Study on the Structure of Nylon 6 Films Iodinated Before Forming. III. Fine Structure Variation of the Amorphous Film Through Deiodination

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ABSTRACT: Amorphous nylon 6 film iodinated before forming with an aqueous solution of 1.0*N* iodine–potassium iodide (I_2/KI) was deiodinated by dipping in water/ethylene glycol (EG) solutions of sodium thiosulfate with various EG contents and temperatures, washed with water, and dried at ambient condition. Structural variation through deiodination and the effects of the deiodination conditions were investigated by X-ray diffractometry and differential scanning calorimetry. The degree of swelling of the films immediately after deiodination and the time required to complete the deiodination were generally increased and decreased, respectively, with increasing temperature and EG content. The amorphous iodinated film was crystallized through deiodination. The α-crystal formation became easier with increasing temperature and EG content in the solution. The crystallinity of the films was higher after drying than before drying, suggesting that the drying induced further crystallization without any significant conversion of crystal type. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 1141–1145, 2009

Key words: nylon 6; films; crystallization; structure; X-ray

INTRODUCTION

Many studies have reported on the crystalline type transition from α to γ when nylon 6 is treated in an iodine–potassium iodide (I_2/KI) solution, and the iodine is subsequently washed in an aqueous solution of sodium thiosulfate.[1–5] Iodine molecules or polyiodide ions interrupt the intermolecular hydrogen bonds and make a complex with nylon 6 chains in both crystalline and amorphous regions.[6–10] That is, they interrupt the hydrogen bonds between the antiparallel chains of the α-crystal in the crystalline region and facilitate the rearrangement into new hydrogen bonds between parallel chains (γ-crystal) during the subsequent removal of iodine.

Abu-Isa[11] reported that the resultant modification after iodination and subsequent washing could be either α- or γ-type crystal, depending on the temperature of the wash solution. For example, the γ-form of nylon 6 was obtained from the complex after washing in ethylene glycol (EG)-water solution only at temperatures lower than 35°C, whereas the α-form was obtained at temperatures higher than 55°C. Using only water as the wash solution, a temperature of 75°C was required before an α modification was observed in the washed samples. However, these results were restricted to the iodination and deiodination of crystalline nylon 6.

On the other hand, we have prepared a new type of nylon 6-iodine complex film, namely, films iodinated before forming (IBF films), by melt-pressing the powders previously iodinated with I_2/KI aqueous solution.[12,13] The structure and crystallization behavior of the IBF films iodinated at a high concentration of 1.0*N* I_2/KI aqueous solution were discussed. The IBF films immediately after iodination had a practically amorphous structure, but slowly crystallized with the lapse of time.[13]

In this study, we prepared completely amorphous IBF film by a procedure previously described[13] and investigated its structural variation according to deiodination and the effects of deiodination conditions. The deiodination was carried out by immersing the amorphous IBF films in water and water/EG blend solutions of sodium thiosulfate at various temperatures. The crystallinity and crystal type of the deiodinated films were evaluated by X-ray diffractometry (XRD) and differential scanning calorimetry (DSC).

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EXPERIMENTAL

Preparation of amorphous IBF film

Nylon 6 pellets (M_v= 35,000, RV = 4.1; Polyscience, Warrington, PA) were used as the starting material. The amorphous IBF film was prepared by heating (melting)-quenching (solidifying) a previously iodinated film. A film prepared by melt-pressing the pellets at 250°C was iodinated with an aqueous solution of 1.0*N* I_2/KI for 24 h and subsequently dried at ambient temperature. The ultimate weight gain was 195%. The iodinated film was then isothermally heated in a well-fitting mold on a hot plate of 250°C under a little pressure to isolate the atmosphere for 5 min and quenched by immersing into dry ice to prevent crystallization. The amorphous state of the resultant film was confirmed by a DSC.

Deiodination

The amorphous IBF film was deiodinated by dipping in water/EG solutions of 0.13 mol/L sodium thiosulfate at 30, 55, 80, and 90°C until the iodine was completely removed. The EG contents were varied as 0, 25, 50, 75, and 100%. After complete deiodination, the film was washed with water and the water on the film surface was wiped away (wet film), after which the film was dried at ambient condition (dry film). In the course of deiodination, the time required to complete the deiodination (t_d) and the degree of swelling of the film after deiodination (DS) were measured. The DS was calculated by the following equation:

$$\mathrm{DS}\,(\%) = \frac{W_s - W_o}{W_o} \times 100$$

where, W_s and W_o are the weights of the wet and dry films, respectively.

