C-19 Diacid-Based Polyamides[1]

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ABSTRACT

The preparation and properties of polyamide hot-melt adhesives derived from Koch C-19 diacid are described. They are comparable to those of commercial C-36 dimer acid-based polyamides for bonding leather and metals and somewhat superior to those of polyamides made from C-19 diacid derived from a hydroformylation process.

INTRODUCTION

Polyamide resins based on fatty acid-derived diacids are well known. Those based on the widely available C-36 dimer fatty acids have achieved considerable commercial significance as hot-melt adhesives, in flexographic inks, and as epoxy curing agents (1). The Diels-Alder adduct of linoleic and acrylic acids (C-21 diacid), also commercially produced, has been converted to polyamides, but few details were reported (2). Considerably more is known about the polyamides made from C-19 diacid (carboxystearic acid).

C-19 diacid has been made from oleic acid by three processes: hydroformylation followed by air oxidation (3, 4) or caustic oxidation (5), hydrocarboxylation (6), and the Koch reaction (7). The first two methods generate C-19 products wherein the added carboxyl group is almost entirely secondary and largely centered about the carbon atoms of the original double bond. In contrast, the Koch process gives a C-19 diacid composed of many more isomers, of which only 25% have secondary carboxyl groups; the major part of the product contains tertiary carboxyl groups because of the fast skeletal rearrangement in the concentrated sulfuric acid catalyst-solvent which precedes the addition of carbon monoxide (7). This different type of carboxyl functionality and the large number of isomers distinguishes the Koch C-19 diacid from the other C-19 diacids to which we refer as "hydroformylation C-19 diacids."

Polyamides made from hydroformylation C-19 diacid have been described in several publications and patents. For example, formulations including the C-19 diacid, azelaic or sebacic acid, and various piperazine derivatives were found to be useful hot-melt adhesives for plasticized polyvinyl chloride (8). Mixtures of this C-19 diacid with combinations of adipic acid, hexamethylenediamine, ethylenediamine, and caprolactam were polymerized and several formulations examined as hot-melt adhesives (9). Although the properties were not promising, it was not apparent whether this was due to the inherent properties of their C-19 diacid, to the particular formulations used, or to the polymerization conditions. Very strong polyamides for use as engineering plastics have been made from hydroformylation C-19 diacid and *bis*(4-aminocyclohexyl)-methane or with benzenedicarboxylic acids and hexamethylenediamine or its derivatives, but no hot-melt adhesive properties were claimed (10). Finally, aminoacids, derivable in principle from hydroformylation C-19 diacid, were polymerized, but the polymers were not examined as adhesives (11). In contrast to the above work, polyamides made from Koch C-19 diacid have never been described except in a patent to one of us (12).

Since the initial aim of our work was to prepare products acceptable to the leather footwear industry, we compared their properties to those of commercial polyamides made from hydrogenated C-36 dimer acid. In the course of this work, we found that the C-19 polyamides had excellent adhesion to metal, so we compared their properties to those of a commercial metal-bonding C-36 dimer polyamide. We also prepared polyamides from hydroformylation C-19 diacid produced by the BASF Company to demonstrate the advantages of Koch C-19 diacid.

EXPERIMENTAL PROCEDURES

Materials

The C-19 diacid was prepared from partially hydrogenated tall oil fatty acid according to the procedure of Lawson et al. (7) and had the following properties: acid value: 320; iodine value: 4; Gardner color: 3; monobasic acid content (by gas chromatography [GC] :1.0%). All other materials were reagent grade.

Procedure

A 500-mL glass resin kettle equipped with a paddle stirrer, nitrogen inlet tube, thermometer with Thermowatch controller, heating mantle, condenser, and addition funnel was charged with 218.7 g (0.666 mol) of C-19 diacid, 48.6 g (0.333 mol) of adipic acid, 5.13 g (0.02 mol) of palmitic acid, and 3.6 g (1 wt %) of Carstab 601 antioxidant. The charge was heated with stirring to 132-140 C to obtain a homogenous mixture, and 121.2 g (1.044 mol) of hexamethylenediamine dissolved in 50 mL of water was added over 15 min. After addition, the air was purged from the reactor by N_2 and the charge heated to 275 C over 20 min. The temperature was maintained at 275 C for 4 hr with N_2 sparging while the water of reaction was distilled. A small sample was removed for acid and amine values at 1 and 3 hr. The N_2 sparging was discontinued and the pressure reduced to 1 torr for 1 hr. The vacuum was broken by N_2, and the polyamide product was cooled to 225 C and poured onto a stainless steel plate to obtain a film for testing.

