Morphology and Thermal Properties of Nylon Copolymers Containing Dimer Acid, Adipic Acid, and Hexamethylenediamine

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ABSTRACT: The effects of the molar ratio of adipic acid to total diacid on the phase morphology and thermal properties of nylon copolymers containing dimer acid, adipic acid, and hexamethylenediamine were investigated. A significant structural transition from the γ form to α and β mixture forms occurred with increasing molar ratio. Meanwhile, the content of the crystals increased markedly. A σ–π* hyper conjugation effect was present in all of the as-prepared samples. A strong σ–π* hyper conjugation effect could decrease the average distance between interchain amide groups and suppress the scission of the C—N bond through the formation of highly combining aza double-bond C=N groups, which would, consequently, make the nylon copolymer much more stable. Differential scanning calorimetry–thermogravimetric analysis results indicate that the low thermal stability of the nylon copolymers with higher molar ratios of adipic acid to total diacid was simply due to the formation of cyclopentanone and caprolactam at 350–420°C, whereas for the nylon copolymers with lower molar ratios, the scission of the C—C bond at 430–500°C directed the pyrolysis of the main chain. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 119: 2511–2516, 2011

Key words: morphology; nylon; thermal properties

INTRODUCTION

In recent years, dimer acid (DA)-based nylons have received a significant amount of attention because of their wide applications in the preparation of engineering and biomaterials as a result of the distinctive properties of DA, such as its nontoxicity, low cost, biodegradability, and low-temperature properties.[1,2]

For practical applications, DA-based nylons are often required to possess high mechanical properties and sufficient thermal stability. Because the bulk phase of most DA-based nylons contains a low volume density of amide groups, DA-based nylons tend to interact weakly with hydrogen bonds. The effects of reinforcing modifiers on the mechanical properties of DA-based nylons have been documented.[3–9] Cavus and Gürkaynak[3] thought that the type and content of the monofunctional reactants were important factors governing the formation of interchain hydrogen bonds caused by the orientation and density of the amide groups, which, thus, remarkably affected the crystallization and greatly influenced the physical properties, such as glass-transition temperature, melting point, heat of fusion, degree of polymerization, number-average molecular weight, and kinematic viscosity, of DA-based nylons. Fan et al.[1] reported that the mechanical properties strongly depended on the molecular weight and flexibility of the diamines used and were further enhanced when shorter chain diamines were added. Similar reinforcement was also observed for many other polar-group-containing modifiers, such as adipic acid,[4] decanedioic acid,[5] caprolactam,[6] and α-amino acid.[7]

Moreover, reaction kinetic studies have been carried out to optimize the processability conditions for industrial production.[10–13] For example, Kale and coworkers[10,11] even found that the reaction between ethylenediamine and DA in the melt phase in the temperature range 124–190°C was second order with an activation energy (E_a) of 76.4 kJ/mol for a conversion of up to 90%, but for higher conversions or conversions with benzyl alcohol as a solvent, the reaction was third order with E_a's of 68.9 or 128.5 kJ/mol, respectively. Heidarian et al.[12,13]

proved that the order of the reaction at conversions above 90% could change from second to third order.

Adipic acid is a potential reinforcement agent for modification because of its low toxicity and tendency to lead molecular main chains to aggregate to form a perfect arrangement, which may then change the crystallization behavior or improve the mechanical properties of DA-based nylons for various application purposes. Most studies have been concerned with mechanical properties, and there has been scarce literature on the correlation between the structure and thermal degradation behavior, although the thermal degradation behavior is strongly dependent on the structure. It is of paramount importance to understand the effect of the structure on the thermal degradation mechanism in the development of a rational technology of processing in high-temperature applications and in the synthesis of firesafe materials. For this reason, in this study, the effect of adipic acid on the morphology and thermal behaviors of nylon copolymers containing DA, adipic acid, and hexamethylenediamine was investigated. Our purpose was to verify whether the crystal forms changed with adipic acid and to determine the way adipic acid affected the thermal degradation properties of the nylon copolymers containing DA, adipic acid, and hexamethylenediamine.

