The Plasticizing Characteristics of Some N,N-Dimethylamides and Ester-Amides of Long-Chain Fatty Acids

ROBERT R. MOD, FRANK C. MAGNE and EVALD L. SKAU,
Southern Regional Research Laboratory,[1] New Orleans, Louisiana 70119

Abstract

The N,N-dimethylamides as well as a few N,N-diethylamides of a number of saturated and unsaturated long-chain fatty acids and fatty acid mixtures have been prepared, characterized, and screened as plasticizers for poly(vinyl chloride-vinyl acetate)copolymer. A number of ester-amides of short-chain 2-, 3-, and 4-hydroxyacids were included. All except the N,N-dimethylamides of stearic, palmitic, and epoxidized rapeseed fatty acids were compatible with the copolymer. Many of the N,N-dimethylamides were highly efficient plasticizers and, except for the dimer acid derivative, were superior to di-2-ethylhexyl phthalate in this respect. A few of the dimethylamides were comparable with di-2-ethylhexyl adipate in low-temperature performance. The N,N,N′,N′-tetramethylamide of dimer acid exhibited no measurable volatility loss in copolymer compositions.

Introduction

Previous investigations in this area have shown that many symmetrical and unsymmetrical N,N-dialkylamides of long-chain fatty acids are good primary plasticizers for polyvinyl chloride resins (1,2). This report, a continuation of that investigation, is concerned with the preparation, characterization, and plasticizer evaluation of a number of N,N-dimethylamides of long-chain fatty acids. A few N,N-diethylamides are also included for correlative purposes, as are some N,N-disubstituted ester-amides of various short-chain hydroxy acids.

Experimental Procedures

The dimethylamine (anhydrous) was a product of the Matheson Company, and the dimethylformamide (reagent grade) was obtained from the Fisher Scientific Company. Diethylamine, hexamethylphosphoric triamide, 3-propiolactone, and 4-butyrolactone were obtained from the Eastman Kodak Company. Oleoyl chloride, palmitoyl chloride, and stearoyl chloride were products of Universal Oil Products Company. The dimer acid (Empol 1014) was a product of Emery Industries. Hydrogenated cottonseed acids were derived from a selectively hydrogenated oil(3), which had an iodine value of 73.0 and a thiocyanogen value of 68.0. Rapeseed and cottonseed fatty acids were prepared by saponification of the respective oils. Linoleic acid, 95% purity, was obtained from the Northern Regional Research Laboratory.

The N,N-Dimethylamides of oleic, stearic, palmitic, and erucic acids were prepared by interaction of the acid chlorides and dimethylformamide (4). N,N,N′,N′-Tetramethylamide of dimer acid was prepared by condensing dimer acid with hexamethylphosphoric triamide (5). N,N-Dimethyl-9,10-dichlorostearamide was obtained by the addition of chlorine to N,N-dimethyloleamide by the procedure of Van Atta et al. (6). The N,N-dimethylamide of hydrogenated cottonseed fatty acids was prepared by interaction of equimolar quantities of fatty acid chlorides and dimethylamine in the usual manner in the presence of an equivalent amount of pyridine. The epoxyamides, Samples 8, 9, 10, and 11, were obtained by treating a benzene solution of the respective amides with the requisite amount of meta-chloroperbenzoic acid to achieve the desired level of epoxidation.

N,N-Dimethyl-3-oleoyloxypropionamide (II) was prepared by the dropwise addition of 72 g of oleoyl chloride to a vigorously stirred benzene solution containing 28 g of N,N-dimethyl-3-hydroxypropinonamide (I) and 19.8 g of pyridine. The intermediate, I, was prepared as described by Gresham et al. (7). Stirring was continued for an additional hour. The reaction mixture was then filtered to remove suspended pyridine hydrochloride, washed successively with aqueous HCl and water, dried over anhydrous sodium sulfate, and stripped of solvent.

N,N-Dimethyl-4-oleoyloxybutyramide (IV) was prepared from 30.5 g of N,N-dimethyl-4-hydroxybutyramide (III) and 72.3 g of oleoyl chloride by the same procedure as that used for preparing II. The intermediate, III, was prepared by adding 10.5 g of dimethylamine to a vigorously stirred benzene solution containing 20 g of 4-butyrolactone, adding 4 g of water, continuing the reaction for an hour, and stripping.

