

Synthesis and Characterization of Polyamide Resins from Soy-Based Dimer Acids and Different Amides

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Received 16 July 1997; accepted 14 September 1997

ABSTRACT: A series of soy-based polyamides with different dimer acids and diamines were synthesized using a condensation polymerization technique. The molecular weight of polyamides prepared from 1,4-phenylenediamine increases greatly with a reaction temperature above 260°C. The physical properties of the polyamides, such as glass transition temperature (T_g), melting point (T_m), decomposition temperature (T_d), crystalline behavior, and mechanical strength strongly depend on their molecular weight and flexibility of diamines used. The aromatic-based polyamides have a higher T_g , T_m , T_d , and stronger mechanical strength than that of aliphatic-based polyamides. X-ray diffraction patterns of the samples indicate that all of the resins synthesized present a typical semicrystalline morphology. Polyamides made from hydrogenated dimer acid possess lower T_g and higher mechanical strength, compared with polyamides from unsaturated dimer acid with different dimer and trimer ratios. These results are analyzed and discussed in accordance with the influence of rigid aromatic segments and the microstructure of different dimer acids. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 68: 305–314, 1998

Key words: polyamide; dimer acid; aromatic; soy-based; condensation

INTRODUCTION

Soy-based dimer acids have been traditionally used to synthesize and formulate hot-melt adhesives, flexographic inks, functional coatings, and engineering materials.^{1–10} Because of their wide applications, the investigations of soy-based polyamides are growing. There are many advantages of using soy-based dimer acids as starting materials, compared with using other monomers because they are nontoxic, less expensive, and potentially biodegradable. The polyamides prepared by condensation polymerization of soy-based dimer acids with different diamines show many interesting physical properties, such as forming extreme

strong bonds to most solid surfaces, having a sharp melting temperature at 90°–120°, reacting fast with epoxy resins, etc. Although many novel formulations and synthesis techniques related to dimer acid-based polycondensation products were disclosed in a recent series of patents,^{11–13} systematic studies focusing on the crystalline structure and thermal and mechanical behaviors of these resins are relatively few. On the other hand, despite extensive research of formulations using different aliphatic amines, the condensation polymerization of a dimer acid with aromatic amines has not been extensively studied. It is well-known that incorporating aromatic segments into a flexible matrix can add exceptional mechanical strength and thermal stability, compared with pure aliphatic segments.^{14–16} The results are attributed to the rigid segmental structure and related crystal morphology. Thus, the study of dimer acid-based polyamides with aromatic seg-

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Journal of Applied Polymer Science, Vol. 68, 305–314 (1998)
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Table I Characteristics of the Monomers

Monomer	Acronym	Structure	T_m /°C
Dimer acid ^a	D1007		Liquid at room temperature
Dimer acid ^b	D1018	Same as above	Same as above
Dimer acid hydrogenated (98% + dimer)	HYDA		Same as above
1,4-Phenylenediamine (99%)	P		143–145
Hexamethylenediamine (98%)	H	$H_2N-(CH_2)_6-NH_2$	42–45
Ethylenediamine (99%)	E	$H_2N-CH_2-CH_2-NH_2$	8.5

^a D1007: 97% dimer, 2% trimer, and 1% monomer acid.

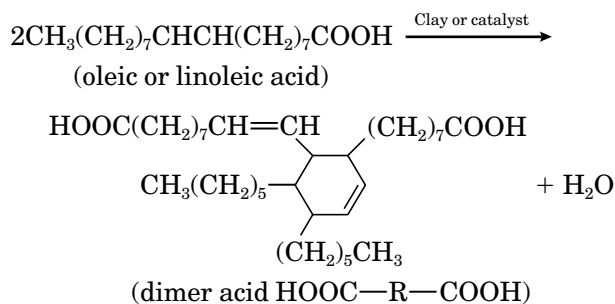
^b D1018: 79% dimer, 15% trimer, and 6% monomer acid.

ments not only possesses value for scientific research, but also can expand commercial utilization of this polymer.