Measurements

XRD scans of the films were obtained by a Rigaku D/max-III-A diffractometer, using nickel-filtered Cu-Kα radiation at 40 kV and 100 mA in reflection mode and at a scanning rate of 5° (2θ)/min. DSC was performed by a TA DSC 2910 under an N_2 atmosphere at a heating rate of 20°C/min. Sample weighing about 3 mg was encapsulated in an aluminum pan.

RESULTS AND DISCUSSION

DS and t_d

Figures 1 and 2 show the variations of DS and t_d with increasing temperature, respectively. The DS was generally increased with increasing temperature. The DS of the films deiodinated with the aqueous solutions of sodium thiosulfate was only about 0.2%, but that with the EG solutions was more than 0.6% and it increased with increasing EG content.

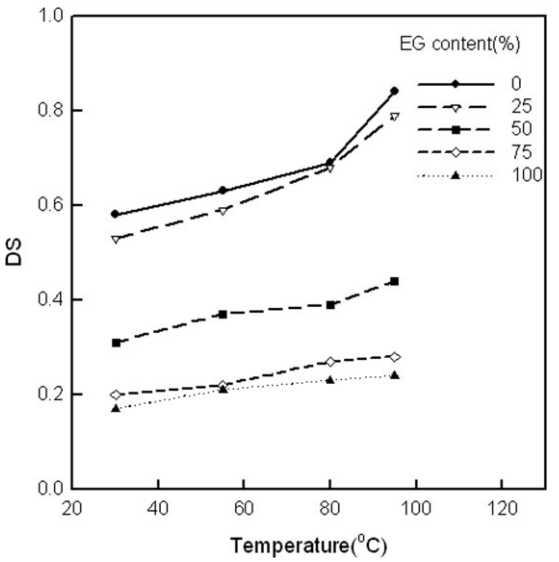

Figure 1 Changes in degree of swelling (DS) of the films immediately after deiodination (wet films) with temperatures.

This may have been caused by the solubility parameter of EG (29.9) being closer to that of nylon 6 (21.5) than to that of water (47.9).[14]

The t_d exhibited the opposite trend to the DS. It generally decreased with increasing temperature and EG content, markedly decreased up to 55°C and 50%, respectively. These trends may have resulted from the high swelling and rapid deiodination induced by the high temperature and high EG

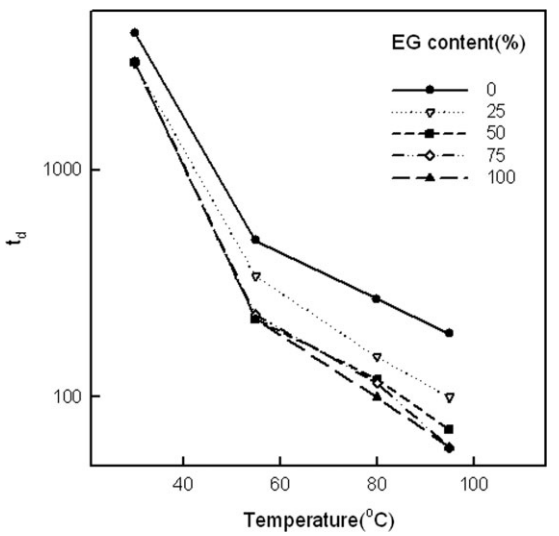

Figure 2 Changes in time required to complete deiodination (t_d) of the amorphous iodinated films with temperatures.

