

Structure and Processability of Iodinated Poly(vinyl alcohol) (III)-Structure of Films Iodinated in Solution before Casting

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Received 10 January 2006; accepted 3 March 2006

DOI 10.1002/app.24579

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Films iodinated at solution before casting (IBC films) were prepared by casting aqueous solutions of 10 wt % poly(vinyl alcohol) (PVA) containing selected quantities of I₂/KI. The quantity of I₂/KI was controlled to obtain 15.2, 39.8, 83.2, 117.0, and 140.1%. The Thermogravimetry (TG) curves of the IBC film exhibited three distinct zones corresponding to the evaporation of H₂O and I₂ molecules (zone I), evaporation of I₂ and partial decomposition of side groups (—OH) (zone II), degradation of the remaining side groups and partial degradation of the main chain (zone III-1), and degradation of the remaining main chain and the char zone corresponding to KI. The crystalline structure of the film with a weight gain of 15.2% was almost the same as that of the pure PVA, and the film with the weight gain of 140% was almost amorphous. The differential scanning calorimetry (DSC) thermograms of the IBC films with a weight

gain of 15.2% and 39.8% indicated endothermic single or double peaks at around 180°C, corresponding to the crystal melting and degradation of side groups; those with weight gains of 83.2% and above indicated exothermic peaks at around 170°C, corresponding to crystallization, and broad endothermic peak at around 180–200°C, corresponding to the crystal melting and degradation of side groups. The dynamic mechanical α_n transition of the IBC film with the weight gain of 140.1% appeared at around 20°C. X-ray diffraction and DSC analysis of deiodinated films show that the crystal structure, on deiodination of all the IBC films, regardless of crystallinity, returned to that of the pure PVA. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 3497–3502, 2006

Key words: poly(vinyl alcohol); film; iodination; casting; structure

INTRODUCTION

Poly(vinyl alcohol) (PVA)–iodine complex has long been investigated since Staudinger et al.¹ found that a blue color was developed by iodination in aqueous solution of PVA. Many people^{2–13} have mainly studied about the structure of PVA–iodine complex.

As the fact that iodine interrupts intermolecular hydrogen bonds and makes complex with polymer chains not only in the crystalline but also in the amorphous regions of several polar polymers was found, the study about PVA–iodine complex has been accelerated.

Hess et al.¹⁴ found new diffraction spots on the X-ray diffraction of PVA fibers which absorbed more than 12 wt % of iodine and concluded that iodine intruded in the crystal phase as well as in the amorphous phase at comparatively heavy iodine sorption. Choi et al.¹⁵ reported that iodine intruded into PVA crystals and formed cocrystal with PVA molecules in the case of 2×10^{-2} mol/L or more of I₂/KI in the soaking solution. In our laboratory, the structure of

the iodinated PVA films possessing various quantities of iodine has been studied through thermal analyses.¹⁶

On the other hand, Lee and coworkers, and Kang and Lee^{17,18} prepared a new type of nylon 6–iodine complex film at 180°C, namely, the film iodinated before forming (IBF films), by melt-pressing the powder previously iodinated in I₂/KI aqueous solutions, much lower than the melt-press temperature (250°C) of pure nylon 6. The IBF films practically have an amorphous structure and 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. Jeong et al.¹⁷ reported that the IBF films could form a relaxed crystalline structure very slowly at appropriate temperature, while Kang and Lee¹⁸ stated that the crystalline structure was induced by deiodination from the IBF films of an almost amorphous state. So, we can know the temperature of the process is lower when the iodinated polymer was used for raw material, and that the amorphous state of polymer by iodination is recovered to the original polymer crystalline lattice by deiodination.