N-(2-Oleoyloxypropionyl)piperidine (VI) was prepared by the dropwise addition of 57.9 g of oleoyl chloride to a well-stirred solution of 27.5 g of N-lactoylpiperidine (V) and 13.9 g of pyridine in 100 ml of benzene. Recovery of VI from the reaction mixture followed the same procedure as described for II. The intermediate V had been prepared by reacting 100 g of piperidine and 69.4 g of ethyl lactate at reflux for 16 hr and concurrently distilling off the liberated ethanol. After removal of excess piperidine by stripping under reduced pressure, the product was vacuum-distilled, dissolved in ethyl ether, and percolated through a column of activated alumina. The adsorbed V was recovered from the column by elution with ethanol, which was then removed by stripping.

N,N-Di-n-butyl-2-oleoyloxypropionamide was prepared in the same manner as VI except for the substitution of di-n-butylamine for the piperidine in preparation of the intermediate, V.

All amide preparations were completely freed of residual acidity by percolation of a hexane solution of the amide through a column of activated alumina. In some instances, Samples 14, 15, 16, and 17, a better recovery of amide was realized by eluting the column with a 1:1 ethanol-benzene mixture.

Densities were determined by pycnometer in a thermostated bath controlled to within 0.1C. Refractive indices were measured at 30.0 ± 0.1C with a precision Bausch and Lomb refractometer.

All the amides were screened as plasticizers for poly(vinylchloride-vinylacetate)copolymer 95:5, (Vinylite VYNW-5), and compared with di-2-ethylhexyl phthalate (DOP), dioctyl adipate (DOA), and dioctyl sebacate (DOS) as controls. The compounding formulation employed was as follows: 63.5% resin,

---

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

35% plasticizer, 0.5% stearic acid, and 1.0% basic lead carbonate. The milling, molding, and testing procedures were the same as previously reported (8,9) except that 10–15 mil sheets were used in the volatility, thermal stability, and extractability tests. Compositions which showed no signs of exudation during 90 days of shelf-storage were rated compatible. Antistatic ratings were established as previously described (2). Extraction loss was determined by measuring the weight loss suffered by duplicate 2-in. discs of plasticized stock after immersion for 24 hr in a 1% aqueous solution of Ivory soap at 60C. The procedural techniques with the exception of the medium, temperature, and the duration of immersion were those described in ASTM 1239–55.

Results and Discussion

The densities, refractive indices, and elemental analyses of the various fatty acid amides are given in Table I, and the plasticizer evaluation data are reported in Table II.

In general, the compatible N,N-dimethyl- and diethylamides of the unsubstituted fatty acids, Samples 3, 4, 5, and 6, exhibit better efficiencies, elongations, and low-temperature characteristics than do di-2-ethylhexyl phthalate (DOP). The N,N-dimethylamides of oleic and erucic acids and the N,N-diethylamide of oleic acid impart excellent low-temperature impact characteristics to the plastic stock and are in this respect comparable with dioctyl adipate. They are not quite as effective in this area however as either N,N-dibutyloleamide (1), or dioctyl sebacate, with brittle points of −63 and −59C respectively.

A comparison of the plasticizing characteristics of Samples 3 and 5 shows that, as the chain length of the acyl moiety is increased from C_{18} to C_{22}, an improvement is effected in the tensile strength and volatility without impairing low-temperature performance. Modulus and elongation are however adversely affected. Although these effects differ in the areas of tensile strength and low-temperature performance with those noted previously in the N,N-dibutylamide series for the identical acyl moieties (1), the results of the N,N-dimethyl series are more in line with expectations and follow a more consistent structure-and-effect rationale than do those of the N,N-dibutyl series.

Unlike N,N-dibutylpalmitamide (1), N,N-dimethylpalmitamide is incompatible. This would indicate that N,N-dimethylamides made from naturally occurring fatty acid mixtures which contain a substantial amount of saturated acids would present a more severe compatibility problem as compared with the corresponding N,N-dibutyl amides (2).

The plasticizing performance of the N,N,N′,N′-tetramethyl derivative of the dimer acid is similar to that of other amide derivatives of this acid previously investigated (1,10,11). In all but one respect their performance is poor. The one noteworthy plasticizing characteristic of all these dimer acid derivatives is the consistently low volatility-loss imparted to the stock. Experimental evidence has been obtained (12) which suggests that advantageous use could be made of this characteristic to obtain a significant reduction in the volatility loss of a more volatile plasticizer by blending it with an appropriate amount of a dimer acid amide.

Addition-chlorination of N,N-dimethyloleamide, Sample 13, improves tensile strength, volatility loss, and soapy water extractability of the plasticized stock but has an adverse effect upon efficiency, low-temperature performance, and thermal stability. Epoxidation in this as in other N,N-disubstituted amide series (1,3,10,11,13) improves compatibility, thermal stability, and volatility but affects low-temperature performance adversely.