Test Methods

Acid and amine values. ASTM D-1980-61 and D-2074-62T with *n*-butanol solvent.

Melt viscosity. Measured in poise (ps) on a Brookfield RTV viscometer with Thermosel set at 205 C; samples conditioned for 24 hr at 50% relative humidity.

Softening point. ASTM E-28-63 using the apparatus described by Lawson (13).

Tensile strength and elongation. ASTM D-638 and D-1708 with samples preconditioned for 24 hr at 24 C and 50% relative humidity. The crosshead speed was 0.2 in./min unless otherwise noted.

Lapshear. aluminum — 1 × 3 × 0.064 in. strips, dichromate etched, were bonded with the resin at a temperature 20 C above the softening point with a bond thickness of 0.001 in. After conditioning at 24 C and 50% relative humidity for 24 hr, they were tested on an Instron TM tester at 0.2 in./min crosshead speed; steel — 1 × 3 × 0.032 in. strips, phosphate-treated, with other test conditions the same.

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TABLE I

Effect of Palmitic Acid Concentration on C-19 Polyamide Properties[a]

Concentration of palmitic acid (moles per 100 moles of diacid carboxyl)	8	5	3	2
Polyamide properties				
Acid value	1.4	2.0	3.1	2.0
Amine value	3.7	2.0	3.3	2.6
Softening point (C)	160-2	160-2	167-8	165-7
Melt viscosity (ps at 205 C)				
initial	27	35	52	131
after 24 hr at 205 C	29	31	55	116
Tensile strength at break (psi)	–	1200	2350	2840
Elongation at break (%)	–	450	320	370

[a]Formulation: C-19 diacid and adipic acid – 2:1 mol ratio; hexamethylenediamine-equimolar; palmitic acid conc. as shown; 1 mol % H_3PO_4; 0.5 wt % 2,6-ditertiarybutyl-*para*-cresol antioxidant; 275 C for 5 hr with last hr under vacuum.

TABLE II

Effect of Adipic and Azelaic Acids on C-19 Polyamide Properties[a]

Dibasic acid mole ratio	Adipic	Adipic	Adipic	Azelaic	Azelaic
C-19 diacid to dibasic	2	2	1	1	1
acid palmitic acid (mol %)	5	5	5	5	5
Polyamide properties					
Acid value	2	3	2	2	2
Amine value	2	3	3	3	5
Softening point (C)	160-2	167-8	195-7	162-4	163-6
Melt viscosity (ps at 205 C)					
initial	35	52	210	67	560
after 24 hr at 205 C	31	55	1000	72	440
Tensile strength at break (psi)	1200	2400	3800	1200	2300
Elongation at break (%)	450	320	100	450	370

[a]Formulation: C-19 diacid and codiacid mol ratio as shown; hexamethylenediamine-equimolar; 1 mol % H_3PO_4; 0.5 wt % 2,6-ditertiarybutyl-*para*-cresol antioxidant; 275 C for 5 hr with last hr under vacuum.

Impact test. Aluminum lapshear specimens prepared as above were conditioned at two temperatures and for 24 hr under water. They were then struck sharply on he edge of a lab bench. The qualitative ratings were: poor – bond failed after light blow; fair – bond failed after heavy blow; good – bond survived heavy blow.

Creep test. 1 × 3 in. strips of leather were bonded at 135 C with 0.3 g of polyamide applied to a 1 $in.^2$ area. After conditioning at 24 C and 50% relative humidity, the specimens were: (a) held at 135 C under a specified load, the time to break being recorded; and/or (b) loaded with 160 g and subjected to a temperature increase of 50 C every 15 min until the bond failed.

Low-temperature flexibility test. 20-mil thick polyamide films were conditioned at the indicated temperature for 24 hr followed by bending the film 180° at that temperature. The sample passed if no cracks were observed.

RESULTS AND DISCUSSION

Because of the relatively unreactive tertiary carboxylic acid groups on the Koch C-19 diacid, we devoted our initial efforts to finding those reaction conditions which would produce a polyamide with a high melt viscosity without degradation. After examination of polymerization temperatures from 225 C to 275 C, various acid, basic, and amphoteric catalysts, and various solvents using a standard formulation, we concluded that 275 C, 1 mol % of phosphoric acid catalyst, and a small amount of water added with the diamine gave a polymer with acid and amine values of 2 or less within 5 hr. Such a reaction temperature is high for polyamidification, but if all traces of oxygen were kept out of the reactor product, colors of Gardner 3-4 were routinely obtained.

