I	+
33	N-Butyl-N-(2-acetoxyethyl)oleamide	2860	1330	360	−45	0.4	C	+
34	N-Cyclohexyl-N-(2-acetoxyethyl)oleamide (A)	3180	1780	380	−31	0.4	C	—
35	N-Benzyl-N-(2-acetoxyethyl)oleamide (M)	3060	1790	400	−33	0.8	C	0
36	N-Cyclohexyl-N-(2-cyanoethyl)oleamide (A)	3030	1710	410	−25	0.5	C	0
37	N,N-bis[2-(3-carbobutoxypropionyloxy)-ethyl]oleamide	3110	1950	390	−33	0.9	I	—
38	N,N-bis[2-(3-carbohexanoxypropionyloxy)-ethyl]oleamide	3040	2010	310	−35	1.2	B	—
39	N,N-Bis(2-cyanoethyl)oleamide (C)			Bleeding after milling			I	—
	Di-2-Ethylhexylphthalate, DOP (Control)	3050	1610	330	−33	1.5	C	0
	Di-2-Ethylhexyladipate, DOA (control)	2890	1290	380	−55	6.0	C	0
	Dioctylsebacate, DOS (control)	2690	1370	350	−59	0.6	C	0

[a] Source of amine; (A) Abbott Laboratories, (C) American Cyanamid Co., (M) Miles Chemical Co., (P) Pennsalt Chemicals Corp.
[b] C = Compatible, B = Borderline, I = Incompatible.
[c] Reference 6.
[d] (—) = Untested composition.

no compatibility problem or any marked low-temperature regression for unsymmetrical di-*n*-alkyloleamides at as high a total alkyl carbon count as 13, *i.e.*, N-methyl-N-dodecyloleamide, Sample 17. N-Butyl-N-dodecyloleamide, Sample 29, was incompatibile. Thus the total alkyl carbon count rather than the carbon count of the larger alkyl substituent is the factor which limits the compatibility of the unsymmetrical dialkyloleamides. That this is also true of the N-alkyl-N-cycloalkyl oleamides is indicated by the fact that N-methyl-N-cyclododecyloleamide, Sample 21, is compatible. Thus, in general, the total N,N-dialkyl or N-alkyl-N-cycloalkyl carbon count consonant with retention of compatibility seems to be about 13.

Of all the unsymmetrical amides tested, the N,N-dialkyloleamides and N-ethyl-N-ethoxypropyloleamide impart the best low-temperature impact properties (brittle points by ASTM D746-57T) to the plastic stock. They are comparable in this respect with the symmetrical N,N-di-*n*-alkyloleamides as well as with the dioctyl esters of adipic, azelaic, and sebacic acids. Although chain branching is generally considered to influence low-temperature performance adversely (8), its effect upon the low-temperature impact characteristics in the N,N-dialkyloleamides is, in general, not severe. That there are exceptions is illustrated by the unusually poor performance of N,N-di-2-amyloleamide, Sample 9, even though its structure is quite analogous to that of N,N-di-2-butyloleamide, Sample 6, and N,N-di-2-propyloleamide, Sample 3.

On the other hand, a limited number of torsional stiffness measurements by ASTM 1043-61T (T_f values) on selected compositions for comparative purposes would indicate that, on a near comparable molecular-weight basis, the branched N,N-dialkyloleamides are not comparable with the normal N,N-dialkyloleamides in low-temperature performance. This is indicated by the T_f values, −58C and −43C, for N,N-dibutyloleamide and N,N-diisoamyloleamide respectively. It is not at all certain however that this adverse performance is exclusively a structurally related response. This is indicated by the fact that the specimens plasticized with branched N,N-dialkyloleamides lost more of their flexibility as a result of the test than did specimens plasticized with N,N-di-*n*-alkyloleamides. This suggests that loss of plasticizer through extraction by the alcohol coolant may also be a contributing factor to the higher torsional stiffness which was obtained. A specimen plasticized with N,N-di-*n*-butyloleamide does not exhibit such subsequent loss of flexibility. The unexpectedly poor performance ($T_f =$ −42C) of N-*n*-butyl-N-*n*-amyloleamide, Sample 28, may also be attributed to the presence of branched isomeric N-alkyl moieties in the product. Their presence has been demonstrated by NMR measurements on the N-*n*-butyl-N-*n*-amylamine used in this preparation. These measurements revealed the presence of a methyl group signal at 1.83δ characteristic of methyl branched hydrocarbons, and the ratio of the intensity of this methyl signal to the terminal methyl signal (CH_3-CH_2-) at 0.9 would indicate that as much as 60% of the amine could consist of branched N-alkyls.

Replacement of one of the N-alkyl substituent groups by either an acyloxyethyl, cyclic, or cyclic-containing group is quite detrimental to low-temperature impact performance. On the other hand, a similar replacement by a furfuryl or an ethoxypropyl group had no effect. The unsymmetrical N,N-disubstituted oleamides,  $C_{17}H_{33}CON{<}^{\text{alkyl}}_{X}$, exhibit essentially the same low-temperature properties as the parent symmetrically N,N-disubstituted oleamides, $C_{17}H_{33}$-  $CON{<}^{X}_{X}$. This becomes readily apparent if the brittle points of Samples 1, 2, 3, 5, and 8 are compared with those of Samples 12, 13, 14, 25, and 28. Even more dramatic in this respect is the comparison between the brittle points of Samples 30, 31, and 33 with that of −45C for the N,N-bis(2-acetoxyethyl)-oleamide (3).