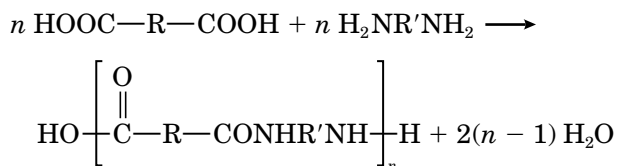
The application of soy-based polyamide as a toner resin for office copiers and laser printers has been developed in our laboratory recently.¹⁷ A potential advantage to using this particular resin in copy toner formulas is that the soy-based polyamide may be biodegradable so that it can be easily deinked by adding certain enzymes during the deinking process. Toners have been typically designed to have a glass transition temperature (T_g) ranging from 50° to 65°C.¹⁸ If the T_g of the resins is below 50°C, the particles tend to stick together, making the material unacceptable as a toner. However, commercially available soy-based polyamides usually have a T_g much lower than 50°C. To synthesize a soy-based toner with a required T_g , a dimer acid with unsaturated segments or an aromatic diamine may be used. The influence of monomer structure and flexibility on T_g of soy-based polyamides was examined in this study.

Soy-based dimer acids can be prepared by condensation of two unsaturated fatty acids, such as

oleic acid (10–59% in soybean oil) or linoleic acid (28–66% in soybean oil) in the presence of a clay or other catalyst,¹⁹



Condensation of dimer acids with diamine produces a polyamide through the reaction of



The commercially available dimer acids invari-

Table II Molecular Weight of Polymers and Their Structure

Monomer	Acronym	Structure	M_n (g mol ⁻¹)
Based on dimer acid 1007 and ethylenediamine	D1007E		10,500
Based on dimer acid 1007 and hexamethylenediamine	D1007H		10,400
Based on dimer acid hydrogenated and 1,4-phenylenediamine	HYDAP		11,500
Based on dimer acid 1007 and 1,4-phenylenediamine	D1007P (160°C)		3,300
	(220°C)	Same as above	7,400
	(260°C)	Same as above	9,000
	(310°C)	Same as above	26,000
Based on dimer acid 1018 and 1,4-phenylenediamine	D1018P	Same as above	9,500

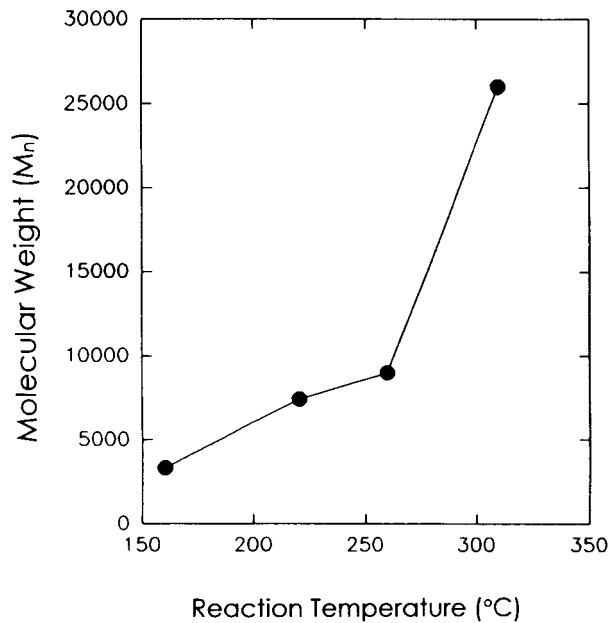


Figure 1 Molecular weight of D1007P versus polycondensation reaction temperature.

ably contain trimer acids. The trimer acid may behave differently from the dimer acid in copolymerization with diamine because the former will result in a three-dimensional polymer structure through a crosslinking reaction. Therefore, the influence of trimer acids on the chemistry and physical properties of soy-based polyamides is also an interest of this study.

To gain a full understanding of the relationship among the monomer structure, polycondensation temperature, and the polymer physical properties, a series of polyamides from different soy-based dimer acids and diamines were synthesized, and the physical properties of soy-based polyamides were investigated by several technologies.

EXPERIMENTAL

Materials

Dimer acid was supplied by the Emery Group of Henkel Corporation (Cincinnati, OH). Empol 1007 and 1018 dimer acids are both yellowish viscous liquids at room temperature with dimer and trimer ratios at 97 : 2 and 75 : 19, respectively. Hydrogenated dimer acid and all of the diamines were purchased from Aldrich Chemical Co. (Milwaukee, WI) and used as received. Their acro-

noms reported purity, molecular structure, and melting point and are listed in Table I.