Control of MW and melt viscosity was achieved by adding

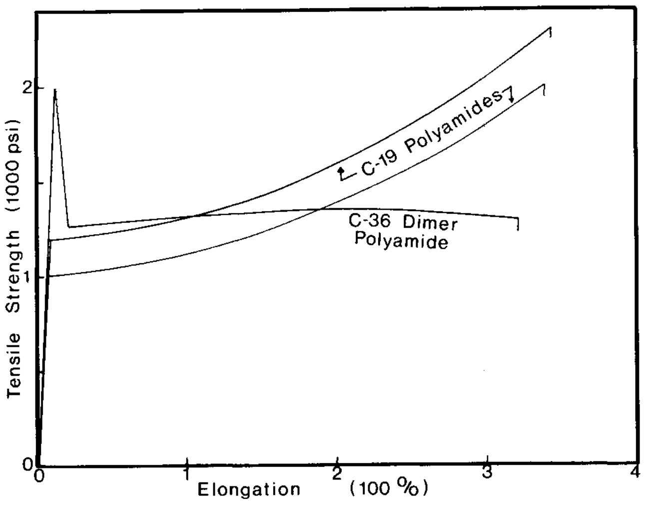

FIG. 1. Stress-strain behavior of C-19 polyamides and C-36 dimer polyamide.

small amounts of palmitic acid as a chain terminator. As shown in Table I, polyamides with satisfactory properties were obtained when 2-5 mol % was used. Interestingly, the softening point was changed minimally when the amount of palmitic acid was increased from 2-3% to 5-8%, although the tensile strength and viscosity were both reduced markedly.

TABLE III

Creep Behavior of C-19 Polyamides and Commercial C-36 Dimer Polyamides

	% Elongation				
	C-19 Polyamides			C-36 Dimer polyamides	
	X	Y	Z	C	D
Hours at 60 C with 100 psi load					
1	3	2	3	2	2
4	4	3	4	3	3
24	5	4	4	4	a
100	5	4	4	6	a
220	5	4	4	7	a
Hours at 82 C with 50 psi load					
1	18	1	8	2	2
4	18	1	8	5	5
24	18	1	8	10	9
100	19	1	8	19	16
220	19	1	8	24	20

Formulations: X – as in experimental section
Y – same but with addition of 1.5% Empol 1040 trimer acid
Z – same but substituting pelargonic acid acid for palmitic

[a]Specimens broke.

Commercial dimer-based polyamide leather bonding hotmelt adhesives have softening points of 160-165 C. Homopolymers of C-19 diacid are highly amorphous and soften at 90-110 C, so the addition of a codiacid is needed to raise the softening point. We examined oxalic, malonic, maleic, terephthalic, isophthalic, suberic, sebacic, azelaic, and adipic acids, but only the latter three were useful in preparing polyamides of the desired tensile strength at a reasonable melt viscosity (see Table II).

The other main component in the C-19 polyamide is the diamine. Ethylenediamine, the principal diamine used in C-36 dimer polyamides, was useless in making the C-19 analog because of imidazoline formation at the high reaction temperature. We settled on hexamethylenediamine.

Comparison of C-19 Polyamides to C-36 Dimer Polyamides

In Figure 1 is shown the stress-strain characteristics for three C-19 polyamides and one commercial polyamide based on hydrogenated dimer acid sold to the leather bonding industry.

The dimer polyamide had a sharp peak in tensile strength followed by a sharp drop as the specimen yielded or "necked down." Further elongation was not resisted by an increase in tensile strength, and the specimen stretched easily until it broke. On the other hand, the C-19 polyamides exhibited

TABLE IV

Comparison of C-19 Polyamides to Commercial C-36 Dimer Polyamides for Leather Bonding

