

Polyamide–Polyether Copolymers: A New Family of Impact-Resistant Thermoplastics

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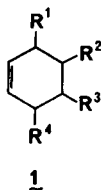
Synopsis

A new family of thermoplastic polyamide–polyether copolymers that display outstanding impact resistance and are especially useful as hot melt adhesives are described. These polymers are prepared by copolymerization of polymerized fatty acid derivatives (dimer diamines) and poly(oxyalkylene) diamines with the typical polyamide monomers sebacic acid and piperazine. Impact resistance is apparently achieved through synergistic interaction between the dimer and the polyether portions of the polymers.

INTRODUCTION

Polyamides based upon polymerized fatty acids, commonly referred to as “dimer” and “trimer” acids, were first described in 1945.¹ These polymers have found major applications as hot-melt adhesives, printing-ink resins, and surface coatings.^{2–4} In general these polyamides have been prepared by melt polycondensation of major amounts (>30 mol % based on total moles of monomers) of dimer acids (or the corresponding dimer diamines) with various shorter-chain dibasic acids and diamines.

Dimer acids are produced by the thermal self-condensation of mixed C₁₈-unsaturated, straight-chain aliphatic acids such as linoleic acid.⁴ As obtained commercially, these acids consist of mixtures of isomers of C₃₆-dibasic acids, although small amounts of “trimer” or higher molecular weight polybasic acids are generally present. Of the many isomeric structures which have been identified as components of “dimer acid,” it is generally agreed that the major components are tetrasubstituted cyclohexenes of the general structure 1, in which two of the R groups are terminated by carboxylic acid groups. Dimer diamines are generally produced by reaction of the acids with ammonia, and dehydration of the resultant ammonium salts to the nitriles followed by hydrogenation to the primary amines:



Our interest in dimer-acid-based polyamides resulted from a desire to develop improved “high performance” hot-melt adhesives, that is, adhesives displaying the properties of:

- (a) relatively high ($>100^{\circ}\text{C}$) melting points (to provide reasonable strength at elevated temperatures);
- (b) very low melt viscosity (for ease of application);
- (c) adhesion to a variety of substrates; and
- (d) good impact strength, especially at low temperatures (e.g., -18°C).

These properties are characteristic of many dimer-acid-based polyamides^{3,4} with the notable exception of impact resistance. A number of attempts⁵ have been made at decreasing brittleness by incorporation of various comonomers, all with limited success.

The present report describes an unexpected synergistic effect on impact strength that we have observed⁶ upon the incorporation of intermediate amounts of dimer acid derivatives and certain polyether derivatives into polyamides.

EXPERIMENTAL

Materials. All monomers were commercial samples used without further purification. Sebacic acid and anhydrous piperazine were obtained from the Aldrich Chemical Co. The dimer diamine utilized was obtained from Humko Sheffield Chemical under the trade name Kemamine[®] DP-3680, amine equivalent weight 303. Poly(oxypropylene) diamine, equivalent weight 1023, was obtained from Jefferson Chemical under the trade name Jeffamine[®] D-2000. Tetrakis-[methylene-3-(3',5'-ditertbutyl-4'-hydroxyphenyl)propionate]-methane, used as an antioxidant, was obtained from Ciba-Geigy, trade designation Irganox[®] 1010.

Polyamide Preparation. A typical polymer synthesis was carried out as follows: a 500-mL three-necked flask, equipped with a mechanical stirrer, inert gas inlet, and a condenser fitted with a Dean-Stark trap, was charged with sebacic acid (40.40 g, 50 mol %), anhydrous piperazine (12.04 g, 35 mol %), Kemamine[®] DP-3680 (30.32 g, 12.5 mol %), Jeffamine[®] D-2000 (20.46 g, 2.5 mol %), and Irganox[®] 1010 (0.1 g, 0.1% by weight).

The flask and its contents were then placed in a Wood's Metal bath previously heated to 160°C and stirred while being purged with nitrogen until the monomer mixture had melted. Stirring under nitrogen was continued and the bath temperature was slowly raised from 160°C to 220°C over a 65-min period, after which time 5.75 mL of water (80% of theory) had been collected. The nitrogen flow was discontinued and the condenser/water trap replaced by a dry-ice-cooled receiver connected to a vacuum line. The reaction vessel was evacuated to a pressure of about 1 torr while the bath temperature was increased to 245°C . Polymerization was continued under these conditions for an additional 20 min, vacuum was broken under nitrogen, and the polymer collected by pouring onto a "Teflon" sheet. The resultant polyamide was a clear gold to amber color in the melt, but became opaque due to crystallization upon cooling.