Polymer Synthesis

Condensation polymerization was used for polymer synthesis. Polymerization conditions and pro-

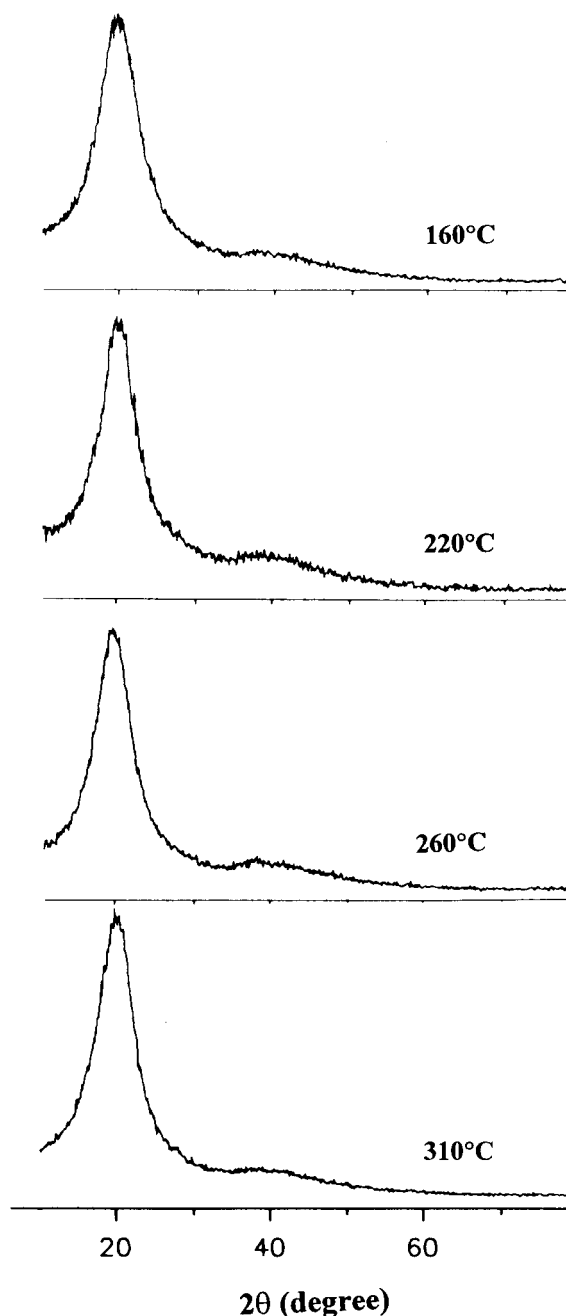


Figure 2 X-ray diffraction patterns for D1007P synthesized at different temperatures.

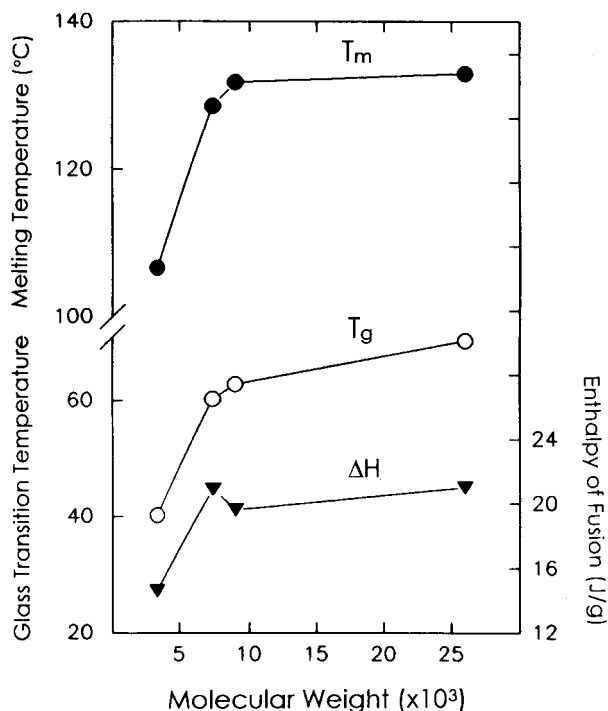


Figure 3 Molecular weight versus T_g , T_m , and enthalpy of fusion for D1007P.

cedures were the same, except that different temperatures and monomers were used. A typical example of polymerization (for sample D1007P) is given as follows: 100 g of dimer acid (equivalent to 0.353 mol acid groups) was charged into a 250-mL, three-necked, round-bottomed flask equipped with a mechanical stirrer, a thermometer, and a nitrogen inlet. The monomer was first heated to 80°C under a nitrogen atmosphere and vigorous stirring; then, 19.2 g of 1,4-phenylenediamine (equivalent to the total acid groups) were added. The reactants were gradually heated to 260°C in 3 h and kept at this temperature for another 5 h under vigorous stirring. Then, the system was allowed to cool down to room temperature. The next day, the reactants were heated again to 260°C and subjected to a vacuum of approximately 2 mm Hg for 4 h. The product was then discharged from the flask.

