Polyamides from Carboxystearic Acid[1]

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ABSTRACT AND SUMMARY

A series of polyamide and copolyamide resins were prepared from carboxystearic acid or methyl carboxystearate, with ethylenediamine, hexamethylenediamine, adipic acid, or caprolactam as coreactants. None of the product formulations appeared suitable for use in hot melt adhesives. More promising were the liquid, reactive polyamides made from carboxystearic acid and polyamines. These products gave excellent adhesion value in scouting tests when used as one component in 2-component epoxy adhesives and coatings. In other applications, C-19 polyamides had enhanced solubility and low melting characteristics to make them attractive as modifiers.

INTRODUCTION

Carboxystearic acid can be made by a variety of methods (1) and has many potential applications (2). Industrial interest in carboxystearic acid as a chemical intermediate remains high. Since our 1972 review (2) a number of patents have appeared for its use in lubricants (3-8), in polyamide adhesives (9-14), in polyesters for urethane foams (15), and in quaternary ammonium surface active agents (16,17).

We have described the synthesis of carboxystearic acid by three routes. Two involve hydroformylation of oleic acid or methyl oleate with either rhodium (18,19) or cobalt carbonyl (20) catalysts followed by air oxidation (21), and one involves direct hydrocarboxylation with palladium catalyst (22). We have described potential lubricant (23) and plasticizer (24) uses, and polyamide resin preparations (25).

In 1974 polyamide resins based on C-36 dimerized unsaturated fatty acids were estimated to represent a consumption of 36 million pounds in the U.S. and expected to increase to 45 million pounds by 1978 (26). More than 50% of the total volume of C-36 dimer acids produced goes into the manufacture of polyamide resins used mainly in printing inks, hot melt adhesives, surface coatings, and adhesives (26). Reactive polyamides were also made from the C-21 dicarboxylic acid derived from the reaction of linoleic acid with acrylic acid. These polyamides are reportedly similar to those made from C-36 dimer acid, but are superior as ink resins because of their low tendency for gelation (27).

Polyamides based on the C-19 carboxystearic acid were expected to have properties complementing those of the C-36 dimer acid and the C-21 dicarboxylic acid. We report now some details on resin preparations from the C-19 carboxystearic acid and evaluations based on scouting tests.

EXPERIMENTAL PROCEDURES

Materials

Carboxystearic acid (CSA), prepared by the hydrocarboxylation of oleic acid (22), had the following typical analysis: 9(10)-carboxystearic acid, 89.1%; dicarboxystearic acid, 8.3%; stearic acid, 1.7%; and hydroxystearic acids, 0.5%. Methyl carboxystearate (MCS), prepared by the hydroformylation of methyl oleate followed by air oxidation and extraction with $NaHCO_3$ (19,28), had the following typical composition: methyl 9(10)-carboxystearate, 90.8%; methyl dicarboxystearate, 6.9%; methyl oleate and stearate, 1.0%; others, 1.3%. Both the carboxystearic acid and the methyl carboxystearate were molecularly distilled.

Ethylenediamine and hexamethylenediamine (Aldrich Chemical Co., Milwaukee, WI) had the respective purities of 93.2% and 98.3% as determined by titration with standard acid. Diethylenetriamine (DET) and triethylenetetramine (TET) were technical grade reagents obtained from Matheson, Coleman, and Bell (Norwood, OH). Tetraethylenepentamine (TEP), also technical grade, was from

TABLE I

Copolyamide Resins from Methyl Carboxystearate, Adipic Acid, and Hexamethylenediamine

Adipic acid, % of total acid		Resin properties			
Mole %	Wt %	MW[a]	Clear T[b] (C)	Flow T[c] (C)	Solubility[d]
		A. 85.8% Methyl carboxyatearate			
0.0	0.0	4400	<RT	95	S
13.3	6.1	---	<RT	100	S
20.9	10.2	---	<RT	150	S hot
23.7	12.2	---	85	140	S
34.1	18.1	---	170	175	S hot
		B. 95.3% Methyl carboxystearate			
0.0	0.0	6500	<RT	105	S
8.0	3.6	6400	<RT	100	S
13.3	6.2	---	RT	120	S
29.5	15.1	---	150	160	S hot
32.2	17.5	---	160	170	I

[a] Molecular wt determined in chloroform solution by vapor pressure osmometry.