Polymer Characterization. Melt viscosities were determined at 232°C (450°F) using a Brookfield Rheolog viscometer. Ball and ring softening points were measured according to ASTM Test Designation E28-67T. Glass transition temperatures (T_g) were recorded as the mean of the range in temperatures observed for two trials measured using a DuPont Differential Thermal Analyzer, Model 900, with programmed heating and cooling rates of $30^{\circ}\text{C}/\text{min}$. Impact strengths were measured on $2.54\text{ cm} \times 2.54\text{ cm}$ bonds between polished maple

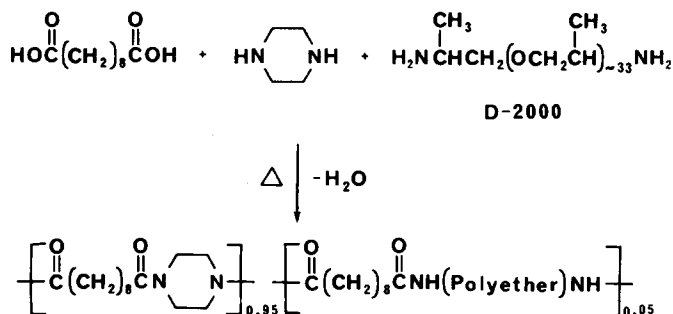
blocks using a pendulum impact tester according to ASTM Test Designation D950-72, and were recorded as the average of three trials.

RESULTS AND DISCUSSION

In our search for impact resistance, we began by speculating that some of the structure-property relationships observed in the field of thermoplastic elastomers^{7,8} should also apply to polyamide chemistry. That is, a polyamide block polymer with the proper balance of crystalline and amorphous segments might provide the flexibility, strength, and impact resistance needed in a high performance hot melt.

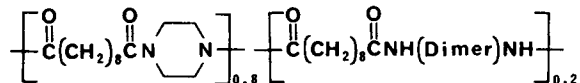
Polyamide-polyether block polymers have been previously prepared by reaction of carboxyl- or amino-terminated polyamides with appropriately functionalized poly(alkylene oxides).⁹ We preferred, in part for practical reasons, to prepare random copolymers *via* standard melt condensation techniques. Poly(piperazine sebacamide), mp 180°C,¹⁰ was chosen as a convenient base polymer for modification.*

Initially a polyamide containing about 30% by weight of amorphous polyether segments was prepared by copolymerization of piperazine and sebacic acid with 2.5 mol % Jeffamine® D-2000 (Scheme 1)[†]:



Polymer 1

Although some improvement in flexibility could be seen by comparison with the base polymer, the new material exhibited poor impact and adhesion characteristics. On the other hand, poly(piperazine sebacamide) modified by copolymerization with 10 mol % Kemamine® DP-3680 (Polymer 12) displayed excellent adhesive properties and high temperature strength:



Polymer 12

* It should be pointed out that similar results have been found with other polyamide base polymers and that the phenomena described herein appear to be general (Ref. 6).

† Throughout this paper, subscripts following the repeat units in the molecular formulae for polymers are being used for convenience as an indication of polymer composition rather than an estimate of the average number of these units in the polymer molecule. In this respect, they represent the mole fraction of the corresponding repeat units in the polymer.

TABLE I
Effect of Piperazine/Kemamine® DP-3680 Ratio on Polyamide Physical Properties

Polymer	Diamine (Mol %)		Viscosity at 232°C (P)	Ball and ring softening point (°C)	T_m (°C)	T_g (°C)	Appearance
	Piperazine	Kemamine DP-3680					
1	47.5	0	27	163	162	-68	Opaque
2	42.5	5	17	150	146	-62	Opaque
3	40	7.5	17	150	142	-61	Opaque
4	37.5	10	35	141	132	-58	Opaque
5	35	12.5	34	135	96 ^b , 122	-12 ^a	Opaque
6	30	17.5	49	123	86 ^b , 114 ^b	-12 ^a	Clear
7	25	22.5	10	81	56 ^b , 82 ^b	-19 ^a	Clear
8	15	32.5	23	79	50, 64	-21 ^a	Clear
9	10	37.5	8	79	52, 72	-20 ^a	Clear
10	5	42.5	80	97	54, 77	-18 ^a	Clear
11	0	47.5	53	100	57 ^b , 80	-16 ^a	Clear

^a Weak, broad transition.