Determination of Molecular Weight

The number average molecular weight of the polyamides synthesized was determined from the combined content of acid and amine end groups.²⁰ Carboxylic end groups were determined by titra-

tion of a 0.5% polyamide solution (pyridine as the solvent) with 0.10*N* methanol sodium hydroxide. Phenolphthalein was used as the indicator. Amine end groups were determined by titration with freshly standardized 0.10*N* propanol hydrochloric acid. Bromcresol green solution was used as the indicator. For all of the titration experiments, at least three replicates, including a blank titration of solvent, were collected for determining the reproducibility.

The number average molecular weight, M_n , was calculated based on the following equation²⁰:

$$M_n = \frac{W}{(C_A V_A + C_B V_B)} \left(\frac{N_m}{1} + \frac{N_d}{2} + \frac{N_t}{3} \right)^{-1}$$

where W is the weight of solid sample titrated; C_A , C_B , and V_A , V_B are the concentrations and actual volumes used from standard solutions of sodium hydroxide and hydrochloric acid, respectively; and N_m , N_d , and N_t are the percentage concentrations of the monomers with one, two, and three functional groups (acid and amide) in the products.

The repeat unit structure of polymers and their

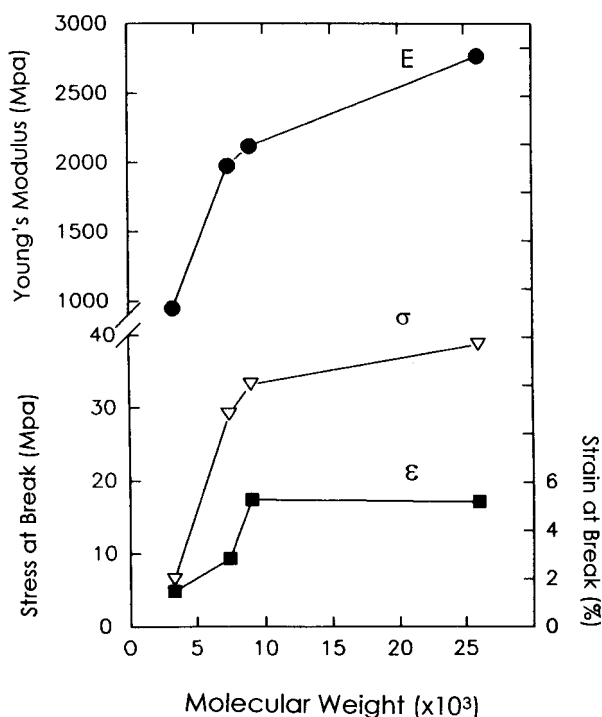


Figure 4 Molecular weight versus Young's modulus, stress at break, and strain at break for D1007P.

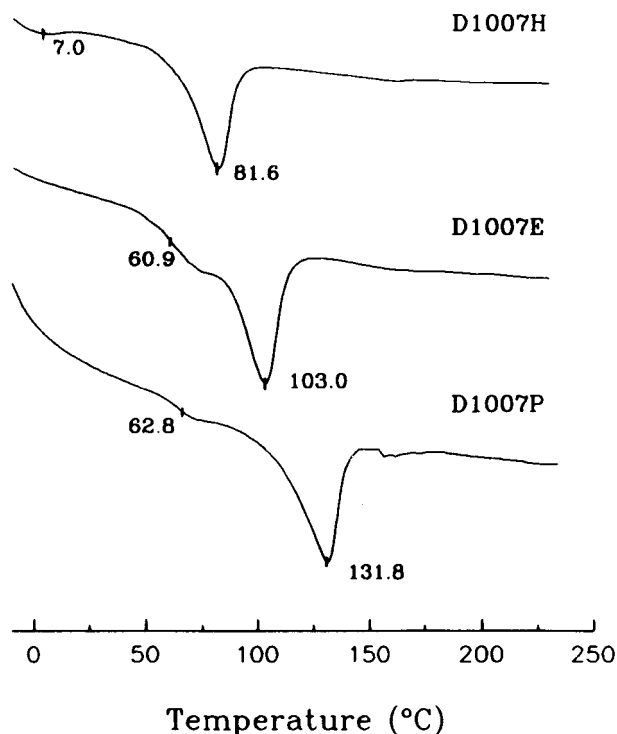


Figure 5 DSC diagrams for D1007E, D1007H, and D1007P.

number average molecular weights are listed in Table II.