	C-19 Polyamides[a]		C-36 Dimer polyamides	
	A[a]	B[b]	C	D
Softening point (C)	164-5	154-7	160-5	165-8
Melt viscosity (ps at 205 C)	45	76	46	40
Acid value	2.1	2.1	5.7	4.9
Amine value	0.7	0.7	1.1	0.9
Tensile strength (psi) at crosshead speed of				
2 in./min	2700	1930	1880	2050
0.2 in./min	2260	2400	1850	2025
Elongation (%) at crosshead speed of				
2 in./min	1900	–	490	475
0.2 in./min	2000	2000	550	525
Creep				
time to break at 135 C with a load of				
-160 g	>24 hr	>24 hr	>24 hr	>24 hr
-454 g	>24 hr	>24 hr	1 hr	40 min
-1000 g	>24 hr	>24 hr	40 min	30 min
temp at break with 160 g load (C)	167	165	158	158
Low temperature flexibility at				
-4 C	fail	fail	fail	pass
0 C	fail	fail	fail	pass
+4 C	fail	fail	pass	pass
Lapshear strength (psi)				
aluminum	1050	1130	860	790
steel	1910	1820	1640	1610
Impact test at				
-18 C	poor	good	fair	poor
25 C	good	good	good	good
25 C after 24 hr H_2O immersion	good	good	good	good

[a]Formulation: C-19 diacid to adipic acid – 2:1 mol ratio; palmitic acid – 2 mol %; hexamethylenediamine-equimolar; 1% H_3PO_4 catalyst; 1 wt % Carstab 601 antioxidant; reacted at 275 C for 5 hr with last hr under vacuum.

[b]Formulation: as above, except C-19 diacid to adipic to sebacic mol ratio – 2:1:1; palmitic acid – 3 mol %.

TABLE V

Comparison of C-19 Polyamide to Commercial C-36 Dimer Polyamide for Metal Bonding

	C-19 Polyamide[a]	C-36 Dimer polyamide
	E	F
Softening point (C)	166-7	135
Melt viscosity (ps at 205 C)	114	>1000
Acid value	3.2	–
Amine value	0.5	–
Tensile strength (psi) at crosshead speed of		
2 in./min	3440	3560
0.2 in./min	3380	3500
Elongation (%) at crosshead speed of		
2 in./min	425	475
0.2 in./min	800	500
Creep		
time to break at 135 C with load of		
160 g	45 min	10 min
454 g	30 min	5 min
1000 g	5 min	2 min
temp to break with 160 g load (C)	171	138
Low temperature flexibility at		
-4 C	fail	pass
0 C	fail	pass
+4 C	pass	pass
Lap shear strength (psi)		
aluminum	1300	1180
steel	1900	1531
Impact test at		
-18 C	good	good
25 C	good	good
25 C after 24 hr H_2O immersion	good	good

[a] Formulation: C-19 diacid to adipic acid mol ratio – 2:1; hexamethylenediamine-equimolar; no palmitic acid; 1 mol % H_3PO_4; 1 wt % Carstab 601 antioxidant; reacted at 275 C for 5 hr, last hr under vacuum.

TABLE VI

Comparison of Polyamides from Koch C-19 Diacid and from Hydroformylation C-19 Diacid

	From Koch C-19 diacid[a,b]	From Hydroformylation C-19 diacid[a,c]
Softening point (C)	166-7	167-170
Melt viscosity (ps at 205 C)	114	520
Acid value	3.2	1.3
Amine value	0.5	2.4
Tensile strength (psi)	3380	3250
Elongation (%)	800	400
Adhesion to stainless steel	excellent	fair

[a] Formulation: C-19 diacid to adipic acid mol ratio – 2:1; hexamethylenediamine-equimolar; 5 mol % palmitic acid added only to the hydroformylation C-19 diacid; 1 mol % H_3PO_4; 1 wt % Carstab 601 antioxidant; reacted at 275 C for 5 hr for Koch C-19 diacid and 250 C for 5 hr for hydroformylation C-19 diacid, last hr under vacuum.

[b] Prepared at Union Camp.

[c] Obtained from BASF Corporation (Ludwigshafen, West Germany).

a lower initial yield strength, which increased smoothly with elongation until breakage. The significance of this behavior is that an adhesive joint bonded by the C-19 polyamide would tend to "give" more easily under stress than that bonded by the dimer polyamide, but would require more ultimate force to break it.

Another important adhesive test for leather bonding is called "hot creep." This refers to the tendency for an adhesive bond to flow or distort slowly under load when warm, and can be measured by subjecting a tensile specimen to a certain force at a certain temperature and measuring the % elongation with time. In Table III, it can be seen that at 60 C and 100 psi the C-19 polyamides had about as low a hot-creep behavior as the two commercial dimer polyamides, and at 82 C and 50 psi they were superior when either a small amount of trimer acid was added or when pelargonic acid was used instead of palmitic acid.