^b Weak transition.

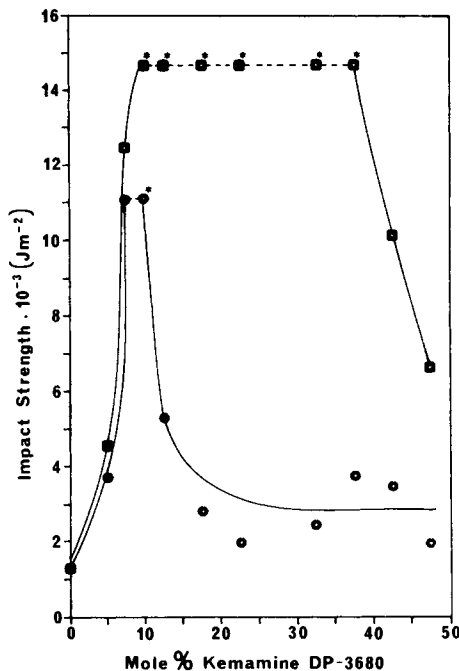
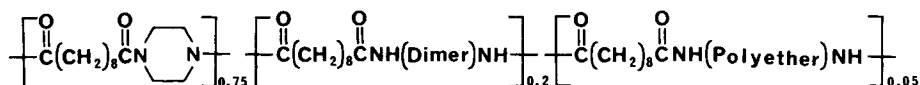


Fig. 1. Impact strengths of modified piperazine sebacamide polymers as a function of dimer diamine level; (O) at -18°C ; (\square) at 21°C ; (\star) exceeded limits of instrument.

Again, however, this copolymer lacked impact resistance. Increasing the Kemamine level to 20 mol % resulted in no improvement. Thus it became apparent that, at least with polyamides having the low molecular weight required for hot melt application, a simple balance of crystalline and amorphous segments would not produce the desired properties.

With this information in hand, we were quite surprised when we prepared a terpolymer containing both Kemamine[®] DP-3680 and Jeffamine[®] D-2000 (10 and 2.5 mol %, respectively, Polymer 4) and found it to display exceptional impact resistance:



Polymer 4

To investigate further this unexpected synergism, a series of polyamides were prepared in which the ratio of piperazine/Kemamine was varied while keeping the Jeffamine level constant at 2.5 mol %. The results are summarized in Table I and Figure 1. This study showed that impact strength at room temperature (21°C) can be developed over a wide range of dimer diamine levels—test specimens bonded together with polyamides containing 10–37.5 mol % Kemamine[®] DP-3680 were capable of absorbing the maximum force delivered by our impact tester without the bonds breaking. However, impact strength at -18°C was very sensitive to composition, with good impact strength being observed only between the limits of 5–15 mol % dimer diamine.

TABLE II
Effect of Piperazine/Jeffamine® D-2000 Ratio on Polyamide Physical Properties

Polymer	Diamine (Mol %)		Viscosity at 232°C (P)	Ball and Ring softening point (°C)	T_m (°C)	T_g (°C)	Appearance
	Piperazine	Jeffamine D-2000					
12	40	10	8	142	137	0 ^a	Opaque
13	39.75	10	48	147	112 ^b , 139	0 ^a	Opaque
14	39.5	10	92	148	117, 140	0 ^a	Opaque
15	39	10	61	147	104 ^b , 138	-6 ^a	Opaque
16	37.5	10	35	141	132	-58	Opaque
17	36.25	10	24	138	95 ^b , 124	-59	Opaque
18	35	10	17	136	98 ^b , 120	-59	Translucent
19	32.5	10	14	131	88 ^b , 113 ^b	-58	Translucent
20	30	10	20	125	70 ^b , 116 ^b	-58	Translucent
21	27.5	10	20	94	—	-60	Clear

^a Weak, broad transition.

^b Weak transition.