Wide-Angle X-ray Diffraction (WAXD) Measurement

WAXD patterns of polyamide resins were obtained with a Diano-XRD 8000 X-ray diffractometer using nickel-filtered Cu-K α radiation. The tube current and voltage are 20 mA and 40 kV, respectively. Measurements were scanned between 0° and 5° 2 θ angle at 0.04° steps. The counting time was 1 s per step.

Differential Scanning Calorimetry (DSC) and Thermal Gravimetric Analysis (TGA)

DSC measurements were performed on a SEICO DSC equipped with a thermal analysis station. TGA measurements were conducted on a SEICO TGA. Both DSC and TGA measurements were performed under nitrogen at a 20°C/min heating rate.

Stress–Strain Analysis

Uniaxial stress–strain measurements of polyamide films were conducted (ASTM D 882-91) using an Instron model 1122 at 20°C and 50% relative humidity. All films were 15 mm in width and 200 (± 50) μm in thickness. A 50-mm gauge length and a 5 mm min⁻¹ crosshead speed were used.

RESULTS AND DISCUSSION

Influence of Reaction Temperature on Polyamides' Molecular Weight and Physical Properties

Synthesis of polyamides using dimer acid and diamine is a typical condensation polymerization, which usually takes place through the elimination of water molecules at certain reaction conditions. The molecular weight of dimer acid-based polyamides can be affected by reaction time, temperature, monomer ratio, catalyst, etc. If other parameters remain a constant, the reaction temperature, which is directly related to the rate of distillation of condensing water, will significantly affect both the polymerization rate and the molecular weight. To explore this factor further, reaction temperatures of dimer acid 1007 with 1,4-phenylenediamine *versus* their number average molecular weights are plotted in Figure 1. It is evident that the molecular weight of polyamide with the aromatic diamine increases with increas-

Table III Thermal and Mechanical Properties of Polyamides with Different Diamines

Sample	T_g (°C)	T_m (°C)	Enthalpy of Fusion (J g ⁻¹)	Decomposition Temperature (°C)	Young's Modulus (MPa)	Stress at Break (MPa)	Strain at Break (%)
D1007E	60.9	103.0	26.1	385.0	2017	27.3	4.4
D1007H	7.0	81.6	28.0	390.0	1322	14.5	7.1
D1007P	62.8	131.8	19.6	406.5	2116	33.3	5.3

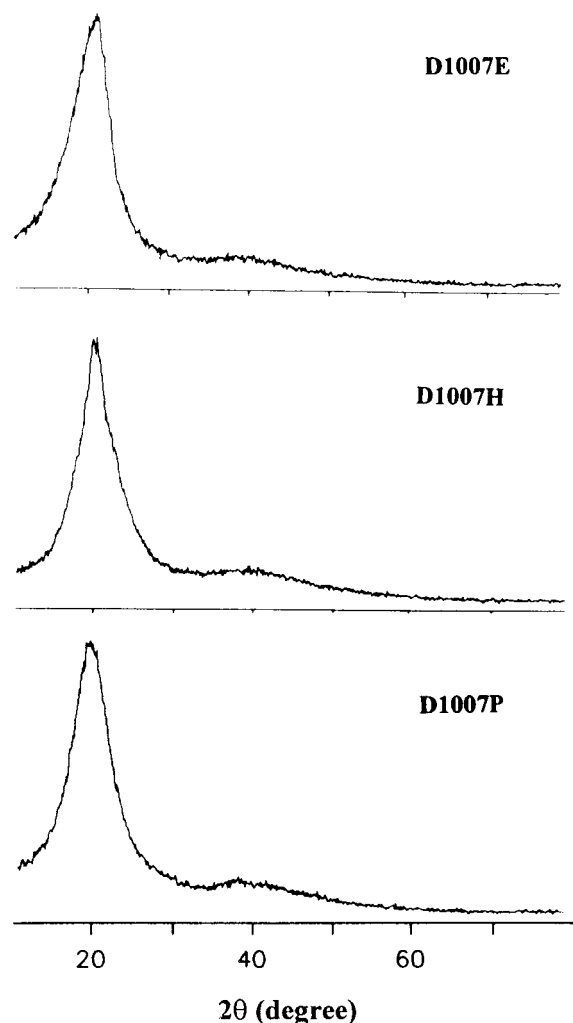


Figure 6 X-ray diffraction patterns for D1007E, D1007H, and D1007P.

