

Study on the Structure of Nylon 6 Films Iodinated Before Forming. I. Comparison with the Film Iodinated After Forming

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ABSTRACT: To examine the possibility of applying the iodination of nylon 6 to forming, a new type of nylon 6–iodine complex films iodinated before forming (IBF film) and the old type of films iodinated after forming (IAF film) were prepared and their structures were investigated and compared with each other. The IBF films from iodinated nylon 6 powders could be obtained by a melt press at 185°C, which is much lower than the melt-press temperature of pure nylon 6 (250°C). It was ascertained that the structure of IAF films is similar to that reported by Lee et al. but the structure of IBF films is very different. The distinctive features of the

IBF films compared with the IAF films are as follows: The IBF films have no excess iodine molecules (I_2) to form a complex with nylon 6 chains because those molecules in the iodinated powders have been evaporated through the melt press. The IBF films have a practically amorphous structure but only a few crystalline portions with a relaxed state which may have been created with iodide-ion-free segments of nylon 6 molecules through the procedure of film forming. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 1138–1144, 2003

Key words: nylon; films; structure

INTRODUCTION

There have been many reports about the structure of nylon 6 iodinated with an aqueous solution of I_2/KI . It has been believed that iodine molecules or polyiodide ions interrupt the intermolecular hydrogen bonds and make a complex with nylon 6 chains in not only crystalline but also amorphous regions. When α -nylon 6 is iodinated, the hydrogen bonds between the antiparallel chains are interrupted and rearranged into new hydrogen bonds between parallel chains (γ -crystal) during the subsequent removal of iodine. So, iodination has been used as a general method for changing the crystal form of nylon 6 from the α -crystal to the γ -crystal.

Murthy and coworkers^{1–5} proposed a structure of the nylon 6–iodine complex crystal such that the I_3^- and I_5^- ions lie between the hydrogen-bonded planes. Chuah and Porter⁶ and Kawaguchi⁷ reported that the complex crystal has two monoclinic unit cells and they determined the lattice parameters. Lee et al.⁸ deduced four steps of complex formation by systematically increasing the concentration of I_2/KI solutions in contact with nylon 6 films.

On the other hand, applying iodination to enhance processability has been attempted, such as the drawing of nylon 6 by Chuah and Porter⁶ and Lee et al.⁸

The iodination is capable of enhancing the drawability of nylon 6 by the role of reducing intermolecular attractions in crystalline as well as amorphous regions. This mechanism may be able to be applied to the forming as well. It is therefore necessary to carry out research about the iodination of nylon 6 before forming. We have made studies about preparing nylon 6 films iodinated before forming, their characteristics, and the removal of iodine from them. In this study, we prepared nylon 6 films iodinated not only before forming but also after forming and investigated the structure of them by comparing them with each other through analyses of a thermogravimeter, differential scanning calorimeter, and an infrared spectrum.

EXPERIMENTAL

Materials and preparations

The nylon 6 was purchased in powder form from Allied Signal (Morristown, NJ). The reported intrinsic viscosity is 1.47 dL/g for the measurement in 88% formic acid. Two types of films iodinated before forming (IBF film) and after forming (IAF film) were prepared by the following procedures:

IAF film

Unoriented film of 0.5-mm thickness was prepared by melt-pressing the powders on a hot stage at 250°C and subsequent slow cooling to ambient. The crystals in the film were predominantly the α form, which was