EXPERIMENTAL

Materials and copolymers synthesis

DA was supplied by Jiangsu Yonglin Chemical Oil Co., Ltd., China with a monomer/dimer/trimer ratio of 0.2 : 98.7 : 1.1. Hexamethylenediamine and adipic acid were purchased from Sinopham Chemical Reagent Co., Ltd., China, and hexamethylenediamine salt of adipic acid was synthesized with the standard chemical salification method. Hypophosphorous acid was obtained from Wuhan Hongxin Chemical Industry Co. Ltd., China.

Hexamethylenediamine salt of adipic acid (2086.7 g; the salification method was based on that given in ref. 14), hexamethylenediamine (242.6 g), hypophosphorous acid (3.0 g), and demineralized water (1552.0 g) were introduced into a 10-L, four-necked reactor equipped with a thermometer, mechanical stirrer, nitrogen inlet (also a dropping funnel), and distilling water outlet. The monomers were first heated to 140°C with stirring in a nitrogen atmosphere, and then, 1137.2 g of DA equivalent to the amine groups of hexamethylenediamine was steadily added over a period of 2 h. The reactants were gradually heated to 285°C within t_1 hours and then subjected to a vacuum of approximately 0.0118 atm for another t_2 hours. The product was drawn off, cooled, granulated, and dried. Eight series of nylon

TABLE I
Polymerization Conditions of the Nylon Copolymers

Adipic acid/ (DA + adipic acid) molar ratio (%)	t_1 (h)	t_2 (h)
0	5	4
10	4	4
25	3	2
40	2	2
50	1	1.5
60	0	1
75	0	0.5
90	0	0.25

copolymers with different molar ratios of adipic acid to total diacid were synthesized according to the synthesis procedure given previously.

The polymerization conditions are listed in Table I. It is worthwhile to note the t_1 and t_2 caused by the incorporation of adipic acid had obvious declines when the molar ratio of adipic acid to total diacid was raised from 0 to 90%. These concentrations of active carboxylic and amino groups were determined by the length of the main chain of the binary acid to be the different collision and the resulting reaction probability between the carboxylic and amino groups, which may account for the discrepancy in the polymerization times among the reaction systems with the different molar ratios.

Characterization

The number-average molecular weight of the prepared nylon copolymers was determined from the combined content of acid and amine end groups[1] by the titration of their solution in benzoic alcohol solvent. This resulted in a number-average molecular weight of about 30, 000 g/mol.

All of the samples were prepared by the casting of 3% solutions of the copolymer nylons in N,N-dimethylacetamide onto glass plates and the evaporation of solvent and formation of films at room temperature; then, traces of solvent were dried in vacuo at 70°C for 72 h. The solution-cast films, whose thickness was about 20 μm, were removed and used directly for Fourier transform infrared (FTIR) and ultraviolet–visible (UV–vis) measurements.

The functional groups of the nylon copolymers were analyzed with a PerkinElmer System 2000 FTIR spectrometer. UV–vis absorption spectra of the samples were collected in air on a UV–vis UV-2500PC spectrophotometer (Shanghai, China). Differential scanning calorimetry (DSC) curves of the annealed samples were recorded on a PerkinElmer Pyris-1 differential scanning calorimeter (Waltham, MA), and thermogravimetric analysis (TGA) was performed
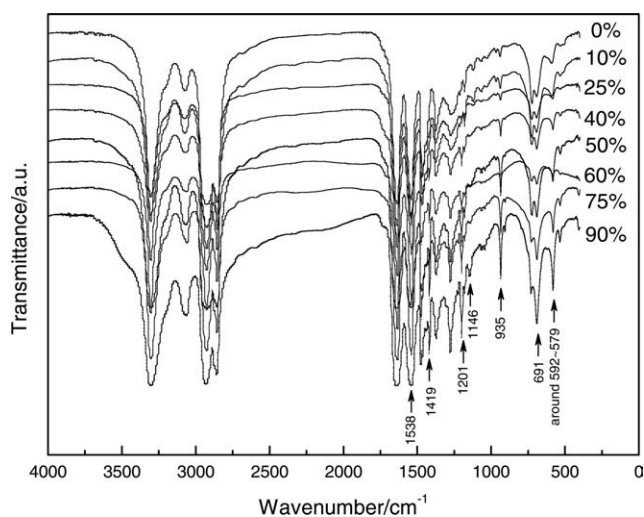
Figure 1 Infrared spectra of the nylon copolymers with different molar ratios of adipic acid to total diacid recorded at room temperature in an ambient atmosphere.