ing reaction temperature. Above 260°C, there is a rapid increase in molecular weight with increasing temperature. This may indicate that the polycondensation reaction resulting from eliminating water in this system can proceed much faster above 260°C. The result is consistent with several recent reports that the optimum reaction temperature of dimer acid and aliphatic diamines is in the range of 260° to 300°C.¹¹⁻¹³ It may also imply that polycondensations of both aliphatic and aromatic diamines with dimer acids have a similar reaction mechanism.

WAXD diagrams of polyamides with aromatic diamine synthesized at different temperatures are shown in Figure 2. All samples have a relatively sharp diffraction peak at $2\theta = 20^\circ$ and a broad shoulder peak around $2\theta = 40^\circ$. There is no

significant variation observed with reaction temperature, except the peak width of the sample prepared at 160°C is a little broad. Compared with the X-ray diffraction diagrams of Nylon's homopolymers, polyblends, and block copolymers,²¹ it was found that dimer acid-based polyamides possess similar X-ray diffraction patterns with Nylons, and can be identified as the semicrystalline polymers. Thermal analysis data can further confirm this conclusion.

Figure 3 presents the thermal behavior of polyamides *versus* their molecular weight. It is seen that T_g , melting temperature (T_m), and enthalpy of fusion (ΔH) gradually increase with the increase in molecular weight. The T_g and T_m of the sample with the largest molecular weight are about 20°C higher than that of the sample with the lowest molecular weight. As T_g reflects the Brownian motion of amorphous chains and T_m represents the chain motion in crystals, higher T_g and T_m may indicate stronger restrained amorphous segments and higher ordered crystals due to an increased molecular weight in the samples. The increase in the enthalpy of fusion with an increase in molecular weight supports the idea that higher molecular weight polyamides may have a higher crystallinity as reported previously.²¹ Results clearly demonstrate that the polycondensation reaction temperature can greatly influence the molecular weight of polyamide and, in turn, affect its T_g , T_m , and crystalline behavior.

The variation of mechanical properties of polyamides with their molecular weight is plotted in Figure 4. Evidently, Young's modulus (E), stress at break (σ), and strain at break (ϵ) all increase with increasing molecular weight. It is well-known that the mechanical properties of solid polymers, especially for semicrystalline polymers, rely closely on their amorphous and crystal morphology.²³ A higher mechanical performance of the sample may indicate that there is a better organized crystal and a less defective amorphous structure through their longer molecular chains. On the other hand, the samples with lower molecular weight could cause lower crystallinity and have more end groups concentrated into their amorphous phase, resulting in poor mechanical performance.

Influence of Aromatic and Aliphatic Diamines on Polyamides' Physical Properties

It has been established that polyamides with aromatic segments could possess better thermal and

mechanical performances than that of aliphatic segments.^{24,25} For further comparison of the influence of both aromatic and aliphatic diamines on the physical properties of dimer acid-based polyamides, ethylenediamine, hexamethylenediamine, and 1,4-phenylenediamine were selected as the monomers for preparation of polyamide resins. The polymers' segmental structure and their molecular weight are listed in Table II. It can be seen from Table II that the molecular weight of D1007E, D1007H, and D1007P (prepared at 260°C) are basically in the range of 10^4 g mol⁻¹.

The DSC curves of the three samples are presented in Figure 5, and related thermal properties are given in Table III. First, it can be seen that the T_g of D1007H (hexamethylenediamine-based polyamide) is only 7.0°C; by contrast, the T_g of D1007P (1,4-phenylenediamine-based polyamide) is 62.8°C. As the T_g represents the chain segments' motion in amorphous phase, the higher T_g of D1007P suggests that the segments' motion in the aromatic diamine could be strongly restrained by their rigid molecular structure. On the other hand, as hexamethylenediamine is more flexible than ethylenediamine, a higher T_g value for D1007E indicates that the flexibility of segments in the aliphatic diamine monomer still plays an important role in effecting their T_g .