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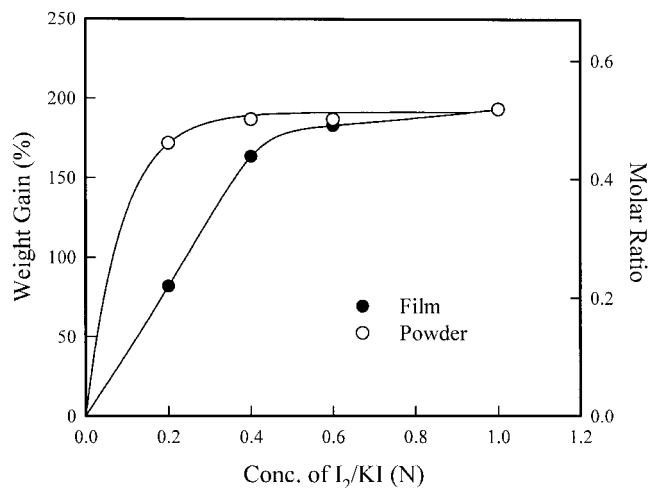


Figure 1 Weight gains and molar ratios of nylon 6 powder and film after treatment with various concentrations of I_2/KI solutions.

confirmed by X-ray diffraction. The film was iodinated by immersing it in 0.2, 0.4, 0.6, and 1.0N I_2/KI aqueous solutions for 24 h at room temperature. The molar ratio of KI to I_2 was fixed at 2.0, in which the I_2 can be dissolved completely. The ratio of nylon 6 to the solution was fixed at 4 g/300 mL.⁹ After removal from the solutions, the films were rinsed with water and air-dried at room temperature for over 3 weeks, which was the necessary time for complete water evaporation and excess iodine sublimation.

IBF film

The powders were iodinated through the same procedures and conditions as those of the IAF film. The iodinated powders were melt-pressed at 185°C to form films. During melting on the press, an atmosphere of N_2 was maintained to protect the nylon 6 from oxidation by the oxidizing action of the iodine.

Measurements

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed by a TA TGA 2950 and a TA DSC 2910, respectively. Both tests were conducted under the atmosphere of N_2 at a heating rate of 20°C/min. In the case of the DSC, the stainless-steel open pans were used to allow the evaporation of iodine. Infrared (IR) spectra were obtained by the film method with an MIDAC PRS-INT 189 FTIR spectrometer.

RESULTS AND DISCUSSION

Iodine absorption

The weight gains and the molar ratios of I_2/KI to the nylon 6 repeat unit for the film and powder after

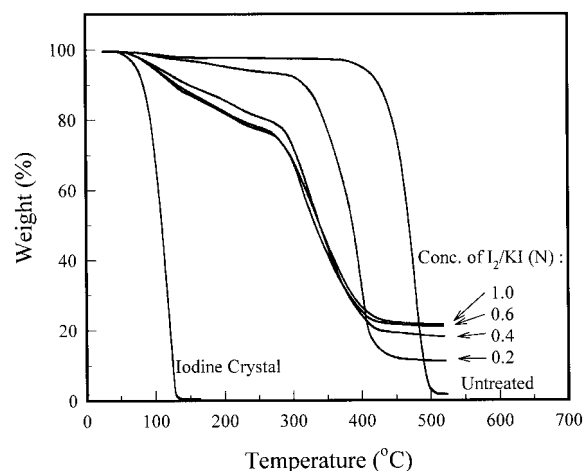


Figure 2 Weight-loss curves for pure iodine crystals, untreated nylon 6 film, and IAF films prepared from various concentrations of I_2/KI solutions by TGA on heating from ambient to 550°C at 20°C/min.

air-drying are shown in Figure 1. They increased markedly with an I_2/KI concentration to 0.6N for the film and to 0.2N for the powder, but above those concentrations, the increasing tendencies practically leveled off. The maximum values for the film and powder were the same. But the minimum concentration of I_2/KI to indicate the leveling-off for the powder was lower due to the greater specific surface area than that for the film.