A more extensive comparison of the C-19 polyamides to the two commercial leather-bonding C-36 dimer products is shown in Table IV. The properties of the former were comparable in most properties and superior in creep, but inferior in low temperature flexibility. Optimization of the formula could probably have improved this.

We had observed that the C-19 polymers exhibited extremely good adhesion to the stainless steel "pour-up" plate, so we compared a higher viscosity product to a C-36 dimer polyamide sold especially for metal bonding. It can be seen from Table V that even though the melt viscosity of the

C-19 polyamides (and hence the MW) was significantly lower than that of the dimer polyamide, the strength and adhesive properties were comparable with the exception of low temperature flexibility.

Comparison of Polyamides Derived from Koch C-19 Diacid and Hydroformylation-Type C-19 Diacid

We found it interesting to compare the properties of similar polyamides prepared from C-19 diacid derived from the Koch process and from C-19 diacid prepared by a hydroformylation-type process and obtained from the BASF Corporation.

From Table VI it can be seen that both C-19 diacids gave polyamides with similar tensile strengths at similar softening points. However, the Koch C-19 diacid-derived polyamide had a much lower melt viscosity and a higher elongation. It also had better adhesion to a metal surface – in fact, it had to be chipped off to be removed, whereas, the hydroformylation-type C-19 diacid-derived polyamide broke off much more easily.

The properties of the polyamide derived from the hydroformylation C-19 diacid were distinctly better than those reported by Kohlhase et al. (9) for a similar polyamide made from the same type of C-19 diacid, hexamethylenediamine, and a slightly lower proportion of adipic acid than we used. It appears from a review of their procedure and those in relevant patents (8,10) that the lack of a vacuum stage at the end of their polymerization may have been responsible for the low viscosity and tensile strength which they achieved. With this modification, we believe that polyamide hot-melt adhesives with good properties could also have been prepared from their C-19 diacid.

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Elimination of Air and Water Pollution by Double-Stage Scrubber[1]

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ABSTRACT

This new scrubbing system has been developed to eliminate entirely air pollution caused by water cooling towers during oil or fat deodorization. It also minimizes water effluent. In industrial application for more than one year, this system is based on the action of two scrubbers placed in series. The first scrubber is a conventional one, whereas the second uses concentrated cooled brine circulating in closed circuit as the condensing medium. A thorough purification of water vapors is thus achieved before the volatiles from the deodorizer enter into the high vacuum bosters. As a practical result of this special scrubbing process, the condensing water of the barometric condensers can be entirely recycled and this water is cooled by means of clean water in a surface heat exchanger requiring minimum maintenance for cleaning.

INTRODUCTION

The severe regulations imposed in all countries to fight pollution caused by the wastewater effluents of various industries are well known.

The leading executives in the Oil Milling Industry are directly concerned by these regulations, for a good deal of wastewater results from processing edible fats and oil. These effluents do indeed contain soaps, fatty materials, and organic components and other pollutants in general.

Purification of this wastewater is desirable in all cases. In the annual balance sheet of a refinery, wastewater purification means an increase in operating costs, the amount of which depends on: (a) The location of the factory with respect to neighboring living quarters and the pollution regulations of municipal or state authorities; and (b) the flowrate and the degree of pollution of the wastewater, either the direct discharge of used water to the river or stream, or the discharge of the same to the public waste treatment works.

In the present paper, we will focus on the effluents from a fat and oil deodorizing plant which, in environmental legislation, is called "condensing cooling water."

During the deodorizing process, a great deal of undesired volatile constituents like fatty acids, aldehydes, ketones, sterols, etc., which are indeed eliminated from the oil by the combined action of vacuum and stripping steam, are finally condensed in the cooling water of the barometric condensers.

Apart from these condensable volatile organics, a certain entrainment of the processed product occurs, which escapes from the deodorizer and finally also adds to pollution of the barometric condenser water. In addition to this water pollution, the use of cooling towers to recycle this water leads to air pollution.

PROCESS

For several years, modern continuous deodorizing plants have been equipped with partial condensation systems to capture the majority of fatty acids. The use of these condensations serves the simple purpose of decreasing sticky deposits in the cooling towers, and recovering some valued volatile materials coming from the deodorizing of certain

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