In this article, therefore, we tried to apply the IBF method of nylon 6 to PVA. As the result of prelimi-

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nary experiments for PVA powder, the maximum adsorption of I_2/KI and the T_m for iodinated PVA film were 88 wt % and 145°C, respectively. From these results, the processability of fusion for iodinated PVA is impossible because the descent of T_m was lower than for nylon 6 and the temperature of decomposition was low, the same as the descent of T_m . So, IBC (iodinated in solution before casting) PVA films were prepared by casting PVA aqueous solutions containing selected quantities of I_2/KI .

There is another good effect for the IBC method, wherein iodine adsorption has no limit unlike in the former method wherein iodine was sunk as a solid state in the I_2/KI aqueous solution, that is, iodine adsorption can be obtained at about 100 wt % in a solid state (powder, film, etc.), but over 150 wt % in the IBC method, which has possibility of the minimum of entanglements between intermolecular chains as well as the disturbance of PVA crystallization.

In the present article, therefore, we made the iodinated PVA films in various quantities of I_2/KI through the IBC method, which was manufactured as a PVA-iodine aqueous state. The crystallinity of the films was investigated for the condition of an amorphous state; the change of structure by deiodination was determined through X-ray diffraction and differential scanning calorimetry.

EXPERIMENTAL

IBC film preparation

The PVA powder from Kuraray Company in Japan was used to prepare films. The PVA films iodinated at solution before casting (IBC films) were prepared by casting the 10 wt % PVA solution containing I_2/KI of 18.6, 43.5, 87.9, 125, and 150 wt % to the PVA (weight gain), which were poured on a glass plate at 60°C and were put under air at 30°C for 24 h. The three kinds of weight gain of I_2/KI (18.6, 43.5, and 87.9 wt %) were controlled in a manner similar to the one described in the work of Oishi and Miyasaka,⁷ and two kinds of those (125 and 150 wt %) were added because more weight gain of I_2/KI was possible in the IBC method.

During the drying period, the weight of samples was checked every day to establish complete water evaporation and excess iodine sublimation. The weight gain was determined from the weight difference of a dry film before and after soaking: 15.2, 39.8, 83.2, 117.0, and 140.1 wt %, respectively.

Deiodination

The iodinated films were deiodinated by dipping in an aqueous solution of 7 wt % sodium thiosulfate and 5 wt % ethylene glycol at 20°C for 3 h, which is enough time for the complete removal of iodine.

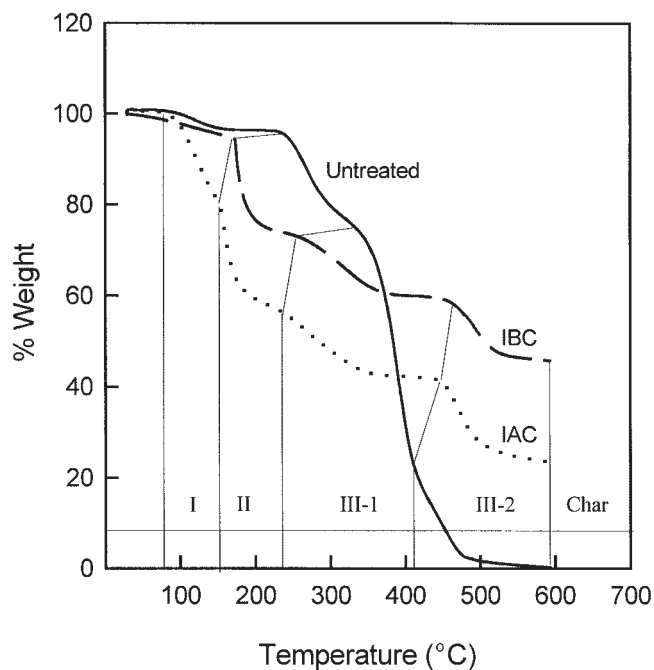


Figure 1 TG curves of untreated film, IAC, and IBC films with weight gain of 89.2% and 140.1% I_2/KI , depicting the different zones.

Measurements

The X-ray diffractometry was performed using Rigaku D/max-III-a with $Cu K\alpha$ radiation.