TGA studies

There may be several different compositions in the iodinated nylon 6: not only effective I_3^- and I_5^- ions to form a complex with the nylon 6 molecule,¹⁻⁶ but also the K^+ ion, molecular iodine (I_2), and potassium iodide (KI), which were recovered from the excess ab-

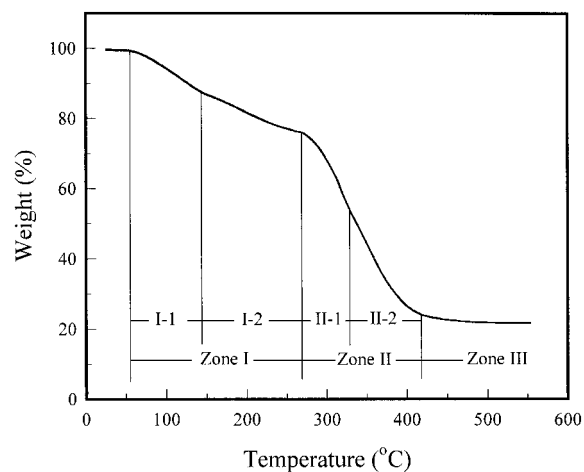


Figure 3 A typical weight-loss curve of IAF film prepared from 1.0N concentration of I_2/KI solution.

TABLE I
Characteristics Indicated by Each Weight-loss Zone on the TGA Curve for the Iodinated Nylon 6 Film

Zone	Component	Source
I-1	I ₂ ↑	Excess I ₂
I-2	I ₂ ↑	N6-I ₅ ⁻ → N6-I ₃ ⁻ + I ₂ ↑
II-1	N6 ↑	Portions of N6 not connected with iodide ions
II-2	I ₂ ↑	N6-I ₃ ⁻ → N6-I ⁻ + I ₂ ↑
	N6 ↑	N6-I ⁻ → N6 ↑ + I ⁻
III	KI	I ⁻ + K ⁺ → KI

N6, nylon 6; ↑, evaporation.

sorbed I₂/KI solution during drying. TGA was used to estimate the weight fraction of each component.

IAF films

Weight-loss curves for the IAF films, iodine crystals, and pure nylon 6 film are shown in Figure 2. The iodine crystals and pure nylon 6 film lost most of their weight rapidly at temperatures from 60 to 140°C and from 400 to 515°C, respectively.

For the IAF film, there are two weight-loss zones widely distinguishable and an ash zone as shown in Figure 3. Chuah¹⁰ confirmed that zone I is from the volatilization of I₂ by pyrolysis at 250°C and presumed that zone II is from the decomposition of the I₃⁻ ions as well as degradation of nylon 6 and that the ash of zone III is composed of KI₃ salts. But Lee et al.⁸ discussed these zones more concretely as follows: Zone I may be from the volatilization of I₂ from not only the excess absorbed solution but also the I₅⁻ ions (I₅⁻ → I₃⁻ + I₂ ↑). But two kinds of I₂ molecules were not confirmed on the TGA curves. Zone II can be divided into two subzones: The lower temperature one (II-1) of rapid weight loss may be from the degradation of pure nylon 6 chains and the higher temperature one (II-2) of slow weight loss may be from both the degradation of the remaining portion of nylon 6 molecules connected with the I₃⁻ ions and the I₂ from a reaction of I₃⁻ + K⁺ → I₂ + KI. Zone III may be composed of KI salts.

In this experiment, zone I can be also divided into two subzones: Zones I-1 and I-2 may be from the volatilization of the excess I₂ and I₂ from the I₅⁻ ions, respectively, which can confirm the above-mentioned assumption that zone I may be corresponding to two kinds of I₂ molecules. The other zones of II and III are similar to the results of Lee et al.⁸ Hence, we can summarize the characteristics being indicated by each zone as Table I.