[b] Temperature at which resin was transformed from opaque or hazy to a clear condition.

[c] Temperature at which visible flow started when the flask was rotated 75°.

[d] Solubility in 95% ethanol. S = soluble at room temperature, S hot = soluble at near bp. I = insoluble.

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[2] Deceased November 20, 1975.

TABLE II

Copolyamide Resins from Methyl Carboxystearate (MCS), Ethylenediamine, and Adipic Acid or Caprolactam

Adipic acid (moles/mole MCS)	Caprolactam (moles/mole MCS)	Ethylenediamine (moles/mole MCS)	Resin properties				
			MW[a]	Flow T[b] (C)	Yield T,[c] C	Appearance'	Cold flow[d]
0[e]	---	1.04	8400	135	31	Clear, hard	0
0	---	1.32	1500	70	28	Clear, sl. tacky	0
0.06	---	1.21	2200	85	27	Clear, hard	+
0.12	---	1.25	2050	80	18	Clear, hard	++
0.17	---	1.32	2000	80	18	Clear, hard	++
0.20	---	1.34	2600	85	25	Clear, hard	++
0.25	---	1.40	2900	145	6,24	Clear, hard, friable	+
0.28	---	1.43	5000	150	22	Hazy, hard	+
0.34	---	1.49	3700	155	-10,24	Hazy, hard, friable	+
---	1.00	1.02	2900	90	19	Clear gum	++++
---	2.00	1.16	2100	85	20	Clear gum	+++
---	2.95	1.15	2500	100	22,109	Hazy gum	++
---	5.00	1.15	4700	175	-21,138	Hazy, hard	0

[a] Molecular weight determined by vapor pressure osmometry in chloroform.

[b] Temperature at which visible flow occurs when flask is heated 0.3-0.6 C/min and tilted about 60° for 20-30 sec. This temperature is 10 to 20 C higher than softening point determined by the ring and ball method.

[c] Measured with a du Pont Model 940 Thermomechanical Analyzer with a 10 C/min temperature rise and with a 1 g weight.

[d] A visual estimate of cold plastic flow of the resin particles. 0 = none, ++++ = maximum cold flow, i.e., 100% fusion of particles.

[e] Purity of MCS for this run was $99^{+}\%$, 90.9% for all other adipic acid runs, 86.2% for the caprolactam runs.

TABLE III

Composition and Properties of Reactive Polyamide Resins

Polyamide resin no.[a]	Component		Polyamide resin in epoxy adhesive (wt %)	Adhesion, Al/Al bond break load (kg/cm²)	Coated steel panels	
	Compound[b]	Mole ratio			Sward rocker hardness	Impact resistance (in lb)
1	CSA TET	1.00 1.50	35	87,92	33	50
2	CSA TEP	1.00 1.26	35	140	31	40
3	CSA TET	1.00 1.26	35	75,84	---	---
4	CSA DET	1.00 1.26	40 50	111 ---	19 30	40 >160
5	MCS DET	1.00 1.25	40	146	4	>160
6	MCS DET	1.00 1.50	35	56	---	---
7	MCS TET	1.00 1.25	40	63,82	---	---
8	MFSPA[c] TET	1.00 1.34	35	200	5	160
Control I[d]			35	73	33	50
Control II[e]			35	59	9	30

[a] Reaction carried out to maximum temperature of 260-264 C for 7 hr, with the exceptions that Run 3 was for 8 hr, Run 7 was at 220 C for 5 hr, and Run 8 was at 248 C for 10 hr.

[b] CSA = 9(10)-carboxystearic acid, MCS = methyl carboxystearate, MFSPA[c] = methyl formylstearate pentaerythritol acetal, DET = diethylenetriamine, TET = triethylenetetramine, TEP = tetraethylene pentamine.

[c] See Figure 1.

[d] Versamid® 140 (General Mills, Inc.).

[e] Genamid® 250 (General Mills, Inc.).

Aldrich Chemical Co. The pentaerythritol acetal of methyl formylstearate (MFSPA) was obtained from R.A. Awl (29).