Soapy water-extractability data show that the extraction losses of N,N-dimethyloleamide- and N,N-dimethylerucamide-plasticized stocks are high, 29.4 and 24.2% respectively. From this standpoint they are inferior to the symmetrical and unsymmetrical higher dialkyl amides (1,2). The loss for N,N-dimethyl-9,10-dichlorostearamide, 11.6%, shows that extractability can be reduced considerably by chlorina-

TABLE I

Densities, Refractive Indices, and Elemental Analyses of N,N-Dimethyl Amides and Ester-Amides

Compound	Density 30C	N_D^{30}	MP °C	%C		%H		%N	
				Exp.	Theory	Exp.	Theory	Exp.	Theory
N,N-Dimethylpalmitamide			37–39	76.18	76.28	13.37	13.16	5.00	4.94
N,N-Dimethylstearamide			44–46	77.20	77.10	13.32	13.27	4.72	4.50
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-Dimethylerucamide	0.8803	1.4656		78.97	78.82	13.04	12.97	3.79	3.83
N,N-Dimethylamides of hydrogenated cottonseed fatty acids	0.8718	1.4595						4.13	4.59
N,N,N′,N′-Tetramethylamide of dimer acid	0.9285	1.4879						4.40	4.55
N,N-Dimethylepoxystearamide[a]	0.9120	1.4611						4.43[g]	4.53[g]
N,N-Dimethylepoxyoleamide[b]	0.9231	1.4712						4.45[g]	4.56[g]
N,N-Diethylepoxyoleamide[c]	0.9230	1.4689							
N,N-Dimethylamide of epoxidized rapeseed fatty acids[d]			41–43						
N,N-Dimethylamide of epoxidized cottonseed fatty acids[e]	0.8908	1.4614							
N,N-Dimethyl-9,10-Dichlorostearamide[f]	0.9681	1.4739							
N,N-Dimethyl-3-oleoyloxypropionamide	0.9394	1.4660		71.85	72.01	11.47	11.82	3.72	3.65
N,N-Dimethyl-4-oleoyloxybutyramide	0.9325	1.4650		72.64	72.86	11.60	11.47	3.58	3.54
N,N-Di-n-butyl-2-oleoyloxy propionamide	0.9140	1.4598		73.39	74.71	11.78	11.81	2.99	3.01
N-(2-Oleoyloxypropionyl)-piperidine	0.9422	1.4724		73.85	73.99	11.21	11.24	3.32	3.35

[a] Oxirane content, 4.45%.
[b] Oxirane content, 3.88%.
[c] Oxirane content, 4.42%.
[d] Oxirane content, 4.04%.
[e] Oxirane content, 2.02%.
[f] Chlorine content, 13.89%.
[g] Before epoxidation.

TABLE II

Plasticizing Characteristics of Some N,N-Dimethyl Amides and Ester-Amides in Poly(vinyl chloride-vinyl acetate) Copolymer (35% Plasticizer)

Sample	Compound	Tensile strength psi	100% Modulus psi	Elongation %	Brittle point °C	Tf	T4	Volatility loss %	Compatibility[a]	Anti-Static rating
1	N,N-Dimethylpalmitamide	2140	950	400	−31	......	......	......	I	
2	N,N-Dimethylstearamide	2830	2050	270	−17	......	......	......	I	
3	N,N-Dimethyloleamide	2400	990	400	−57	−45	−19	2.23	C	+
4	N,N-Diethyloleamide	2520	1130	400	−57	−50	−21	2.15	C	+
5	N,N-Dimethylerucamide	2600	1350	360	−57	−45	−15	0.48	C	+
6	N,N-Dimethylamide of hydrogenated cottonseed fatty acids	2460	1100	410	−51	−33	−12	4.54	C	+
7	N,N,N′,N′-Tetramethylamide of dimer acid	3120	2010	400	−11	− 7	+11	0.00	C	0
8	N,N-Dimethylepoxystearamide	2320	960	370	−37	−36	−17	1.93	C	+
9	N,N-Dimethylepoxyoleamide	2360	980	400	−39	......	......	1.24	C	+
10	N,N-Diethylepoxyoleamide	2430	1020	340	−35	−30	−11	0.92	C	+
11	N,N-Dimethylamide of epoxidized rapeseed fatty acids	2570	1260	340	−33	......	......	......	I	
12	N,N-Dimethylamide of epoxidized cottonseed fatty acids	2480	980	430	−39	−36	−13	2.66	C	+
13	N,N-Dimethyl-9,10-dichlorostearamide	2820	1410	350	−37	−32	− 7	1.65	C	+
14	N,N-Dimethyl-3-oleoyloxypropionamide	2570	1180	380	−45	−33	− 8	0.68	C	+
15	N,N-Dimethyl-4-oleoyloxybutyramide	2510	1130	380	−45	−39	0	0.64	C	+
16	N,N-Dibutyl-2-oleoyloxypropionamide	3020	1730	360	−39	......	......	1.14	C	
17	N-(2-oleoyloxypropionyl)-piperidine	3090	1630	360	−31	......	......	1.33	C	
	DOP	3050	1610	330	−33	−26	− 2	1.5	C	0
	DOA	2890	1290	380	−55	......	......	6.0	C	0
	DOS	2690	1370	350	−59	−58	−17	0.6	C	0