Three important zones, indicating the distinctive features of iodine in the IAF films, are zones I-1, I-2, and III, which correspond to the excess I₂, I₅⁻ ions, and total polyiodide ions (I₃⁻, I₅⁻) connected to nylon 6 molecules, respectively. So, the variation of the percent weight loss of each zone indicates a variation of the content of the corresponding component. Table II shows the percent weight loss obtained directly from the TGA curve (WL_m), percent absorption of I₂/KI (AI), and percent weight loss standardized on the subject of the unit weight of pure nylon 6 (WL_s) for each zone. The AI and WL_s were obtained by the following equations:

$$AI (\%) = \frac{\text{Weight gain}}{\text{Weight gain} + 1} \times 100$$

$$WL_s (\%) = \frac{WL_m}{AI + 100} \times 100$$

Figure 4 shows the changes of the WL_s for zones I-1, I-2, and III. With an increasing concentration of I₂/KI, the WL_s for the zones I-1 and III corresponding to the excess I₂ and the total polyiodide ions increase with a tendency similar to that of the weight gain (see Fig. 1). But the real increase of WL_s for zone I-2 does not appear until a 0.4N I₂/KI concentration, which means that I₅⁻ ions can be built up at higher concentrations than 0.2N.

IBF films

Weight-loss curves for the IBF films are shown in Figure 5. The overall appearances of the curves are similar to those for the IAF films, but they do not show zone I-1 corresponding to the excess I₂. This may be

TABLE II
Percent Absorption of I₂/KI (AI), Percent Weight Loss Obtained Directly from the TGA Curve (WL_m), and Percent Weight Loss Standardized on the Subject of the Unit Weight of Pure Nylon 6 (WL_s) of IAF Films for Each Zone

Concentration of I ₂ /KI (N)	AI	Zone I-1		Zone I-2		Zone III	
		WL _m	WL _s	WL _m	WL _s	WL _m	WL _s
0.2	45.1	5.0	9.1	1.9	3.5	11.0	20.0
0.4	62.0	9.0	23.7	10.6	27.9	18.0	47.4
0.6	74.7	11.0	31.2	11.5	32.6	20.7	58.6
1.0	65.9	11.0	32.3	13.0	38.1	21.0	61.6

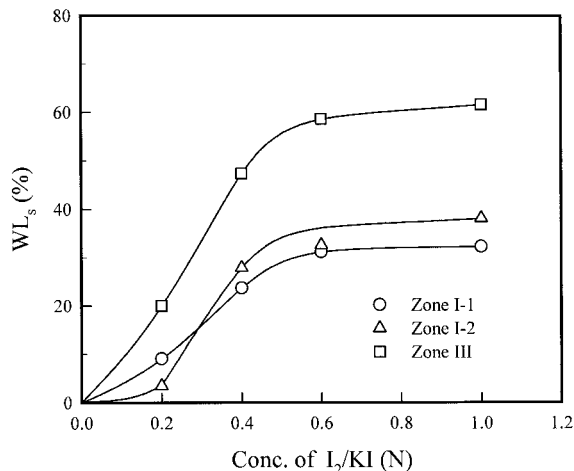


Figure 4 Changes on weight loss standardized on the subject of the unit weight of pure nylon 6 (WL_s) for zones I-1, I-2, and III with increasing concentration of I_2/KI .

due to a previous evaporation of the majority of the excess I_2 , which has been contained in the iodinated powders, through the melt press. The melt press was carried out at $185^\circ C$, which is higher than the temperature range of zone I-1 ($60-140^\circ C$). Furthermore, it is presumed that the evaporation of a considerable portion of the I_5^- ions connected to the nylon 6 molecules is capable through the melt press, because the temperature of the melt press is a little higher than is the onset temperature ($160^\circ C$) of zone I-2.

We were not able to calculate the AI and WL_s because a quantitative analysis of the I_2 evaporated through the melt press was impossible. Only the WL_m for zones I-2 and III, therefore, are shown in Figure 6. They increased markedly with the I_2/KI concentration to 0.2N and then practically leveled off in the same manner with the weight gain for the powder.