Thermogravimetry (TG) and differential scanning calorimetry (DSC) were performed by a TA TGA 2950 and a TA DSC 2910, respectively. Both tests were conducted at the heating rate of 20°C/min under the atmosphere of N_2 . For DSC, stainless steel open pans were used to allow the evaporation of iodine.

The dynamic mechanical thermal analysis (DMTA) for the undrawn films was performed by Rheometric Sci. DMTA 3E under the atmosphere of N_2 at the heating rate of 4°C/min.

RESULTS AND DISCUSSION

Structure of IBC films

TG analysis

The reports on the TG analysis for the pure PVA were described in our previous work.¹⁶ Figure 1 shows the TG curves of the IBC film whose maximum weight gain of I_2/KI was 140.1% and the IAC (iodinated after casting) film whose maximum weight gain of I_2/KI and the results of the IAC film have been discussed in our previous work.¹⁶

The step of the TG curves for the iodinated film is the same as in our previous work.¹⁶ They show four or five loss zones associated with the degradation and

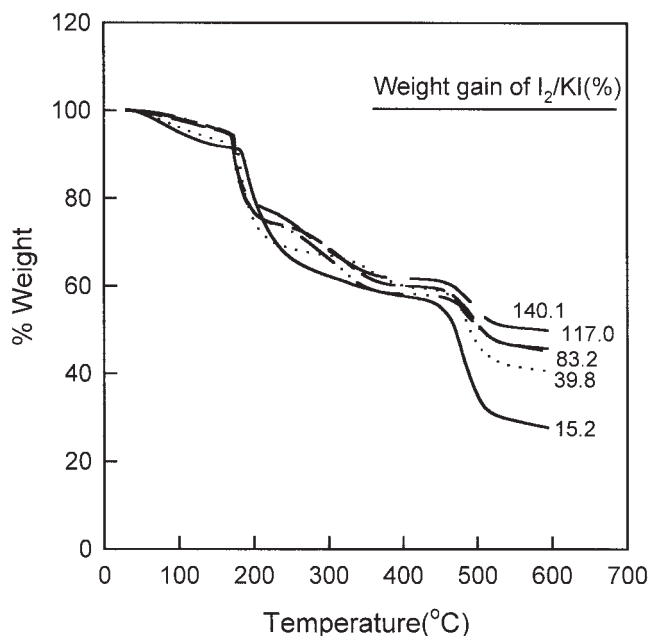


Figure 2 The TG curves of IBC films.

evaporation of excess I₂ molecules (zone I) and I₂ molecules from I₅⁻, partial OH side groups on PVA (zone II) and I₂ from I₃⁻, remaining OH groups and partial main chains (zone III-1), remaining main chains and a very small amount of residue from PVA (zone III-2). The char of KI salts remained.

Compared with the weight loss curve of the IAC film, the set-on temperature of each zone of the IBC film is the same as that of the IAC film, but the loss ratio of zone I is smaller and the quantity of loss remains larger than that of the IAC film. The zone I is associated with the evaporation of I₂ molecules, which were not conformed with PVA molecules, reformed by I₃⁻ of I₂/KI aqueous solution and K⁺ in the dry process. Compared with both IAC and IBC films in terms of the quantity of I₂ reformation, I₃⁻ was easily connected with PVA in an aqueous state (IBC film) rather than PVA in a solid state (IAC film). Therefore, I₃⁻ remaining in the IBC film and I₂ reformed from that were smaller than those of the IAC film, which was the first reason the quantity of loss zone I of the IBC film is smaller than that of the IAC film. Second, the IBC film was really an amorphous state whose structure was relaxed. Therefore, I₂ was easily evaporated in the dry state in contrast to the crystalline state of the IAC film.

It was estimated that the char might be KI salt reformed degradation.¹⁶ The quality of the IBC film was much greater than that of the IAC film. This resulted from the KI salts absorbed in IBC film much greater than that of the IAC film.