on a PerkinElmer TGA-7 thermobalance at a heating rate of 20°C/min in a nitrogen atmosphere.

RESULTS AND DISCUSSION

FTIR spectroscopy analysis

Figure 1 presents the FTIR spectra for the as-prepared samples as a function of adipic acid/ total diacid molar ratio. The band around 1201/ 1146 cm^{-1} was attributed to the skeletal vibration of N—C=O. The absorption peaks indicated the presence of amide groups in the nylon copolymers.

The band due to N—H bending and C—N stretching was seen around 1538 cm^{-1}, which was previously assigned to the α form of various nylons as the amide II band, according to Bradbury and Elliot[15] and Arimoto.[16] Besides the amide II band, the 950–500-cm^{-1} region of the spectrum was informative in light of the phase content and was especially sensitive to the crystal form, which appeared at 935/691 cm^{-1} as the amide IV/V band for the α form.[17–24] The peak around 580 cm^{-1}, as the amide VI band, has been assigned to the α and β mixture forms.[20–24] The band around 1419 cm^{-1} originated from the scissoring mode of the CH$_2$ units.[20,24,25] The more the molar ratio increased, the greater the intensity of these main absorption bands was, which indicated an increasing content of the α and β crystal forms with increasing molar ratio.

On the basis of previous XRD studies by Fan et al.,[1] a diffused peak at $2\theta = 20°$ was assigned to the γ crystal form for the sample with a 0% molar ratio. The intensity of the main bands shown in Figure 1 corresponding to the α and β crystal forms was very weak and was hardly even observed with

increasing molar ratio from 0 to 25%. At the same time, the intensity of the band at 592 cm^{-1}, associated directly with the γ crystal form, remained constant. However, as the molar ratio increased from 25 to 40%, the band at 592 cm^{-1}, assigned to C=O bending, abruptly redshifted approximately 13 cm^{-1}. This strongly suggested that the strengthening of hydrogen bonds favored the disappearance of the γ crystal form and the emergence of the α and β crystal forms.

Clearly, when the short adipic acid segments were locally incorporated into the DA-based nylon, the strong intermolecular hydrogen bonds led molecules to aggregate to form a more perfect morphology. This resulted not only in an obvious increase in the content of the α- and β-form crystals but also in a significant structural transition from the pseudohexagonal γ form to the more stable α and β mixture forms. Perhaps the structural transition of the nylon copolymer took place between 25 and 40%.