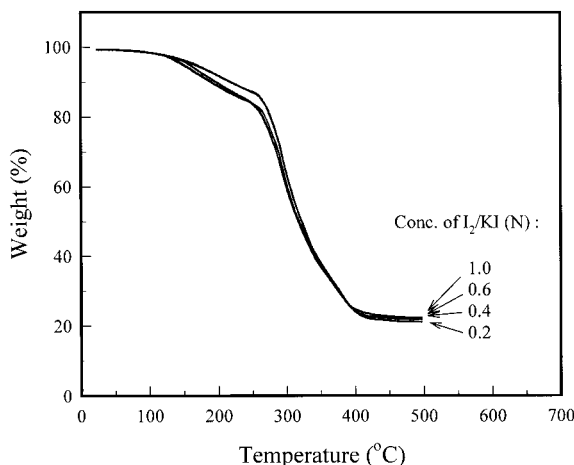


Figure 5 Weight-loss curves for IBF films prepared from various concentrations of I_2/KI solutions by TGA on heating from ambient to $550^\circ C$ at $20^\circ C/min$.

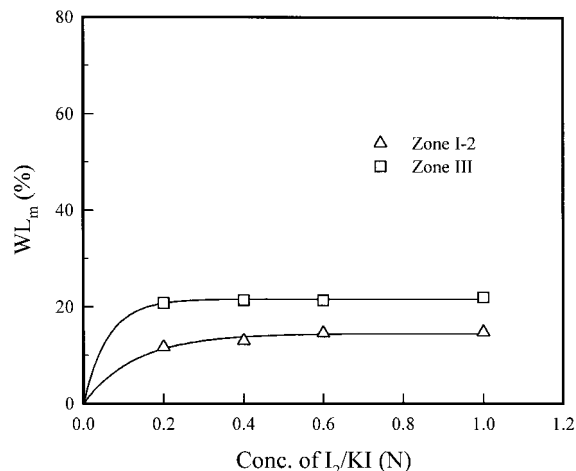


Figure 6 Changes on weight loss obtained directly from the TGA curve (WL_m) for zones I-2 and III with increasing concentration of I_2/KI .

Variation of crystal structure

Lee et al.⁸ deduced four steps of formation of a nylon 6-iodine complex with a systematically increasing concentration of I_2/KI solutions through analyses of X-ray diffraction and DSC, as shown in Figure 7: The pure nylon 6 α -crystal has antiparallel packed chains which are hydrogen-bonded to each other [Fig. 7(a)].

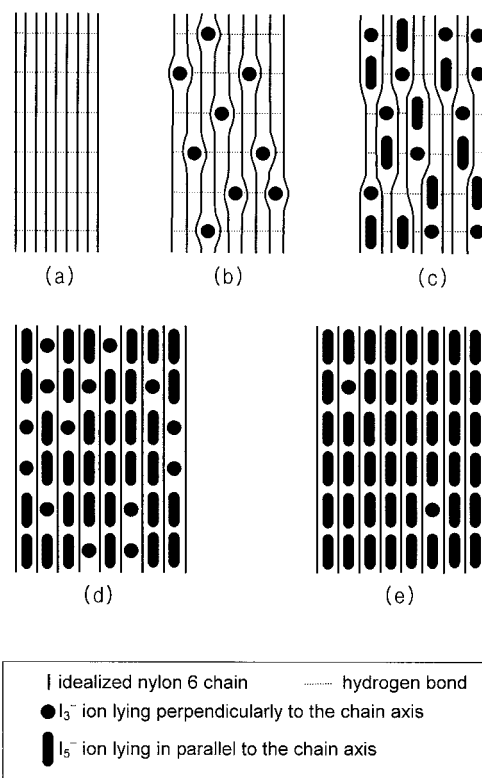


Figure 7 Models showing steps to form nylon 6-iodine complex crystal with increasing content of $K^+I_3^-$, partially revised in more logical manner from the suggestion by Lee et al.⁸