Figure 2 shows the TG curves of IBC films iodinated with various weight gain of I₂/KI. Generally, with

increasing I₂/KI, the weight loss of each zone was decreased and finally the quantity of remaining KI was increased. This quantity of KI was related to K⁺ as mentioned earlier. Although the weight loss of zone I for 15.2% and 39.8% was prominently large, the possibility of I₂ reforming was little. It is estimated that I₂ reforming was not evaporated in the dry state for a fine crystal structure as X-ray results show later.

X-ray analysis

Figure 3 shows X-ray diffraction scans of the IBC film with I₂/KI. Generally, with the increase in I₂/KI, the intensity of diffraction peaks decreased, and the peaks at 140.1% of I₂/KI nearly disappeared. Therefore, the structure of the IBC film was relaxed by the intrusion of iodide ions (I₃⁻ or I₅⁻) and the crystal relaxation of the IBC film increased and nearly reached an amorphous state at 140.1% of I₂/KI.

In the case of the IAC film from our previous work, the PVA-iodine complex crystal structure shows itself from 15.2% (0.1mol/L), because I₃⁻ can evenly intrude into the PVA crystal even though with a small amount of I₃⁻.

But, in the case of the IBC film, crystallization was formed differently, that is, the diffraction peak at $\theta = 19.5^\circ$ appeared in 15.2% I₂/KI, which is similar to the PVA crystal. The I₃⁻ ions intruded PVA chains first and then crystallization occurred. This is because PVA chain segments do not combine with I₃⁻ but form the original PVA crystal because of small I₃⁻ ions.

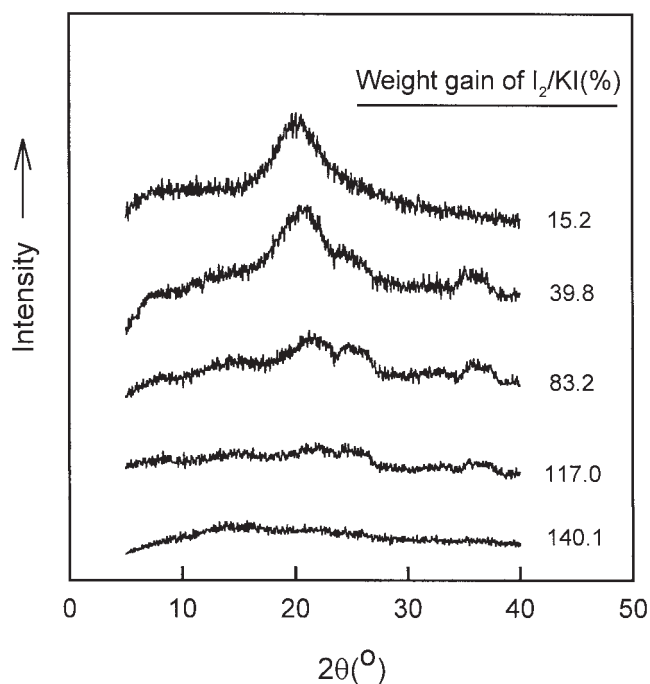


Figure 3 The X-ray diffraction scans of IBC films.