Similarly, with the variety of T_g , the melting temperature of three samples increases with a decrease in diamine flexibility also. Especially, the melting temperature of D1007P (131.8°C) is almost 50°C higher than that of D1007H (81.6°C). The higher melting temperature in D1007P may indicate that its aromatic segments in the crystal phase are strongly interacting and need more energy to change their configuration and initiate them to move. The lower melting temperature of D1007H may result from its flexible chain structure. Besides, D1007P's thermal decomposition temperature from TGA data is about 20°C higher than that of D1007E and D1007H, respectively, indicating its excellent heat-resistant properties.

Interestingly, it was found from Table III that the enthalpy of fusion of the three samples decreases with the increase in flexibility of diamine. The more flexible the segment, the higher the value of enthalpy of fusion. According to calorimetry theory,²⁶ for a semicrystalline polymer, the degree of crystallinity can be calculated by the ratio of the enthalpy of fusion of the sample to that of its perfect crystalline polymer. Because aromatic-based polyamide has stronger segments

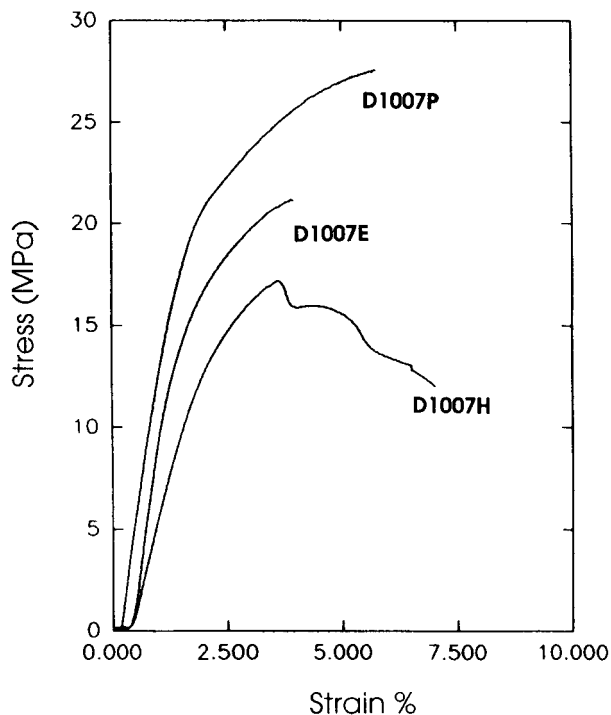


Figure 7 Stress-strain curves for D1007E, D1007H, and D1007P.

interaction and lower flexibility than that of an aliphatic one, it is expected that hexamethylenediamine-based polyamide should move easily at melting point, which results in a lower enthalpy of fusion in its perfect polymer crystal. A higher enthalpy of fusion of an aliphatic-based polyamide sample from the experiment (Table III) and an assumed lower enthalpy of fusion of its perfect crystals suggest that the hexamethylenediamine-based polyamide may have the highest crystallinity. This conclusion is also supported by X-ray diffraction data (Fig. 6) [i.e., sample D1007H has a relative sharper diffraction peak ($2\theta = 20^\circ$)], compared with D1007E and D1007P.

The stress-strain curves of the three samples are shown in Figure 7. As expected, D1007P has the highest Young's modulus and stress at break; D1007E is intermediate; and D1007H has the lowest modulus and stress at break (Table III). Furthermore, D1007P and D1007E seem to be brittle in character, where there is no obvious yield point and ductile region observed. In contrast to D1007P and D1007E, D1007H possesses a typical ductile fracture feature, where there exists a clear yield point and a longer deformation region. Its average strain at break reaches to 7.1%. The results may still be attributed to the rigid aromatic and flexi-

Table IV Thermal and Mechanical Properties of Polyamides with Different Dimer Acids

Sample	T_g (°C)	T_m (°C)	Enthalpy of Fusion (J g ⁻¹)	Decomposition Temperature (°C)	Young's Modulus (MPa)	Stress at Break (MPa)	Strain at Break (%)
HYDAP	44.2	132.1	21.2	400	3191	40.7	2.6
D1018P	58.4	125.5	18.1	406	2541	38.3	4.4
D1007P	62.8	131.8	19.6	406	2116	33.3	5.3

ble aliphatic chain segments in their amorphous phases, respectively. It is well-known that tensile fracture in semicrystalline polymers generally occurs in their amorphous region, because heterogeneities such as chain ends and ruptured bonds most likely concentrate in the amorphous region, and these could lead to "disruption points" and stress concentrations.²⁷ The higher mechanical strength and Young's modulus in D1007P are evidently related to its rigid aromatic segments, which can effectively resist formation of stress-induced microcracks or crazes during the deformation process. As for D1007H, plastic deformation occurs as soon as the stress is applied to it, due to its flexible segments, and leads to a decrease in mechanical properties.