UV–vis spectroscopy analysis

UV–vis spectroscopy provided information about the σ–π* hyper conjugation effect between the σ orbit of the N—H bond and the π* orbit of the C=O bond for the as-prepared samples with various adipic acid/total diacid molar ratios. A sharp absorption band around 190–300 nm assignable to σ→π* electronic transition was observed in Figure 2. With increasing molar ratio from 0 to 25%, the wavelength of the spectra at maximum intensity blueshifted 16 nm and then redshifted 33 nm with a further increase in the molar ratio from 25 to 50%. Similar behavior was observed with an increase in the molar ratio from 50 to 100%. The blueshifts
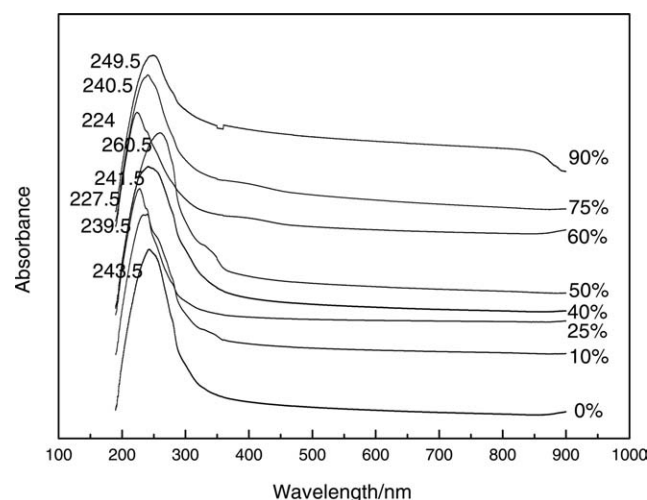

Figure 2 UV–vis absorption spectra of the nylon copolymers with different molar ratios of adipic acid to total diacid.
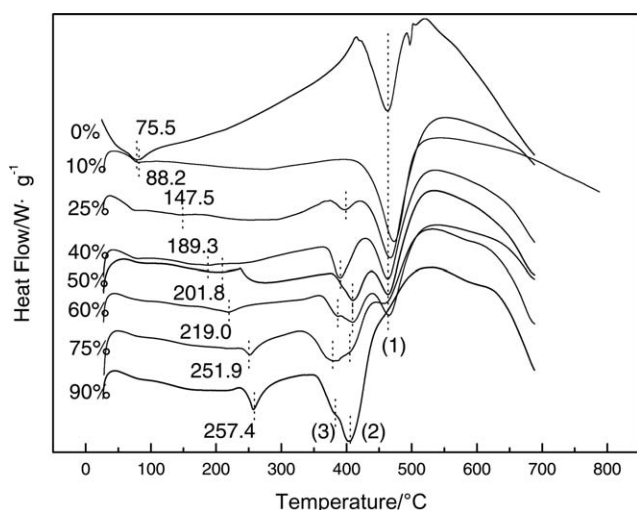
Figure 3 DSC curves of the nylon copolymers in a nitrogen atmosphere as a function of the molar ratio of adipic acid to total diacid.

associated with weakening of hydrogen bonds showed the increasing average distance between the interchain amide groups, whereas the redshifts associated with the strengthening of hydrogen bonds showed the decreasing average distance between the interchain amide groups. The shifts were unchanged proportionally with the molar ratio, which was unexpected and indicated that the shifts were due to the cooperative generation of changes in both the volume density of amide groups and the σ–π^* hyper conjugation effect. The difference in the chain length of DA and adipic acid led to the periodic change of average distance between the interchain amide groups.

Thermal properties

The DSC melting curves of the as-prepared samples in N_2 in Figure 3 showed that a series of stepwise annealing treatments at steadily increasing temperatures resulted in only a single endothermic peak at 80–260°C, which indicated that the nylons were just the random copolymers not the homopolymers. As the molar ratio increased, the annealing peak at lower temperatures shifted to higher temperatures and was accompanied by an increase in its peak area magnitude. This may have been due to the difference in both the crystal content and the force of the hydrogen bonds, as shown in Figures 1 and 2.

The endothermic behavior of the as-prepared samples was very complicated at 350–500°C. The samples exhibited only an endothermic peak (peak 1 in Fig. 2) around 462°C with increasing molar ratio from 0 to 10%. For molar ratios higher than 25%, four changes were noticed: a decrease in the intensity of peak 1, a gradual increase in the intensity of

the endothermic peaks (peaks 2 and 3 in Fig. 2) around 350–430°C, the overlap of peaks 2 and 3, and a significant shift in the latter two peaks toward low temperatures.

