Synthesis and Characterization of Soy-Based Copolyamides with Different α -Amino Acids

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ABSTRACT: A series of soy-based copolyamides with different amino acid contents was synthesized by a condensation polymerization technique. The physical properties and enzymatic degradation properties were investigated. It was found that the introduction of amino acids into this type of copolyamide does not enhance the biodegradation ability but does improve the swelling properties of the copolyamides in water at a relative high pH and temperature. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 1081–1088, 1999

INTRODUCTION

Incorporating α -amino acids into polyamide matrix has been reported in a series of recent publications.¹⁻⁴ The idea of using different amino acids in these researches stems not only from the fact that α -amino acids are very reactive monomers with diamines and diacids but also that amino acid-containing copolyamides are endowed with various interesting properties, such as decreasing crystallinity, increasing solubility in various solvents, and, most importantly, enhancing bio- and chemical degradation behaviors. However, no study has been reported in the literature regarding the synthesis and characteristics of amino acid-containing polyamides using a soy-based monomer.

Soy-based polyamides obtained from condensation copolymerization of soy dimer acids and different diamines are widely used as hot-melt adhesives and coating materials.⁵ Recently, we successfully used soy-based polyamides as toner resins for copiers.⁶ It was also found in our study that the waste papers printed by the soy-based toners were easily deinked if the toner particles

could be swelled during waste paper repulping. This result provides new information to the toner producers for developing a deinkable toner for office copiers. Generally speaking, the swellability of a polymer can be enhanced by introducing ionic groups into a copolymer backbone because ionic groups in a polymer backbone can increase the affinity between polymer chain and water molecules and, at the same time, reduce the crystallinity of the polymers. Soy-based polyamides, due to their special molecular structure of dimer acid, possess relatively excellent thermal and mechanical performance.^{6,7} However, because of their high crystallinity, poor swellability and bioand chemical degradation characteristics were observed. One of the effective methods to improve these characteristics is to incorporate amino acids into the polyamides backbone so that the crystallinity can be decreased and the affinity between polymer and water molecules can be increased. Although soy-based copolyamides with some amino acids have been explored in a previous study,⁶ the effect of different functional groups in amino acids on the polyamide properties has not been studied, and this effect may be significant for some amino acids but unimportant for others. For example, phenylalanine has a similar molecular structure to tyrosine, except that tyrosine carries an extra phenolic group in its para position of benzene ring. If both amino acids are in-

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| Monomer | Acronym | Structure | $T_m\left(^{\circ}\mathrm{C} ight)$ |
|---------------------------------|---------|---|-------------------------------------|
| Dimer acid | D1016 | $CH = CH(CH_2)_7COOH$ $CH_3(CH_2)_5 \qquad (CH_2)_7COOH$ $CH_3(CH_2)_5 \qquad (CH_2)_7COOH$ | Liquid at room temperature |
| 1,4-Phenylene– diamine (99%) | Р | H_2N N NH_2 | 143–145 |
| L-Tyrosine | Т | $\begin{array}{c} H_2N-CH-COOH \\ \\ CH_2 \\ \downarrow \\ OH \end{array}$ | 135 |
| L-Phenylalanine | РН | HO-CH-COOH \downarrow CH ₂ | 270-275 |
| L-Glutamic acid | G | $\begin{array}{c} \mathrm{HOOCH_{2}CH_{2}CHNH_{2}} \\ \\ \mathrm{COOH} \end{array}$ | 148 |

Table I Characteristics of the Monomers

corporated into copolymer chains, respectively, it could be expected that the tyrosine-based copolymer may appear to have much larger swelling ability than phenylalanine-based copolyamide due to the hydrophilic character of the phenolic hydroxyl group in tyrosine.

The objective of this study is to investigate the effect of different amino acids on the physical properties of soy-based polyamides. A series of amino acids with different functional groups was selected in this study. The copolymers' thermal, mechanical, and swelling behavior in water were compared and analyzed in accordance with amino acid's molecular structure and different functional groups. The biodegradation of these soybased polyamides was examined.

EXPERIMENTAL

Materials

Dimer acid used in the synthesis was supplied by Emery Group of Henkel Corporation (Cincinnati, OH). Empol 1016 dimer acid is a yellowish, viscous liquid at room temperature with the ratio of dimer, trimer, and monomer at 97 : 2 : 1. 1,4-phenylenediamine, L-glutamic acid, and L-phenylalanine were purchased from Aldrich (Milwaukee, WI). L-tyrosine (1-3[4-hydroxyphenyl]-alanine) was obtained from Sigma (Louis, MO). All chemicals were used as received. Their acronyms, reported purity, molecular structure, and melting point are listed in Table I.