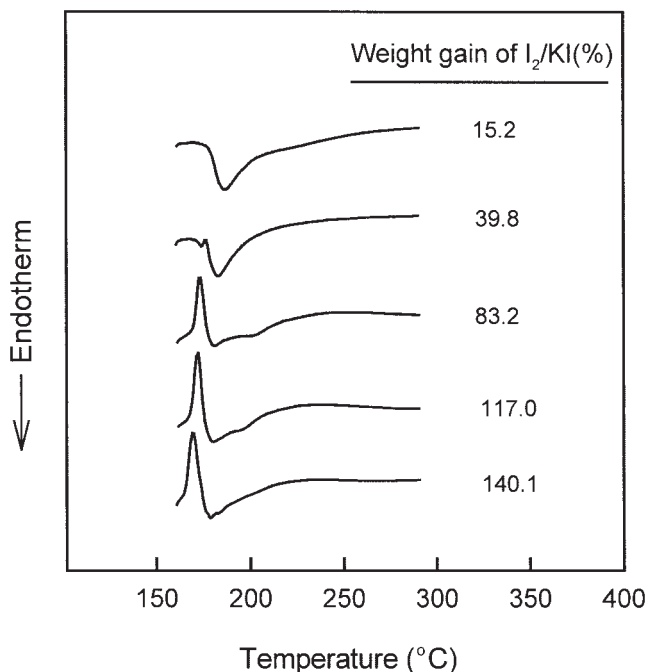


Figure 4 The DSC thermograms of IBC films.

Over 39.8% of I_2/KI , several diffraction peaks appeared at $2\theta = 7.5^\circ, 14.5^\circ, 20.5^\circ, 26^\circ, 32.5^\circ,$ and 35.8° . The diffraction peaks at $2\theta = 7.5^\circ$ (001), 14.5° (101), 20.5° (102), 26° (003), and at $2\theta = 32.5^\circ$ (002), 35.8° (110) were assigned to the substitution model of PVA-iodine complex and the PVA original crystal, respectively. This shows that the PVA-iodine complex and the original PVA crystal are mixed in the IBC film. With increasing I_2/KI , the original PVA crystal decreased and the crystal of PVA-iodine complex increased.

DSC analysis

Figure 4 shows DSC thermograms of the IBC film with I_2/KI . There was a different tendency between 15.2, 39.8% of I_2/KI and 83.2, 117.0, 140.1% of I_2/KI .

In the case of 15.2, 39.8% of I_2/KI , a big endothermic peak appeared at 180°C , corresponding to the decomposition of OH side groups. The small endothermic peak at a temperature lower than 180°C of 39.8% corresponded to the melting of the crystal. Referring to the afore-mentioned X-ray results, the peak of crystal-melting should appear at higher than that of 39.8% of I_2/KI . This was estimated to be included in the decomposition peak that followed. The reason the peak of the melting crystal of lower I_2/KI was higher than that of the IAC film was thought to be because of the presence of not only the PVA-iodine complex crystal but also the PVA original crystal in IBC samples. Also, the peak of decomposition appeared at a temperature higher than 170°C . This was due to the

decrease in the weight loss of zone I, which is associated with I_2 of oxidation from TG results.

In the case of 83.2, 117.0, and 140.1% of I_2/KI , there were sharp exothermic peaks at 170°C and they were followed by broad double endothermic peaks. The exothermic peak at 170°C must be corresponding to the crystallization of the IBC film, which was formed on heating of DSC because the degree of crystallinity was very low. The endothermic peak, the melting crystal peak, and OH group degradation followed. The melting temperature of the IBC crystal was higher than that of the IAC film, which was estimated for the PVA original crystal and formed by heating DSC thermograms with PVA molecules, not combined with iodine but relaxed. The OH degradation temperature was higher than that of the case of 15.2 and 39.8% of I_2/KI , because of the low quantities of I_2 and the weight loss of zone I, referring to the TG results.

DMTA results

Figure 5 shows the DMTA for the pure PVA, IAC film weight gain (89.2% of I_2/KI), and IBC film weight gain (140.1% of I_2/KI). The peak of the α_a dispersion at 70°C for the untreated film is known to be assigned to the glass transition temperature (T_g) of PVA. The peaks of both IAC and IBC films were observed at 60 and 20°C , respectively, lower than that of the untreated film. Such a drop of T_g by iodination may be resulted from the rupture of intermolecular hydrogen bonds by iodine. Especially, the drop in T_g of the IBC