[a] C = Compatible, I = Incompatible.

tion, but this value is still undesirably high as compared with that for any of the diester controls.

The amide-plasticized stocks are, except for those plasticized with an epoxyamide, inferior to that of a DOP-plasticized stock in both short- and long-term thermal stability. But epoxyamide-plasticized stocks exhibit a superior long-term stability although they are still slightly deficient, vis-a-vis DOP stocks, in short-term stability. The arbitrary terms "short-" and "long-term thermal stability" refer to instrumental reflectance characteristics of the plastic composition during the first 75 minutes of the thermal test period and those for the period beyond the initial 75 minutes respectively.

The amides listed in Table II, with the exception of the N,N,N′,N′-tetramethylamide of dimer acid, are effective antistaticizers for the poly(vinyl chloride) compositions at the plasticizing concentrations. This finding follows the same pattern previously observed for other N,N-disubstituted amides involving the same acyl moieties (2).

The ester-amides (Samples 14, 15, 16, and 17) exhibit better volatility-loss characteristics and poorer low-temperature performance than the N,N-dimethyl or diethyl amides of the unsubstituted fatty acids but are otherwise comparable. Although they are structurally quite unrelated to the N,N-bis(2-acyloxyethyl)amides of long-chain fatty acids previously investigated (2,13), their low-temperature performance characteristics are, with the exception of Sample 17, strikingly similar. In the area of compatibility characteristics they are vastly superior to the N,N-bis(2-acyloxyethyl)amides (13).

From the limited data in Table II it would appear that the acylated amides of 2-hydroxyacids are less desirable plasticizers in terms of efficiency, low-temperature performance, and volatility-loss characteristics than the identical derivatives of the 3- or 4-hydroxyacids. This deficiency is most apparent in the low-temperature performance. Though the acylated 2-hydroxyacid amide in one instance carries the most favorable N-substituent for low-temperature performance, the butyl group, it is less satisfactory in this respect than either the 3- or 4-hydroxyacid amides which utilize the less favorable N-methyl substituent.

REFERENCES

1. Mod, R. R., F. C. Magne and E. L. Skau, JAOCS *42*, 941–944 (1965).
2. Magne, F. C., R. R. Mod and E. L. Skau, Ibid. *44*, 235–238 (1967).
3. Magne, F. C., R. R. Mod and E. L. Skau, Ibid. *38*, 291–293 (1961); *38*, 294–296 (1961).
4. Coppinger, G., J. Am. Chem. Soc. *76*, 1372–1373 (1954).
5. Kopecky, J., and J. Smejkal, Chem. and Ind. 1529–1530 (1966).
6. Van Atta, G. R., D. F. Houston and W. C. Dietrich, JAOCS *24*, 209–212 (1947).
7. Gresham, T. L., J. E. Jansen, F. W. Shaver, R. A. Bankert and F. T. Fiedorek, J. Am. Chem. Soc. *73*, 3168–3171 (1951).
8. Magne, F. C., R. R. Mod and E. L. Skau, Ind. Eng. Chem. *50*, 617–618 (1958).
9. Fore, S. P., F. C. Magne and W. G. Bickford, JAOCS *35*, 469–472 (1958).
10. Mod, R. R., F. C. Magne and E. L. Skau, Ibid. *41*, 237–240 (1964).
11. Mod, R. R., F. C. Magne and E. L. Skau, Ibid. *41*, 781–782 (1964).
12. Magne, F. C., R. R. Mod and E. L. Skau, unpublished.
13. Magne, F. C., R. R. Mod and E. L. Skau, JAOCS *40*, 541–545 (1963).

[Received November 29, 1967]