Peaks 2 and 3 overlapped, which implied that at least two overlapping steps took place and that there might have been some consecutive reactions. This was consistent with the observations of Herrera et al.[26] of a two-step model with competing reactions but was in conflict with the single-stage degradation put forward by Ghosh et al.[27] According to the literature,[26,28] one may speculate that the peak 3 was due to cyclopentanone formation and peak 2 originated from caprolactam formation because cyclopentanone has a relatively stable pentatomic ring. Peak 1 was probably due to the scission of the C—C bond with higher dissociation energy in the molecular skeleton of DA.

TGA of the sample with a 50% molar ratio in N_2 showed a weight loss of about 1.22% at 236°C (Fig. 4). However, for the sample with a 10% molar ratio, the weight losses were about 1.41% at 172°C and 0.67% at 257°C. This initial weight loss at 172°C did not result from a loss of physisorbed water but from a loss of structural water from the surface of the sample, whereas the weight losses above 200°C may have been caused by the polymerization reaction of a small amount of terminated groups. This implies that, for the two samples, their terminated groups had more chances to collide with each other, which was correlated to the average distance between macromolecules, as shown in Figure 2.

As shown by differential TGA (Fig. 5), the pyrolysis of the main chain occurred over 350°C and finished at around 500°C. The residue left was about
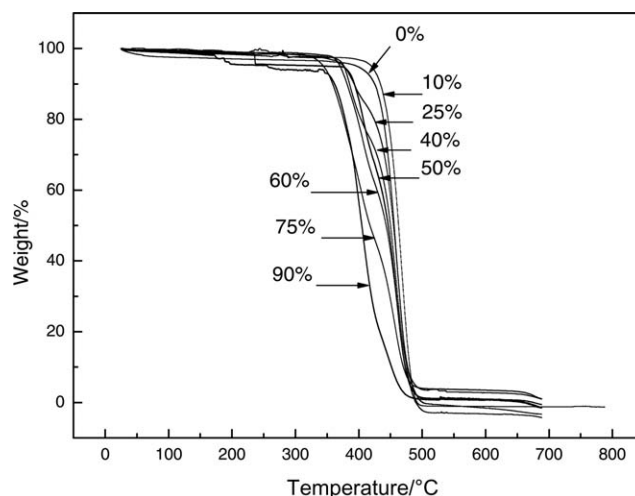

Figure 4 TGA curves of the nylon copolymers in a nitrogen atmosphere as a function of the molar ratio of adipic acid to total diacid.
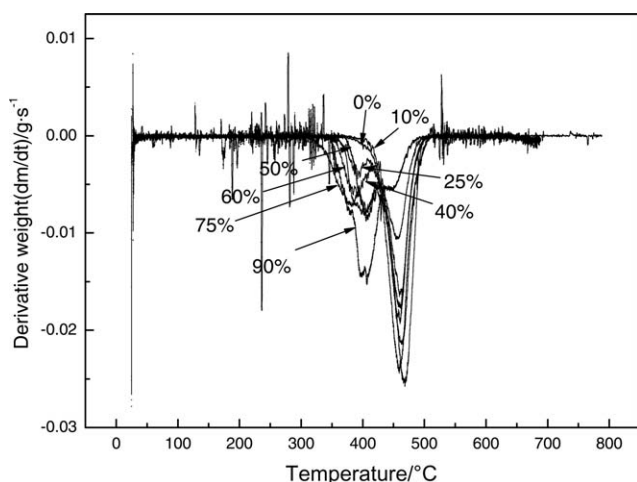
Figure 5 Differential thermogravimetry curves of the nylon copolymers in a nitrogen atmosphere as a function of the molar ratio of adipic acid to total diacid.