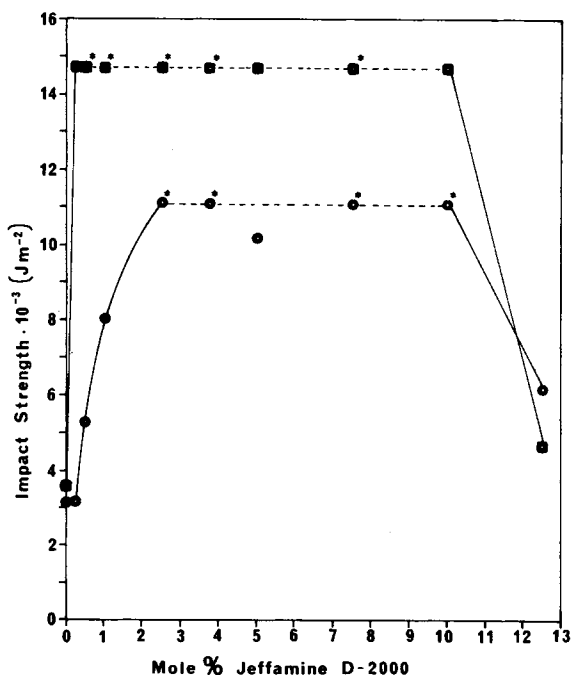


Fig. 2. Impact strength of modified piperazine sebacamide polymers as a function of poly(oxyalkylenediamine) level (O) at -18°C ; (□) at 21°C ; (★) exceeded limits of instrument.

The effect of the amount of polyether segment in the polyamides was studied next by holding the Kemamine® DP-3680 level constant at 10 mol % (Table II and Fig. 2). As mentioned above, polymers without the Jeffamine component (e.g., Polymer 12) have poor impact resistance. However, incorporation of as little as 0.25 mol % polyether (about 3% by weight) produced excellent room temperature strength (Polymer 13) while slightly higher levels (Polymer 15) were needed to give good low temperature properties. Above about 10 mol % Jeffamine® D-2000, the polyamides became quite soft and lost impact strength at room temperature.

The data tends to indicate that the ability of the polymer to crystallize or phase-separate upon cooling must be an important factor in the development of impact strength at lower temperatures. This phase separation, as evidenced by the opaque appearance and/or a dramatic lowering of the glass transition temperature (T_g) of the polymer, is apparent only at about 15 mol % dimer diamine or less. In this regard, it might be argued that Polymers 1 and 12 do not adequately assess the influence of the amount of amorphous character on impact resistance since Polymer 4 has a much higher proportion of amorphous components (57% by weight of units derived from the polyether and dimer diamines). However, when less than about 7.5 mol % dimer diamine is present in the monomer charge (e.g., Polymer 2), phase separation develops in the melt during polymerization. This inhomogeneity increases during the polymerization process and, although it does not prevent the attainment of reasonable molecular weights, it undoubtedly contributes somewhat to the poorer physical properties of the resultant polyamides. Apparently, phase separation cannot be too distinct or

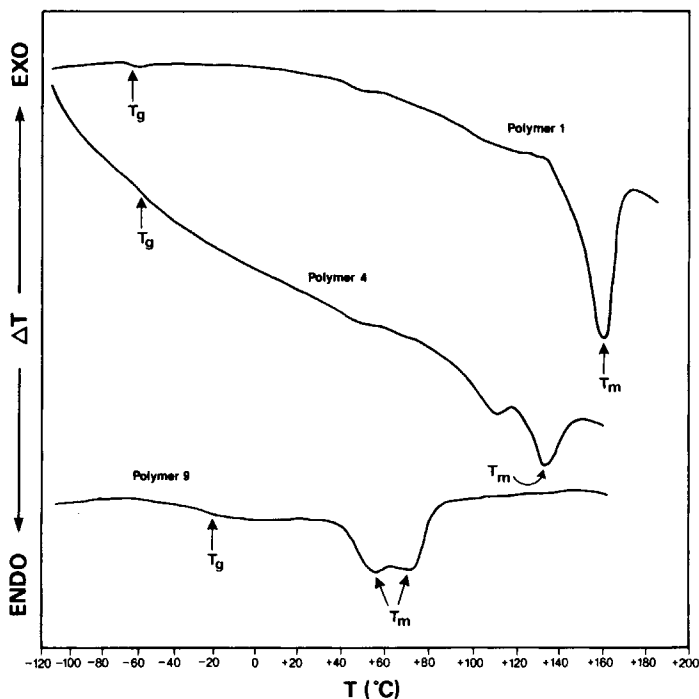
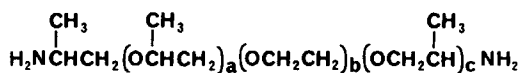