N-Methyl-N-alkyl oleamides, excepting those involving an N-*sec*-carbon linkage, are the most efficient of the unsymmetrically disubstituted oleamides which were tested and are, in this respect, slightly better than the corresponding symmetrically substituted N,N-dialkyloleamides (6). The benzyl radical and all N-*sec*-carbon substitutent radicals such as 2-propyl, 2-butyl, 2-amyl, as well as alicyclic radicals such as cyclohexyl, and cyclododecyl are almost invariably detrimental to plasticizer efficiency in the oleamides. The data of Table II for Samples 4, 7, 10, 21, 26, 27, 32, 34, 35, and 36 show that in compositions incorporating such moieties the 100% modulus is almost always in excess of 1600 psi, the upper limit for compositions which do not incorporate such moieties. The effect of this type of N-substitution is most strikingly illustrated in the N-alkyl-N-(2-acetoxyethyl)oleamide series, Samples 30–33, where the introduction of an isopropyl radical, Sample 32, instead of an *n*-alkyl radical results in both a higher modulus and a higher brittle point.

Volatility losses of the substituted-amide plasticized compositions were, in general, lower than that for DOP plasticized compositions but were, for at least half of the compositions, in excess of that for a DOS plasticized composition. In general, lower volatility losses are associated with the disubstituted oleamides of higher molecular weight and volatilities are, as expected (8), usually lower for the N-N-di-*n*-alkyloleamides than for the corresponding oleamides involving a branched N-alkyl substituent.

A selective screening of a number of compositions plasticized with unsymmetrical N,N-dialkyloleamides indicated that their thermal stabilities were comparable with those of compositions plasticized with symmetrical N,N-di-alkyloleamides (6). The soapy-water extractability of a number of the unsymmetrical N,N-dialkyloleamides was found to range from 20 to 22%, about the same as previously reported for N,N-di-*n*-butyloleamide (6) and for long-chain amides in general, but considerably higher than that of the diester plasticizer controls. The extractability is considerably lower, 11.7%, for the tetraester amide, Sample 37.

Interesting conclusions can be drawn from the antistatic evaluation data for the N,N-disubstituted oleamides of Table II as combined with the corresponding unpublished data for the symmetrical N,N-dialkylamides of various other acids previously investigated (6). Those which did not contain a cyclic

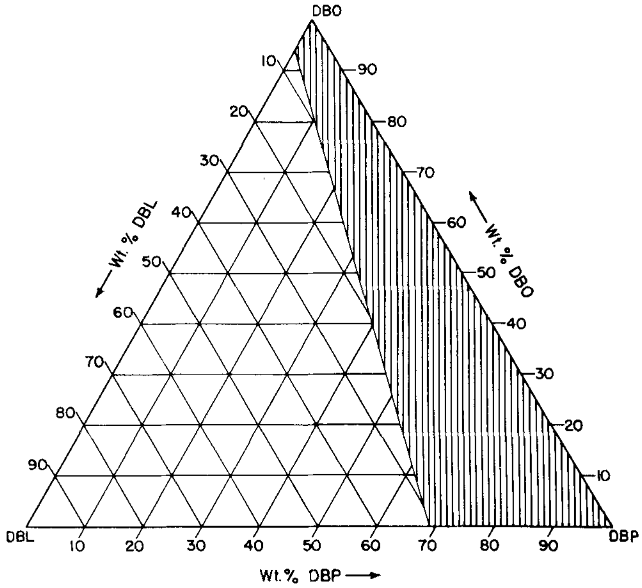


FIGURE. I

Fig. 1. Ternary composition-compatibility diagram for mixtures of N,N-di-*n*-butyloleamide (DBO), N,N-di-*n*-butyllinoleamide (DBL) and N,N-di-*n*-butylpalmitamide (DBP). Shaded area represents compatible compositions.

or branched acyl moiety or an N-cyclic substituent were found to be effective antistaticizers when employed as the plasticizing component of a PVC composition. With a few exceptions those amides which incorporated a cyclic or branched acyl moiety or an N-cyclic substituent were found to be ineffective.

The ternary composition-compatibility diagram (Fig. 1) for the N,N-di-*n*-butylamides of oleic (DBO), linoleic (DBL), and palmitic acids (DBP) in Vinylite (VYNW-5) was developed to determine approximately what proportion of these acid moieties could be tolerated, in the derived N,N-dialkylamides, with retention of compatibility as a PVC plasticizer. The experimental procedure followed in establishing the diagram was the same as that previously described (2). Although the compatible proportions depicted in the diagram would probably not apply exactly to the lower or higher N,N-dialkylamides of the same fatty acids, they are nevertheless sufficiently representative of these to permit a realistic prediction of the compositional adjustments which might be required in a commercial fatty acid mixture to promote compatibility in the N,N-dialkylamide product. Comparison of this ternary diagram with others previously published (2,4) shows that the N,N-dibutyl group is a more effective compatibilizing moiety for amide mixtures which involve acyls of these three fatty acids than the morpholino group but not quite as effective as the piperidino group.

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