Enzymes used in polymer degradation experiments are shown in Table II.

Copolyamide Synthesis

Copolymers were synthesized by condensation polymerization. Among feeding comonomers, the content of amino acids was varied while the dimer acid and phenylenediamine were kept stoichiometrically constant. A typical example of polymerization for a copolymer with 11 mol % of feeding glutamic acid is given as follows: 50 g of dimer acid (equivalent to 0.174 mol acid groups) was

| Enzyme | Supplier | Unit Definition | pH Used | Temperature (°C) |
|-----------|--------------------|--|------------|---------------------|
| Trypsin | Sigma Chemical Co. | Hydrolyses 1 mmol <i>p</i> -toluene sulphonyl-L-arginine methyl ester per min @ pH 8.1, 25°C | 8.1 | 25 |
| Esterase | Sigma Chemical Co. | Hydrolyses 1 mmol ethyl butyrate per min @ pH 8.0, 25°C | 8.0 | 25 |
| Xylanase | Fluka Chemical | Hydrolyses 1 mmol remazol brilliant blue R-xylan per min @ pH 5.4, 30°C | 5.4 | 25 |
| Cellulase | Fluka Chemical | Hydrolyses 1 mmol OBR-hydroxyethylcellulose per min @ pH 4.8, 30°C | 4.8 | 25 |
| Lipase | Fluka Chemical | Hydrolyses 1 mmol oleic acid per min @ pH 8.0, 37°C | 8.0 | 25 |

Table IIEnzymes Used

charged in a 250-mL three-necked round-bottom flask equipped with a mechanical stirrer, a thermometer, and a nitrogen inlet. The dimer acid was first heated to 80°C under a nitrogen atmosphere and vigorous stirring, then 9.6 g of 1,4phenylenediamine (equivalent to the total acid groups) and 3.6 g of L-glutamic acid were added, respectively. The reactants were gradually heated to 250°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 250°C and subjected to vacuum of approximately 2 mmHg for 4 h. The product was then discharged from the flask.

Differential Scanning Calorimetry and Thermal Gravimetric Analysis

Differential scanning calorimetry (DSC) measurements were performed on a SEICO DSC equipped with a thermal analysis station. Thermogravimetric analysis (TGA) measurements were carried out on a SEICO TGA. Both DSC and TGA measurements were performed under nitrogen at 20 and 10°C heating rates, respectively.

Enzymatic Degradation Tests

Enzymatic degradation tests were conducted in the presence of different enzymes at the optimum pH (provided by the supplier; see Table II) and at 25 and 35°C. Dilute sulfuric acid (0.2N) or sodium hydroxide (0.2N) was used for pH adjustment.

In weight loss measurements, each polymer film contains 0.2 g of sample with a surface area of 15

 \times 10 mm². The enzyme solutions were prepared by dissolving 0.045 g of an enzyme in 30 mL of distilled water. The sample films were placed in selected enzyme solution. After required reaction time, the samples were washed in distilled water and dried in an oven to a constant weight at 50°C. The difference between the weights of polymer films before and after interaction with enzyme solution was recorded. The effect of enzymatic degradation on the samples was further studied by measuring the total organic carbon (TOC) component in the solutions, corresponding to the amount of water-soluble hydrolyzed products with a TOC instrument (Shimadzu, Japan). Incubating conditions of the polymer films for TOC tests were basically the same with the weight loss measurements. However, blank TOC tests were carefully conducted in the buffer solutions containing either only the enzymes or only the polymers. These results were deducted late from the results of enzymatically incubated solutions to determine the net TOC values, which were due exclusively to the enzymatic hydrolysis of polymers.

Swelling Test

Water uptake of the samples was determined in aqueous solutions under different pH values at 70°C for 24 h. The experiment was conducted as follows: dry polymer film samples with a fixed surface area and thickness $(10 \times 10 \times 0.01 \text{ mm}^3)$ were carefully weighed before being placed in a 100-mL vial containing a certain pH value solution. The vial was put into an isothermal water bath with a fixed temperature for 24 h. The polymer sample was then taken out from the solution,





washed with distilled water, wiped using a filter paper, and weighed. The weight ratio of dry and wet samples was recorded.

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 are 15 mm in width and 200 (\pm 50) μ m in thickness. A 50 mm gauge length and a 5 mm/min crosshead speed were used.

RESULTS AND DISCUSSION

Synthesis of Copolyamides with Different Amino Acids

In order to study the influence of the functional groups and molecular characteristics of amino acids on the copolymer's chain structure and morphology, as well as their physical properties, three different amino acids (Table I) were selected as reaction monomers. Among them, glutamic acid possesses the strongest polar effect due to its carboxylic acid group, and tyrosine has a relatively weaker polar effect because phenolic hydroxyl is less polar than that of carboxylic acid. It is expected that if the charge strength in copolyamide varies systematically, the physical properties of copolymers, including their swelling, mechanical, and thermal behavior, will sustain significant difference.