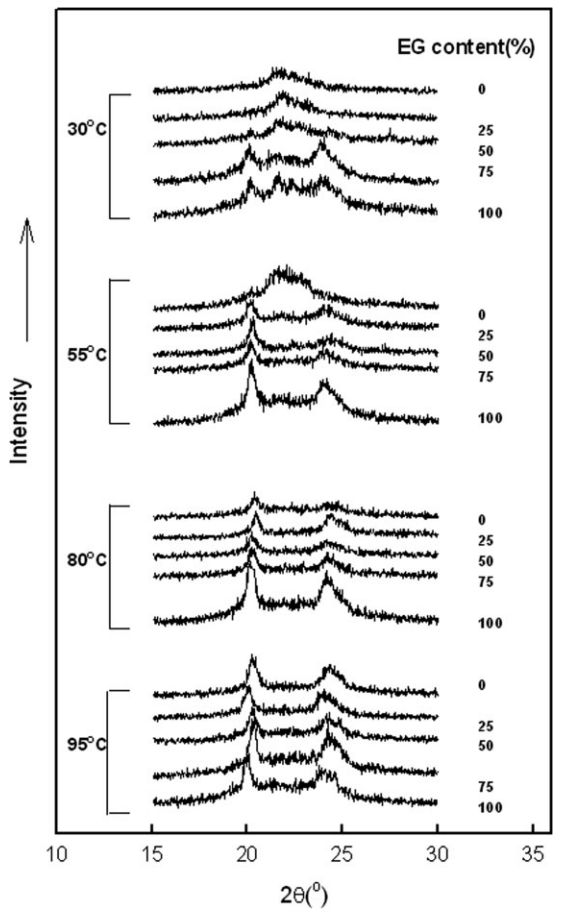

Figure 3 X-ray diffraction scans of the films immediately after deiodination (wet films).

content. On the basis of these results, we estimated that the proper conditions for rapid deiodination with minimized swelling are a temperature of 55°C and an EG content of 50%.

Fine structure variation

It is well known that the iodinated crystalline nylon 6 retains its crystallinity after deiodination, but the crystal type could be changed from α- to γ- according to the deiodination condition. It was reported that the α-type crystal reformed more easily at a higher temperature[6] and in an EG/water solution than a pure aqueous solution of sodium thiosulfate.[11]

However, the iodinated film used in this experimental was amorphous. Therefore, we investigated the following viewpoints: Does the iodinated film maintain its amorphous state after deiodination? If not, which deiodination stage (immersing in the sodium thiosulfate solution or subsequent drying) does the crystallization occur in, and which type of crystal is formed? To settle these questions, we conducted XRD and DSC analyses for the wet and dry films, respectively.

TABLE I
The Crystal Types of the Films Immediately after Deiodination (Wet Films)

	EG content (%)				
Temp. (°C)	0	25	50	75	100
30	γ	γ	γ	α, γ	α, γ
55	γ	α	α	α	α
80	α	α	α	α	α
95	α	α	α	α	α

XRD

The nylon 6 is known to exhibit strong (200) and (002 + 202) diffraction peaks at $2\theta = 20.2°$ and 24.0°, respectively, for the α-crystal and $2\theta = 21.8°$ and 22.7°, respectively for the γ-crystal.

Figure 3 shows the XRD scans of the wet films. All the films exhibited peaks corresponding to the characteristics of the original nylon 6 crystals, indicating that the amorphous IBF films were crystallized throughout the deiodination. At the lowest EG content and temperature(≤50% at 30°C, 0% at 55°C), the peak corresponding to the γ-crystal ($2\theta = 21.8°$) was mainly exhibited. However, with increasing EG

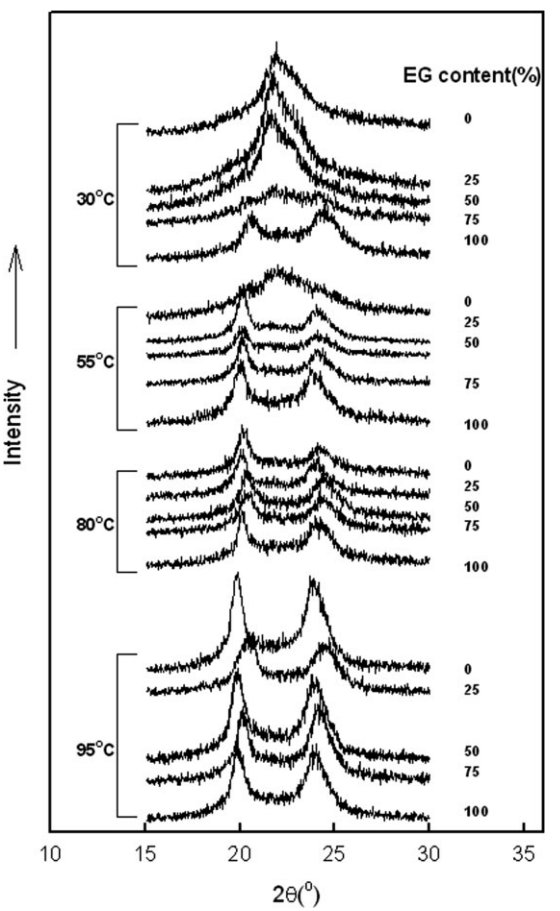

Figure 4 X-ray diffraction scans of the films after deiodination and drying (dry films).