Polymerizations—Small Scale

Copolyamide resins from hexamethylenediamine: To a 25-ml distilling flask were charged methyl carboxystearate (9.45 g, 85.8% purity, 0.0237 mole), the nylon salt from adipic acid and hexamethylenediamine (0.95 g, 0.00362 mole), and hexamethylenediamine (3.20 g, 96.8% purity, 0.0267 mole). These amounts of reactants correspond to 13.3 mole % (6.1 wt %) of adipic acid of the total dibasic acid present. Polymerization was carried out under a nitrogen atmosphere and in a Wood's metal bath with gradual heating to 138 C in 3 hr, to 240 C in 7 hr, and finally at 240 C for 6½ hr. The product (12.10 g, 99.5%) was a clear, tough resin that had the properties indicated in Table I. Copolyamides with various amounts of adipic acid and 95.3% methyl carboxystearate were prepared in a similar manner. The product resins had Gardner colors ranging from 3 to 7.

Copolyamide resins from ethylenediamine: Similar preparations with ethylenediamine are listed in Table II. The final polymerization times were 4.5 hr at 240 C. The product resins had Gardner colors ranging from 6 to 13.

Reactive polyamides: To a 50-ml distilling flask were charged 16.38 g (0.051 mole) of carboxystearic acid and 11.22 g (0.077 mole) of triethylenetetramine. The mixture was blended by heating and rotating the flask on a steam bath. Polymerization was carried out under a nitrogen atmosphere and in a Wood's metal bath with gradual

TABLE IV

Large-Scale Laboratory Preparation of Polyamide and Copolyamide Resins from Carboxystearic Acid or Methyl Carboxystearate

Polyamide resin	A	B	C	D	E
Composition, mole ratio					
Carboxystearic acid, 99+%	1.00	---	---	---	1.00
Methyl carboxystearate	---	1.00	1.00	1.00	---
Adipic acid	---	0.44	---	0.36	---
Caprolactam	---	---	5.00	---	3.77
Hexamethylenediamine	1.00	1.58	---	---	---
Ethylenediamine	---	---	1.15	1.48	1.18
Resin properties					
Molecular weight[a]	6775	---	---	2100	3100
Flow T,[b] C	120	165	170	190	140
Yield T,[c] C	21	43	15,134	---	---
Appearance	Clear, tough	Hazy, leathery	Hazy, hard, tough	Hazy, hard	Hazy, tough
Cold flow[d]	0	+	0	+	++

[a] Molecular weight determined by vapor pressure osmometry in chloroform.

[b] Temperature at which visible flow occurs when flask is heated 0.3-0.6 C/min and tilted about 60° for 20-30 sec. This temperature is 10 to 20 C higher than softening point determined by the ring and ball method.

[c] Measured with a du Pont Model 940 Thermomechanical Analyzer with a 10 C/min temperature rise and with a 1 g weight.

[d] A visual estimate of cold plastic flow of the resin particles. 0 = none, ++++ = maximum cold flow, i.e., 100% fusion of particles.

TABLE V

Carboxystearic Acid Polyamide Resin Properties[a]

Test	A	B	C[c]	D[c]	E[d]	Control[e] (C-36 dimer acid)
Tensile strength (ASTM D-412), psi						
@2.0 in./min	830	400	635	565	430	1850
@0.2 in./min	240	160	---	---	---	1800
Elongation (ASTM D-638-68), %						
@2.0 in./min	2000	1800	400	200	600	540
@0.2 in./min	2000	2000	---	---	---	600
Al/Al shear, psi	775	800	---	---	---	900
Steel/steel shear, psi	700	750	---	---	---	1660
Impact resistance, ft lb/in.	0.18	0.14	---	---	---	0.18
Softening point (ring and ball), C	102	160	---	---	---	160
Melt viscosity at 204 C, cps						
Initial	3200	1500	1100	---	12,800[d]	4600
24 hr Stability	3300	4000[f]	---	---	---	5000

[a] Formulations given in Table IV.

[b] Tests carried out by a commercial laboratory.

[c] Soluble only in hot solvent.

[d] Melt viscosity at 160 C.

[e] Versalon 1160 (General Mills, Inc.).