Effect of Different Dimer Acids on Polyamides' Physical Properties

To study the effect of the molecular structure of a dimer acid monomer on the polymer's molecular weight and physical behavior, dimer acid 1018 (79% dimer, 15% trimer, and 6% monomer acid) and hydrogenated dimer acid (98%+ dimer acid) were also reacted with 1,4-phenylenediamine for preparing polyamides. Their segmental structure and molecular weight are compared in Table II. At the same polymerization conditions, it can be seen that D1007P and D1018P have a similar molecular weight and HYDAP's molecular weight is higher than that of D1007P and D1018P. Theoretically, compared with D1007P, D1018P is expected to have more crosslinks, branched structures, and relatively larger molecular weight polydispersity, due to its higher content of trimer and monomer acids. Because both the contents of trimer and monomer acids are higher in 1018 than in 1007, where the trimer acid may result in an increase and monomer acid may cause a decrease in molecular weight, it was not surprising that a similar molecular weight was obtained for

D1007P and D1018P. It should be mentioned that the end group analysis method used to calculate molecular weight in this case is only based on the amount of end groups in the system; it cannot represent the molecular structure factor, let alone the polydispersity. The higher molecular weight of HYDAP may be attributed to its higher purity of dimer acid, which could construct the fine and long liner macromolecular chain.

Table IV lists the thermal and mechanical properties of HYDAP, D1018P, and D1007P. First, we can see that HYDAP's T_g is almost 20°C lower than that of D1018P and D1007P. This result may be attributed to the fact that the hydrogenated dimer acid has less rigid saturated segments,²⁸ because an unsaturated dimer acid may likely form a conjugated molecular complex²⁹ through its double bonds and restrict the segments' motion accordingly. As for D1018P and D1007P, it is reasonably assumed that, within experiment error, they have the same T_g . Although the hydrogenated dimer acid gives a significantly lower T_g than the nonhydrogenated one, the T_m for these two types of polyamides is almost the same. However, we did find that the melting temperature of D1018P was 6°C lower than that of D1007P and HYDAP. The lower melting temperature may imply a lower-ordered crystalline morphology due to its more heterogeneous molecular structure (more trimer acid content) in D1018P. The lower enthalpy of fusion of D1018P may further confirm this point. For more details about their crystalline structure, we conducted X-ray diffraction measurements for these samples; unfortunately, we did not find more useful information to discern their difference, except a common sharp diffraction peak at $2\theta = 20^\circ$.

It can also be seen from Table IV that HYDAP possesses the higher Young's modulus and stress at break, compared with D1007P and D1018P. This may be a result of its large molecular weight and relative homogeneous crystalline structure.

Comparing D1018P with D1007P, the higher tensile stress and Young's modulus for D1018P may be attributed to the more microcrosslinking structure in its amorphous phase.

CONCLUSIONS

The molecular weight of soy-based polyamides through polycondensation reaction of different dimer acids and diamines can be effectively controlled by controlling the reaction temperature. The optimum reaction temperature that can synthesize higher molecular weight polymers is in the range of 260° to 300°C. Polyamides prepared from 1,4-phenylenediamine possess higher T_g , T_m , and decomposition temperature, and show stronger mechanical strength than that of aliphatic polyamides. The results can be attributed to the influence of flexibility of aromatic and aliphatic diamine segments on the polymers' crystallization behavior and different morphology. X-ray diffraction data indicate that dimer acid-based polyamides are typical semicrystalline polymers. A polyamide made from a hydrogenated dimer acid has a lower T_g and higher mechanical strength, compared with polyamides made from an unsaturated dimer acid. This indicates that the flexibility of the dimer acid and its macrostructure, such as the content of monomer and trimer acids, still play a role in effecting the polymer's properties.

The financial support of the Ohio Soybean Council is greatly acknowledged. Dr. Emmanuel Karikari and Dr. Issifu Harruna of Clark Atlanta University are thanked for helping conduct X-ray diffraction measurements and for allowing us to use their DSC instrument.

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