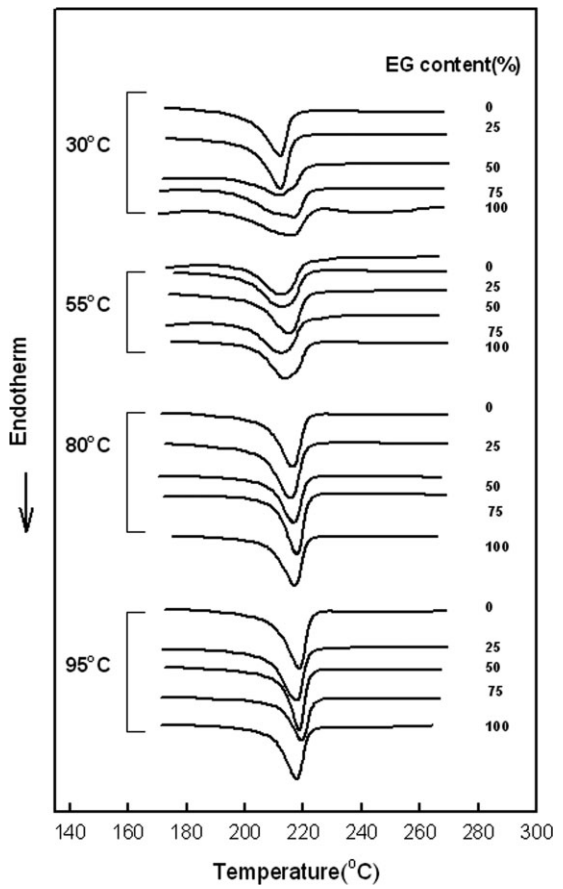

Figure 5 DSC thermograms of the films immediately after deiodination (wet films).

content and temperature, peaks corresponding to the α-crystal (2θ = 20.2° and 24.0°) also appeared and were strengthened while the γ-crystal peak was rapidly weakened and disappeared. This result indicated that the higher temperature and EG content enhanced the α-crystal formation, which is similar to the case of deiodination for the crystalline nylon 6.[6–8,11]

The improved α-crystal formation was attributed to the enhanced molecular activity due to the higher temperature and the increased DS on account of the higher EG content.

The resultant crystal types of the wet films according to the EG content and temperature are shown in Table I.

Figure 4 shows the XRD scans of the dry films. Although the shape of all the diffraction peaks was generally similar to that of the wet films (Fig. 3), their strength was generally higher than that of the wet films, indicating that additional crystallization proceeded during the drying without significant conversion of crystal type. This additional crystallization was ascribed to the high swelling of the wet film after deiodination.

DSC

DSC was carried out to obtain more information and support the aforementioned XRD results. The melting temperatures (T_m) of the α- and γ-crystals have been reported as 219, 222, or 223°C and 214 or 217°C, respectively[6,11,15]: Despite this variation, T_m of the α-crystal was always higher than that of the γ-crystal.

The DSC thermograms for the wet films are shown in Figure 5. Generally, although most of the melting peaks in the case of deiodination at 30 and 55°C were double or broad peaks, those at 80 and 95°C were sharp single peaks. This indicates that the films deiodinated at the lower temperatures had both α- and γ-type crystals, whereas those at the higher temperatures had only α-type crystals. The peaks for the EG contents of 0 and 25% at 30°C and for the EG content of 0% at 55°C were relatively sharp single peaks at the lower temperature, corresponding to the γ-crystal. These results were well coincident with the aforementioned XRD results. The enhanced α-crystal formation induced by the increase of EG content was well supported by the DSC results of the films deiodinated at 30°C, as shown in Figure 5. The films deiodinated in the