0%. For the sample with a 0% molar ratio, the decomposition began at 426°C. As the molar ratio increased from 0 to 10%, the decomposition temperature increased about 11°C, which indicated that the stability of sample improved. The strong decrease in the thermal stability of the sample with increasing molar ratio from 10 to 90% could be attributed to the formation of cyclopentanone at 350–400°C and the formation of caprolactam at 370–420°C. As shown in Figures 4 and 5, the TGA and differential thermogravimetry curves of the samples displayed two distinct regions of weight loss. Meanwhile, their maximum rate of corresponding regions in Figure 5 increased continuously along with the decrease in the maximum rate of decomposition at 440–500°C. This indicates that the incorporation of adipic acid into the DA-based nylons deteriorated the thermal stability of the DA-based nylons significantly. For the samples with 50 and 90% molar ratios, the decomposition temperature showed a considerable increase at about 16 and 25°C, respectively, compared to the samples with 40 and 75% molar ratios. The strengthening of σ–π* hyper conjugation decreased the average distance between interchain amide groups and then resulted in the formation of highly combining aza double-bond C=N groups.[28] On the other hand, polymerization between amino groups and carboxyl groups, which eliminated the unstable terminated groups, may have retarded the thermal degradation of the samples.[29]

To further investigate why the nylon copolymers with lower molar ratios had excellent stability, the decomposition processes were simplified, and some fundamental assumptions were introduced. The decomposition reaction was presumed to be basi-

cally a rate-determining step where the Arrhenius equation was applicable; however, the diffusion of pyrolysis gases was assumed to be under an equilibrium state. On the basis of these assumptions, it was possible to establish eq. (1) and to interpret it as a function of known factors:

$$d\alpha/dt = k_0\exp(-E_a/(RT))(1-\alpha)^n \qquad (1)$$

where α is the extent of the reaction, t is the reaction time, k_0 is the pre-exponential factor, E_a is the activation energy, T is the thermodynamic temperature, and n is the apparent reaction order.

The kinetic parameters n and E_a of the pyrolysis steps were determined with a combination of the Coats–Redfern and Levenberg–Marquardt methods.[30,31] It turned out that the n values were 1.5 for peak 1, 3.0 for peak 2, and 5.1 for peak 3. The E_a values were 274 kJ/mol for peak 2 and 195 kJ/mol for peak 3. Meanwhile, E_a decreased slightly with increasing molar ratio. E_a for peak 1 was 340 kJ/mol. This value was very close to that corresponding to the dissociation energy of the aliphatic C—C bond (E_a = 347.5 kJ/mol). This confirmed that it was the scission of the C—C bond in the molecular skeleton of DA rather than the C—N bond that played a dominant role for peak 1 in the thermal degradation of the nylon copolymers under the given conditions. Moreover, the depolymerization energy of aliphatic C—N bonds, with a value of 277 kJ/mol, was in contradiction with the E_a value of 340 kJ/mol. Thus, we concluded that, for peak 1, the occurrence of an atactic dissociation reaction of C—C bonds was predominant over that of the depolymerization reaction of the main chains.

CONCLUSIONS

The results of this study demonstrate that the molar ratio of the adipic acid to total diacid was a key parameter governing the phase morphology and thermal properties of the nylon copolymers containing DA, adipic acid, and hexamethylenediamine. The content of the crystal phase increased significantly with increasing molar ratio. Meanwhile, a significant structural transition from the γ form to α and β mixture forms occurred. The σ–π* hyper conjugation effect was present in all of the as-prepared samples. A strong σ–π* hyper conjugation effect could have decreased the average distance between the interchain amide groups and suppressed the scission of the C—N bond through the formation of highly combining aza double-bond C=N groups, which, consequently, made the nylon copolymers much more stable.

The DSC–TGA results indicate that the low thermal stability of the nylon copolymers with higher molar ratios of adipic acid to total diacid were

simply due to the formation of cyclopentanone and caprolactam at 350–420°C, whereas for the nylon copolymers with lower molar ratios, the scission of C—C bonds directed the pyrolysis of the main chain; that is, atactic dissociation became a predominant reaction. This indicates that long-chain nylons may have different thermal degradation mechanisms and stabilities compared with short-chain nylons.

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