Fig. 3. DTA traces of representative polyamides from Table I as a function of temperature.

impact resistance again will be lost. To circumvent this problem, a modified poly(piperazine sebacamide) containing 12.5 mol % Jeffamine® ED-900 (a polyoxyethylene-based diamine of about 900 molecular weight) was prepared. Although this polyamide contained 58% by weight amorphous segments derived from the polyether and all components were compatible in the melt, it still displayed very poor impact properties. Thus it is also apparent that all three diamine components must be present to develop impact strength:



ED-900 ($a+c \approx 3.5$; $b \approx 20.5$)

A reasonable explanation of the results might involve the domain size in these phase-separated polymers as well as the sharpness of the phase boundaries. The importance of the dimer component may be due to an ability to increase compatibility between the crystalline polyamide and amorphous polyether domains. When present in amounts \geq about 5 mol %, it allows effective dispersion of the crystalline domains throughout the amorphous matrix and thus helps maintain crystallite size in the proper range to produce toughening. At about 5 mol % or less dimer component, the crystalline domains may become too large and/or phase boundaries perhaps become too sharp, with the result that the polymer becomes brittle, particularly at the low molecular weights needed for hot melt application. On the other hand, as the level of dimer derivative increases, compatibility between the phases increases until, at about 17.5%, either the

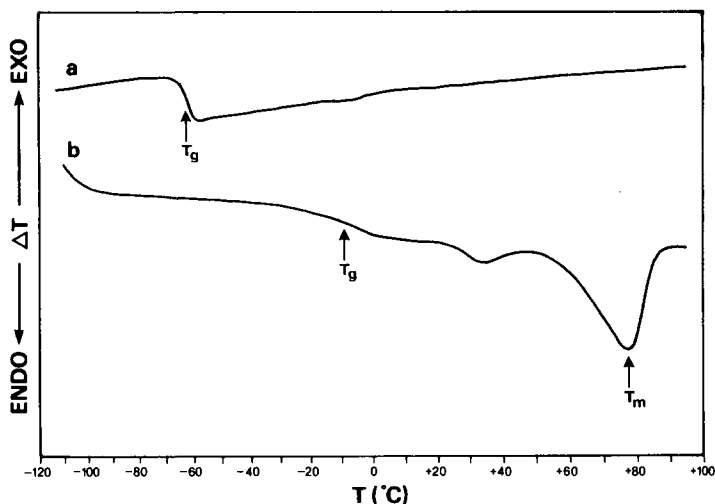


Fig. 4. DTA traces of homopolyamides of sebacic acid with (a) Jeffamine® D-2000 and (b) Kemamine® DP-3680.

crystalline domain size becomes too small to promote toughening or the polymer becomes completely homogeneous. The fact that room temperature impact strength is maintained up to about 50 mol % dimer content suggests that the former may be the case, and that smaller crystallite sizes may still effect toughening at the higher temperature. Some support for this hypothesis is found in the nature of the DTA traces as a function of increasing dimer diamine level (Fig. 3). In Polymer 1 (no dimer diamine), both T_g and T_m appear quite sharp and distinct. As the level of dimer diamine increases (Polymers 4 and 9), both transitions become broadened and move closer together. For comparison, Figure 4 shows the DTA traces for the homopolymers of sebacic acid with Jeffamine® D-2000 and Kemamine® DP-3680, respectively. The similarity between that of the latter and that of Polymer 9 is striking.

Although thorough experimental verification is beyond the scope of this paper, the above explanation is quite analogous to what is known concerning the dispersion of rubber particles in glassy polymers to produce toughened plastics (e.g., high-impact polystyrene).^{11,12} The existence of a critical particle size range for toughening is well established, while rubber-matrix adhesion, which might correspond to the sharpness of the phase boundaries in our case, has also been found to be of prime importance.

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