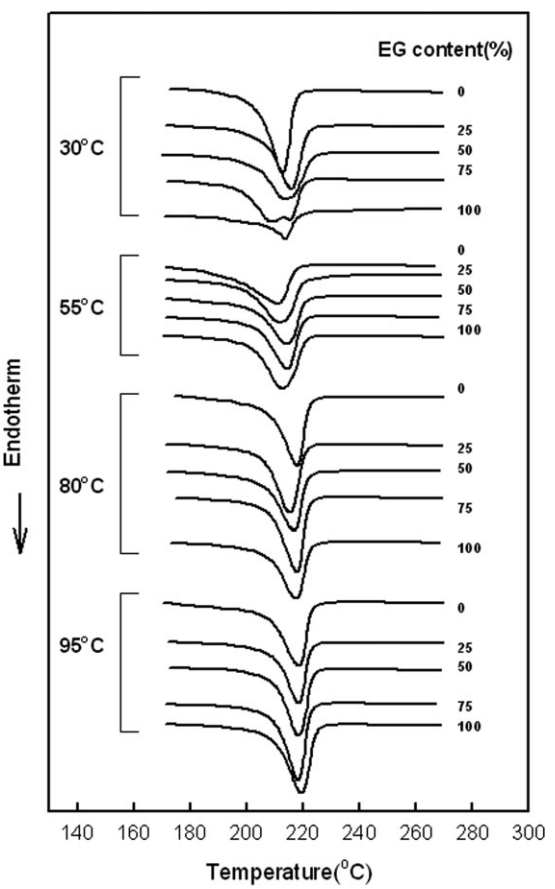

Figure 6 DSC thermograms of the films after deiodination and drying (dry films).

TABLE II
The Heat of Fusions (Δ*H* [unit, J/g]) of the Nylon 6 Films Immediately after Deiodination (Wet Films) and Drying (Dry Films).

	EG content (%)									
	0		25		50		75		100	
Temp. (°C)	wet	dry	wet	dry	wet	dry	wet	dry	wet	dry
30	52.9	73.2	48.9	72.6	43.3	73.4	50.6	78.7	56.8	68.7
55	49.8	77.8	44.4	73.0	65.8	71.5	58.2	70.0	45.1	72.4
80	56.2	86.4	60.8	85.9	55.3	83.4	44.9	90.5	54.7	83.8
95	58.4	85.3	62.8	88.1	62.6	83.5	38.5	90.8	42.3	82.0

solutions with EG contents of 0 and 25% exhibited only sharp single melting peaks at about 210°C, corresponding to the γ-crystal. However, for the film deiodinated in the solution with an EG content of 50%, a new peak at about 220°C corresponding to the α-crystal appeared with shoulder form, and its relative intensity to the lower temperature peak increased with increasing EG content.

The DSC results for the dry films, shown in Figure 6, were also mostly coincident with the aforementioned XRD results (Fig. 3). Especially, the peak intensities were higher than those of the wet films in all cases. The heat of fusion (Δ*H*) for the wet and dry films was therefore determined and is indicated in Table II. The variation of Δ*H*, especially for the wet films, did not present any consistent tendency according to the deiodination temperature and EG content, which may be attributed to the conflict between the conditions (temperature and DS) and crystallization time. The higher temperature and DS due to the higher EG content during deiodination are positive conditions for crystallization (i.e., a crystallinity supporting factor), but they must shorten the deiodination (*i.e.,* crystallization) time (i.e., a crystallinity suppressing factor). In the dry film, the effect of the deiodination temperature on Δ*H* exhibited a substantially consistent tendency. Δ*H* increased with increasing deiodination temperature. The Δ*H* of the dry films was much greater than that of the wet films, which would have supported the aforementioned the additional crystallization during the drying.

The dependence of the resultant crystal types on the deiodimation temperature in this experiment was similar to that reported by Abu-Isa[11] despite the structural difference of samples before deiodination in terms of the amorphous or crystalline state.

CONCLUSIONS

Amorphous nylon 6 film IBF with an aqueous solution of 1.0*N* I_2/KI was deiodinated by dipping in water/EG solutions of sodium thiosulfate with various EG contents and temperatures, washed with water, and dried at ambient condition. The DS of the films immediately after deiodination and the time required to complete the deiodination were generally increased and decreased, respectively, with increasing temperature and EG content.

The amorphous iodinated film was crystallized through deiodination. The α-crystal formation became easier with increasing temperature and EG content in the solution, which is similar to the case of deiodination for the crystalline nylon 6. There were only γ-crystals in the films deiodinated at the lower EG content and temperature (0, 25% at 30°C and 0% at 55°C), both α- and γ-crystals in the films deiodinated at the higher EG content and the lower temperature (50, 75, 100% at 30°C and 25, 75, 100% at 55°C), and only α-crystals in the films deiodinated at the higher temperature (80 and 95°C). The crystallinity of the films was higher after drying than before drying, suggesting that the drying induced further crystallization without any significant conversion of crystal type.

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