[f] The only resin that retained its color. Both samples A and B as well as the control formed surface skins.

heating to 225 C in 1½ hr, to 250 C in an additional 2 hr, and to 264 C in an additional 4 hr to a total of 7½ hr. The product (23.31 g) had a Gardner color of 4, a visible cold flow time (flask rotated 70°) of 5-6 sec, and an amine value of 438.4 mg KOH/g (Polyamide resin no. 1, Table III). Similar procedures were used for other resins listed in Table III.

Polymerizations—Large Scale

Nylon salt preparation: To a 3-liter Erlenmeyer flask containing hexamethylenediamine (168.8 g, 1.427 mole) was added slowly and with stirring a hot solution of carboxystearic acid (482.8 g, 1.40 mole, 95.2% purity) in 250 ml of absolute ethanol. Occasional cooling was necessary because of the heat evolved in this neutralization reaction. Additional ethanol was used to rinse the flask to make a total of about 340 g of ethanol. The product was a rigid paste that was allowed to digest at 65-70 C for 20 hr, then at room temperature for several days. The paste was filtered, and the filter cake was washed with 760 g of ethanol in eight portions. The white crystals were dried at 0.1 mm of Hg and 40 C for 4 days to give 484.6 g of the nylon salt (77.9%). Concentration of the filtrate yielded another 77.9 g (12.5%).

Polyamide preparation: To a 3-liter resin kettle were charged 554.7 g (1.247 mole) of the above nylon salt and 170 g of water used as a transfer agent. The kettle was sealed to its top with silicone grease, and the top was fitted with a thermometer and a nitrogen inlet and outlet. After flushing the interior with nitrogen and while maintaining slow flow of nitrogen, the kettle was immersed in a Wood's metal bath. The temperature of the melt (bath temperature) was gradually increased to 105 C (127 C) in 2 hr, to 139 C (164 C) in 4 hr, to 220 C (240 c) in 6 hr, and to 265 C (305 C) in 8 hr. Removal of water during polymerization provided adequate agitation. When cooled to 140-150 C, the melt was poured into Teflon dishes. The product yield was 499.5 g (98.0%). The product had a Gardner color of 1, a density of about 0.9635, and was tough and tack-free. Differential thermal analysis showed a small, sharp peak at 3.8 C and a large and broad dual peak at 76 C and 89 C. Elemental analysis: Theor. for 20 repeat units: C, 73.32; H, 11.81; N, 6.59, Found: C, 73.10; H, 11.80; N, 6.67.

This sample (polyamide resin A, Table IV) and other formulations were tested by a commercial laboratory with the results indicated in Table V.

Copolyamide with adipic acid: To a 2-liter round-bottomed flask equipped with a thermometer and a nitrogen inlet and outlet were charged methyl carboxystearate (361.7 g, 85.8% purity, 0.9065 mole), adipic acid (57.69 g, 0.3947 mole, 30.3 mole % of total dibasic acids), and hexamethylenediamine (171.5 g, 96.8% purity, 1.4286 moles). Methanol (81 g) was used as a transfer and wash medium, and 0.02 g of silicone fluid was added as an antifoam agent. The flask was flushed with nitrogen, and a slow flow of nitrogen was maintained during the reaction. The temperature of the melt (bath temperature) was gradually increased to 107 C (132 C) in 2 hr, to 174 C (196 C) in 8 hr, and to 224 C (241 C) after 15 hr. The product (525.6 g, 99.9%) was a slightly opaque, yellow-brown (Gardner color = 5½) very slightly tacky resin. The sample (B, Table IV) was tested by a commercial laboratory with the results indicated in Table V.

Test procedures: Tensile and elongation tests were carried out according to ASTM D-412 and ASTM D-638-68 procedures. Samples A and B, Table V, having a tendency to shatter upon impact when attempts were made to cut specimens with a die, were cast into molds to prepare dumbbell test strips. The latter were conditioned at 77 F and 50% relative humidity for 24 hr before testing. Two crosshead speeds were used to demonstrate rate of force effect on tensile and percent elongation.