The synthesis results indicated that three amino acids are all quite reactive with dimer acid and phenylenediamine. Among the reaction conditions, the reaction temperature is the most important, that is, a lower temperature leads to lower molecular weight (determined by the hardness of the polymer and the viscosity of the polymer solution) and poor mechanical properties. The optimum reaction temperature range selected was 250-300°C. Besides, the protection of nitrogen is also important for this condensation reaction because phenylenediamine is very sensitive to oxygen. Without the nitrogen, the polymers will appear dark brown in color, indicating that phenylenediamine is being changed into a quinoid structure.



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Figure 1 DSC measurements for tyrosine-containing copolyamides.

It should be pointed out that glutamic acid and tyrosine have three functional groups in their chain segments; therefore, several chainlinkage combinations as well as crosslinking structure could be created among them. However, based on fundamental organic chemistry, the most possible chain structures for three copolymers are shown in Table III.

The content of amino acid will significantly affect the apparent physical properties of the copolymers. Accordingly, the melting point and the viscosity of melted copolymers decrease with increasing content of amino acid. For the copolyamides containing less than 25 mol % of amino acid, the final products are brittle solids. However, for the copolyamides containing more than 30 mol % of amino acid, the final products are soft and tacky at room temperature. The thermal and mechanical properties of the copolymers can further prove this conclusion.

Thermal Properties

The thermal analysis results of three copolyamides are shown in Figures 1-3, respectively. Evidently, the copolymer's T_g (glass transition temperature) and T_m (melting temperature) are gradually decreased as the amino acid content is increased. First, at 11 mol % of amino acid, the copolymer with glutamic acid has higher T_g and T_m compared to other copolymers. It should be noted that the ratio of amine groups to carboxyl is higher than that for glutamic-containing polyamides (glutamic has two carboxyl groups but only one amine group), which suggests that there are some free carboxyl groups in the polyamide backbone. Therefore, the enhanced T_g and T_m may be attributed to the strong hydrogen bonding among these free carbonyl acid groups and protons. However, there is no obvious difference in



Figure 2 DSC measurements for phenylalanine-containing copolyamides.



Figure 3 DSC measurements for glutamic acid-containing copolyamides.

their T_g and T_m for the copolymers with tyrosine and phenylenediamine. This may reflect that hydrogen bonding among hydroxyl groups is really weak, which could not effectively affect their T_g and T_m . Interestingly, when amino acid content increased to over 22 mol %, the three copolymers' T_g and T_m were basically showing the same values, except for the T_g of glutamic acid-containing copolymer, which was 13.4°C at 26% molar content.

The influence of the amino acid content on the melting temperature of the copolyamide measured by DSC is shown in Figures 1–3. It can be clearly seen that the melting peak of crystals for three series of amino acid-containing polymers is gradually reduced with increasing mole content of amino acid. Compared to homopolyamide (without amino acid), the decrease in T_g and T_m of copolymers may be attributed to the presence of heterogeneous segments of amino acid in the soybased homopolyamide. These heterogeneous seg-

ments will interrupt the original regular chain structure and crystalline morphology of the polymer and inhibit crystallization during the cooling of the polymer.

Mechanical Properties

The mechanical properties of copolyamides are shown in Table IV. Clearly, the three copolymers' mechanical performance gradually declines with increasing amino acid content. Compared to the homopolymer, the three copolymers' Young's modulus and stress at break decline greatly; however, strain at break appears a little different. For the copolymer with glutamic acid, the strain at break lowered slightly; but for the others with tyrosine and phenylalanine, the strain at break gradually increases with increasing amino acid. The results may indicate that copolymer with glutamic acid possesses more brittle characteristics due to strong molecular interaction. As for the copolymers with tyrosine and phenylalanine, the relative weak molecular interactions cause these amino acids to act as internal plasticizers, which leads to molecular chain slipping during stretching and increases the strain at break accordingly.

Biodegradation Test

To examine the enzymatic hydrolysis behavior of soy-based polyamide resins, six different enzymes that had been used for the polymer degradation in previous studies⁸⁻¹¹ were used in the experiment. It was reported that nylon-66 can be degraded by trypsin, papain, and α -chymotrypsin, although the degradation of the polymer is slow.¹² It was also reported that by incorporating amino acids into polyamides, the biodegradation of the polyamides will be improved.^{13,14} However, experimental results from our study indicate that the weight loss of the polymer film is less than 0.05% for all of the enzymes after 1 week's reaction with enzyme solutions. Within the experiment error, these weight losses could be reasonably considered as insignificant.