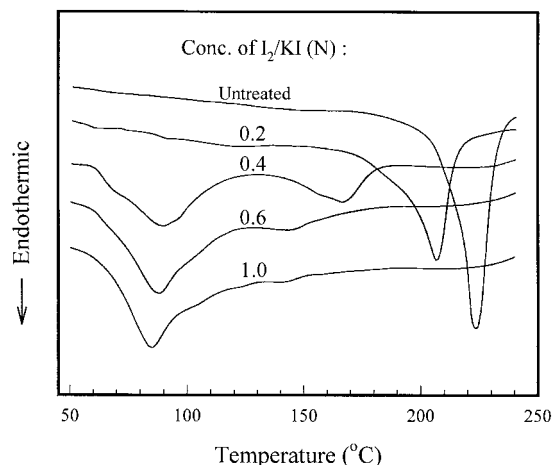


Figure 8 DSC thermograms of untreated nylon 6 and IAF films prepared from various concentrations of I_2/KI solutions.

At the lower content of $K^+I_3^-$, the overall starting crystal phase is maintained, with chains being displaced segmentally by I_3^- ions lying perpendicularly to the chain axis [Fig. 7(b)]. At the higher content of $K^+I_3^-$, there are two distinctive crystal phases: an original nylon 6 crystal phase with a shorter intermolecular distance and a complex crystal phase with a longer intermolecular distance which is composed of two subphases including the I_3^- ions and the I_5^- ions lying parallel to the chain axis [Fig. 7(c)]. At a further higher content of $K^+I_3^-$, there is only the complex crystal phase composed of the two subphases with an increased fraction of the subphase including the I_5^- ions [Fig. 7(d)]. At the highest content of $K^+I_3^-$, the dominant crystal phase includes the I_5^- ions [Fig. 7(e)]. In this research, the process of complex crystal formation was reviewed through not only the DSC but also the IR spectrum analyses for the IAF films and examined for the IBF films as well.

IAF films

The crystalline region of an α nylon 6–iodine complex can have three different portions of an α -crystal retained and two complex crystals with I_5^- and I_3^- ions. Lee et al.⁸ reported the result of DSC analysis for nylon 6–iodine complex films prepared by treatment of an α -nylon 6 film with aqueous solutions of I_2/KI of various concentrations (0.1–2.0N). The DSC thermograms indicated three kinds of melting peaks at around 65 and 85 and higher than 120°C, which may be associated with the portions of the α -crystal retained and the complex crystal with I_5^- and I_3^- ions, respectively. With an increasing concentration of I_2/KI , the melting peak associated with the α -crystal shifted to lower temperature and became broader and its area decreased and finally disappeared; the melting

peak associated with the complex crystal with I_5^- ions appeared at the concentration of 0.3N, increased, and became sharp; the melting peak associated with the complex crystal with I_3^- ions appeared at the lowest concentration, increased and decreased, and then disappeared at the highest concentration.

It can be confirmed by Figure 8 that the results of the DSC analysis for the IAF films in this research are very similar to those reported by Lee et al.⁸: The DSC thermogram for the untreated nylon 6 film indicated a sharp melting peak of the α -crystal at 220°C, but the melting peak for complex films shifted to lower temperature and became broader and smaller, then practically disappeared at 1.0N with an increasing concentration of I_2/KI . The peak at around 65°C, which may be associated with the melting of the complex crystal with I_3^- ions, appeared at 0.2N, increased a little at 0.4N, left trace on the curve at 0.6N, and disappeared at 1.0N. The peak around 85°C, which may be associated with the melting of the complex crystal with I_5^- ions, appeared at 0.2N, then increased and sharpened gradually with an increasing concentration of I_2/KI . These results can be readjusted according to the concentration of I_2/KI : The crystals corresponding to 0.2, 0.4, 0.6, and 1.0N may have phases of the α -crystal and the complex crystal with I_3^- ions, the α -crystal and the complex crystals with I_3^- and I_5^- ions, the α -crystal and the complex crystals with I_5^- ions, and only the complex crystals with I_5^- ions, respectively. We can therefore summarize that the crystalline structure corresponding to 0.2, 0.4, 0.6, and 1.0N may be applicable to the models of (b), (c), (d), and (e) in Figure 7, respectively.