For the aluminum/aluminum shear strength tests, panels (0.064 in. thick) were given a dichromate etch and then bonded with polyamide resin at 20 C above the resin softening point. The bonded areas were 1 in. x 1 in., and bond thickness was 1 mil. The specimens were conditioned as above and tested ad a crosshead speed of 0.2 in./min.

Bonderized (phosphate-treated), 0.032-in. thick steel panels were used for the steel/steel shear strength tests and were prepared and conditioned as above.

Impact resistance tests were carried out according to ASTM D-256, Method A.

RESULTS AND DISCUSSION

Three application areas were of particular interest for the polyamide resins from carboxystearic acid or methyl carboxystearate: flexographic printing inks, hot melt adhesives, and reactive polyamides for curing epoxy adhesives. For printing inks, the polyamide should have a softening point of about 100 C and should be soluble in 95% ethanol. For hot melt adhesives, the polyamide resin should have a softening point of about 160 C. For curing epoxy resins, reactive polyamides must impart tensile shear strength and be suitable as a structural adhesive (30).

Although these properties could best be achieved through the use of high purity compounds, most of our experiments were carried out with materials of lower purity and hence of lower potential cost. However the lower the purity, the lower were molecular weights and softening points or flow temperatures:

Purity, %	MW	Flow T, C
99+	8400	135
99+	6775	120
95.3	6500	105
85.8	4400	95

In order to compensate for the lower flow temperatures, various amounts of adipic acid (Tables I, II) or caprolactam (Table II) were added to make copolyamide resins. However, those copolyamides containing more than about 10 wt % (20 mole %) adipic acid became less soluble in ethanol as the concentration increased. The copolyamides also exhibited an undesirably high degree of cold plastic flow, unless very large amounts of adipic acid or caprolactam were present. Terephthalic acid had much greater effect in raising flow temperatures: 265 C at 10 wt % and 320 C at 23 wt %.

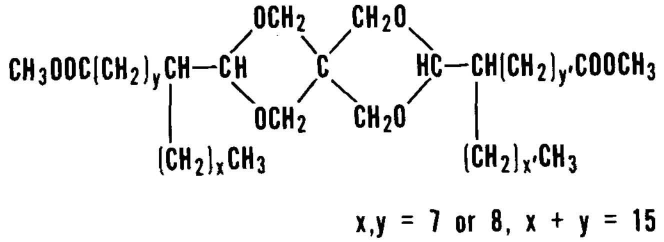

FIG. 1. The pentaerythritol acetal of methyl 9(10)-formylstearate.

It should be noted that both carboxystearic and methyl carboxystearate of low purity contained 7-8% of trifunctional materials. No attempts were made to determine the effects of these materials on polyamide properties.

Formulations of methyl carboxystearate containing 3 to 6 wt % adipic acid were soluble and flowed at sufficiently high temperatures to be suitable for ink applications (Table I). However, additional tests and formulations are required for a full evaluation of this application.

For hot melt adhesive applications, various formulations of carboxystearic acid with adipic acid and diamines and caprolactam showed poor tensile strength (Table V). These results suggest the presence of chain-stopping contaminants other than monofunctional materials. However, the elongation properties obtained with these formulations were uniquely superior to the control resin derived from C-36 dimer acid. The aluminum to aluminum shear strength and impact resistance obtained with the resins from carboxystearic acid were equivalent to those from the control. Improved tensile strength may be achieved by reformulation of these polyamides with other co-diacids (13) and diamines (12-14).

Better results were obtained with reactive polyamides made from carboxystearic acid and polyamines that show great promise in epoxy resin applications. Aluminum to aluminum adhesion and hardness were better with the carboxystearic acid-based resins than with the C-36 dimer polyamide control resins (Table III). Their impact resistance was the same as the controls, but it was markedly improved in formulations with diethylene triamine (resins 4 and 5, Table III).

A polyamide resin prepared from the pentaerythritol acetal of methyl formylstearate (Fig. 1) produced resins of outstanding adhesion and impact resistance. However, the resin was a very viscous liquid at room temperature and showed poor hardness (resin 8, Table III). The liquid reactive polyamide products are promising because of their excellent adhesion value in epoxy resins and coatings. In the other applications, the enhanced solubility and lower melting points of C-19 polyamides compared to C-36 dimer acid polyamides would make them attractive as modifiers.

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