To confirm the above results, the total organic carbon (TOC) measurements for all amino acidcontaining samples were conducted under the same incubating conditions as used in the weight loss experiment. It was still found that within the experimental error, the TOC data (not present here) did not show any significant variations for all samples. Both weight loss and TOC data may

| | Young's Modulus | Stress at Break | Strain at Break | |
|-----------------------|-----------------|-----------------|-----------------|--|
| Copolyamide | (MPa) | (MPa) | (%) | |
| Homopolymer | 2116.0 | 33.30 | 5.30 | |
| Copolymers with tyros | sine: | | | |
| 11 mol % | 330.8 | 6.84 | _ | |
| 22 mol % | 281.2 | 7.94 | 9.05 | |
| 26 mol % | 105.9 | 2.30 | 15.1 | |
| Copolymers with gluta | amic acid: | | | |
| 11 mol % | 242.9 | 5.89 | 3.27 | |
| 22 mol % | 288.8 | 5.94 | 2.92 | |
| 26 mol % | 192.6 | 2.65 | 2.38 | |
| Copolymers with phen | ylalanine: | | | |
| 11 mol % | 183.2 | 9.26 | 13.09 | |
| 22 mol % | 118.7 | 6.57 | 31.90 | |
| 26 mol % | 48.0 | 3.35 | 41.89 | |

Table IV Mechanical Properties of Copolyamides

suggest that soy-based polyamides are nonbiodegradable under these conditions.

The reasons for the difference in the biodegradation characteristics between the polyamides reported in the literature^{13,14} and the soy-based amides made in this study are complicated. It has be known from the above discussion that the polyamides prepared from soybean dimer acids have a semicrystalline structure. It is generally accepted that the enzymatic hydrolysis of a semicrystalline polymer may take place in two stages.¹⁵ First, enzyme molecules will preferentially penetrate into the amorphous region through swelling of the polymer and then selectively scissor off molecular segments with special chemical linkages. Second, when potential biodegradable chemical linkages were exhausted in the amorphous phase, the hy-



Figure 4 Water uptake at different pHs for tyrosinecontaining copolyamides.

drolysis moved to degrade the segments in crystalline region. Because of the swelling and hydrolysis of the amorphous region, the enzyme molecules attach to the crystal part of the polymer easily, resulting in damage to the semicrystalline structure. The effect of swellability of polymer on the biodegradation was also reported by Hayashi et al.¹⁶ Based on this theory, polymer's structure and swelling property should play a very important role in the enzymatic degradation process.

Swelling Behavior

The swolling of the polymers at 70° C in different pH solutions are shown in Figures 4–6, respectively. Compared with homopolyamide (Fig. 4),



Figure 5 Water uptake at different pHs for phenylalanine-containing copolyamides.



Copolyamide with glutamic acid

Figure 6 Water uptake at different pHs for glutamic acid-containing copolyamides.

the water uptake percentages of the three copolyamides gradually increase with the increase in the amino acid feeding content. As discussed previously, several possible factors may contribute to these results. First, incorporating amino acids actually introduces more hydrophilic functional groups into the polymer chain, which can attract more water molecules into polymer matrices. Second, reacting amino acid with dimer acid and phenylenediamine could effectively decrease the molecular weight and reduce the crystallinity. Therefore, the water molecules penetrate into the polymers more easily, resulting in an improvement of polymer swolling in aqueous solutions.

From Figures 4–6, little changes of water uptake percentage for the three copolymers at lower pH conditions can be observed. However, there is a remarkable increase of water uptake at high pH values for three polymers, especially at pH 12. These results are expected because both phenolic and carboxyl groups in the amino acids can form a salt under alkaline conditions.

It was noted that glutamic acid contains more carboxyl groups than tyrosine and phenylalanine do. Therefore, it is expected that the glutamic acid-containing copolyamide should have the highest degree of swelling in alkaline solution. Figure 6 shows that the water uptake for the copolyamide with 26 mol % of glutamic acid reaches 100% at pH 12, which supports the above assumption.

CONCLUSIONS

The amino-acid-containing soy-based copolyamides can be synthesized by condensation polymerization of soy-based dimer acids, diamines, and amino acids. The copolymers did not show significant enzymatic degradation properties under the conditions used in this study. However, the copolyamides containing glutamic acid are swollable in aqueous solutions at high pH and temperature. The type and the content of the amino acids in the copolyamides are two important factors affecting the chain structure and crystalline morphology, as well as the physical properties of the copolymers.

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