Figure 9 shows IR spectra for the IAF films, and the variations of the bands related to crystallinity with the concentration of I_2/KI are summarized in Table III. With an increasing concentration of I_2/KI , all the bands at 1478, 1418, 1028, 961, and 930 cm^{-1} assigned

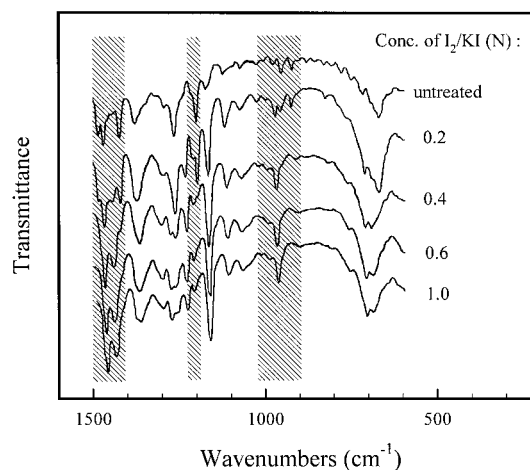


Figure 9 IR spectra of untreated nylon 6 and IAF films prepared from various concentrations of I_2/KI solutions.

TABLE III
Variation of Some IR Bands Related to Crystallinity of Nylon 6 with Concentration of I₂/KI

IR band	Assignment	Reference	IAF film				IBF film			
			Concentration of I ₂ /KI				Concentration of I ₂ /KI			
			0.2	0.4	0.6	1.0	0.2	0.4	0.6	1.0
1478	α-crystalline	Manley ¹¹	↓	D	D	D	↓	↓	↓	↓
1464	Amorphous	Manley ¹¹	—	—	—	—	—	↑	↑	↑
1439	γ-Crystalline	Abu-Isa ¹²								
	Amorphous	Manley ¹¹	—	↑	↑	↑	—	↑	↑	↑
1418	γ-Crystalline	Abu-Isa ¹²								
	α-Crystalline	Manley ¹¹	↓	D	D	D	↓	↓	↓	↓
1200	Crystalline	Chuah and Porter ^b	—	↓	↓	↓	—	—	↓	↓
1028	α-Crystalline	Perkins ¹³	—	↓	↓	↓	—	↓	↓	↓
980	Amorphous	Perkins ¹³	↑	↑	↑	↑	↑	↑	↑	↑
961	α-Crystalline	Perkins ¹³	—	—	—	—	↓	↓	↓	↓
930	α-Crystalline	Perkins ¹³	—	—	—	—	↓	↓	↓	↓

↑, increase; ↓, decrease; D, disappearance.

to the α-crystal decreased and/or disappeared, but those at 1464, 1439, and 980 cm⁻¹ assigned to the amorphous structure did not change or increase. (Abu-Isa¹² noted that the bands at 1464 and 1439 cm⁻¹ are also associated with the γ-crystal, but there is no reason to notice the γ-crystal in this case.) These results can support those of the DSC: Especially, the result that all the bands assigned to the α-crystal but the one at 1028 cm⁻¹ disappeared at concentrations of 0.6N and this supports strongly that the crystalline structure corresponding to 0.6N is applicable to the model of (d) in Figure 7.

Figure 10 shows DSC thermograms for the IBF films. Above all, that all the thermograms are similar to one another may have resulted from the similar weight gains of the powders used. Only a very weak endothermic peak was indicated on each thermogram, which shows that all the IBF films practically have an amorphous structure. This amorphous structure may

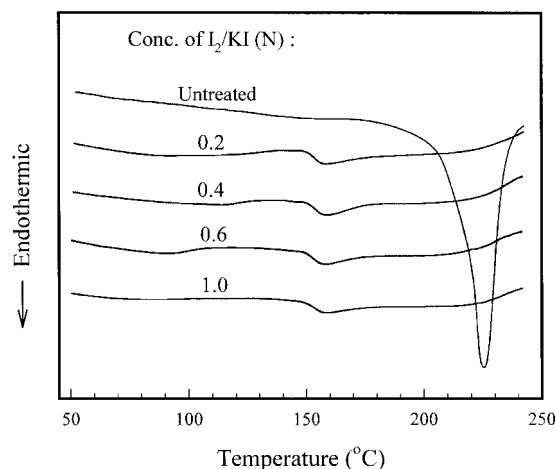


Figure 10 DSC thermograms of untreated nylon 6 and IBF films prepared from various concentrations of I₂/KI solutions.

have resulted from the disturbance of crystallization by the iodide ions connected to the nylon 6 molecules. The weak peak is estimated as being associated with the melting of nylon 6 crystals relaxed by its temperature of 155°C, which is in the range corresponding to the melting temperatures of the α-crystals of IAF films.

We can therefore assume that the crystalline structure of the IBF films, even though it is very weak, was created with iodide-ion-free segments of the nylon 6 molecules through the film-forming procedure. At this point, it is necessary to recall the data of the molar ratios of I₂/KI to the nylon 6 repeat unit for the powders, which were used to prepare the IBF films, shown in Figure 1. Even the maximum molar ratio was only 0.52, which means there was a considerable extent of the iodide-ion-free segments on the nylon 6 molecules.

Figure 11 shows the IR spectra for the IBF films, and the variations of the bands related to the crystallinity with the concentration of I₂/KI are summarized also

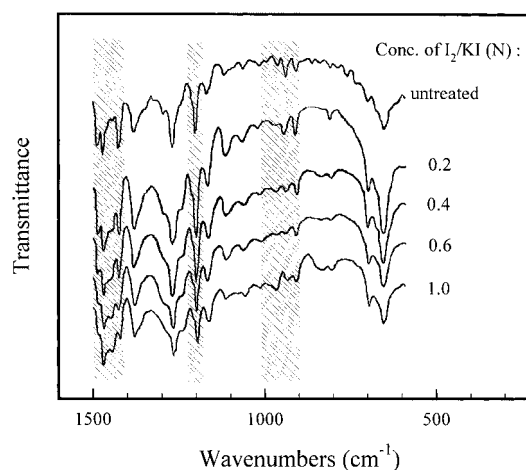


Figure 11 IR spectra of untreated nylon 6 and IBF films prepared from various concentrations of I₂/KI solutions.

in Table III. With an increasing concentration of I_2/KI , all the bands at 1464, 1439, and 980 cm^{-1} assigned to the amorphous structure increased gradually, and those at 1478, 1418, 1200, 1028, 961, and 930 cm^{-1} assigned to the crystalline structure remarkably decreased but did not disappear. These results support the above assumptions that the IBF films have a practically amorphous structure but have little of the crystalline structure of nylon 6 in the relaxed state. On the other hand, Abu-Isa¹² noted that the bands at 1464 and 1439 cm^{-1} are associated with the γ -crystal. So, the increase of those bands may suggest enrichment of not only the amorphous structure but also the γ -crystalline structure, namely, the crystalline structure of the IBF films is capable of being of γ -form as well as of α -form.

CONCLUSIONS

A new type of nylon 6 film iodinated before forming (IBF film) and the old type of films iodinated after forming (IAF film) were prepared. The IBF films from iodinated nylon 6 powders could be obtained by a melt press at 185°C , which is much lower than the melt-press temperature of nylon 6 (250°C).

It was ascertained that the structure of IAF films is similar to that reported by Lee et al.⁸ but the structure

of IBF films is very different. The distinctive features of the IBF films compared with the IAF films are as follows: The IBF films have no excess iodine molecules (I_2) because of previous evaporation of those molecules in the iodinated powders through the melt press to form the film. The IBF films have a practically amorphous structure with only a few crystalline portions in the relaxed state which may have been created with the iodide-ion-free segments of nylon 6 molecules through the procedure of film forming.

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