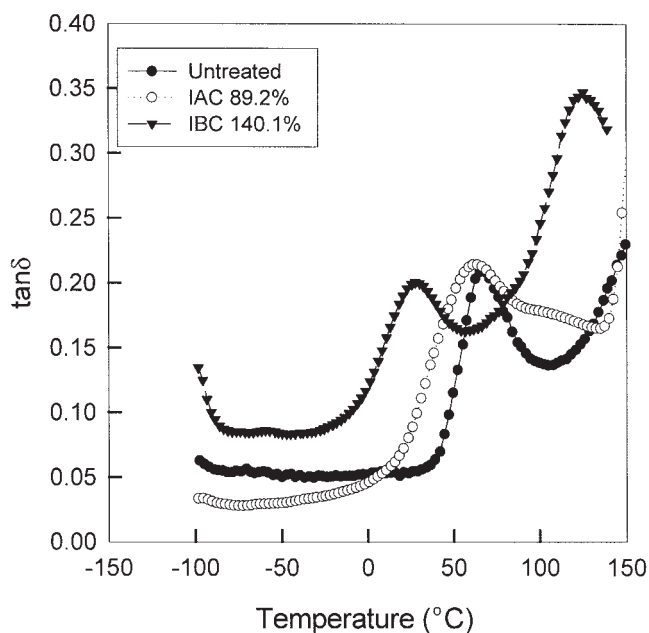


Figure 5 The curves of $\tan \delta$ versus temperature for untreated, IBC, and IAC films.

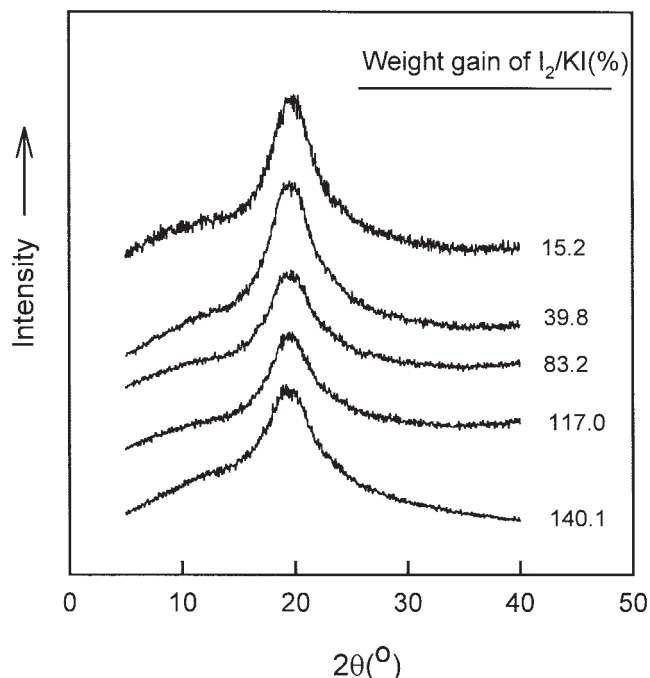


Figure 6 The X-ray diffraction scans of films obtained by deiodination of IBC films.

film extremely decreased to nearly an amorphous state.

In addition, the intensity of the $\tan \delta$ for the untreated film began to increase rapidly at around 150°C, which is estimated as the beginning of the α -relaxation temperature (T_α) peak. It is known that PVA has a unique crystalline relaxation, referring to α -relaxation at T_α (150°C), even lower than its melting point (230°C). Other flexible polymers such as polyamide with strong hydrogen bonds do not exhibit crystalline relaxation. For the IAC film, a very broad peak likely corresponding to α -relaxation is observed at 110°C, lower than T_α of the untreated film. Such a drop in T_α by iodination confirms that iodine ruptures the intermolecular hydrogen bonds in the crystalline region of PVA. For the IBC film, the clear peak by T_α is shown at 120°C. But the IBC film was in the amorphous state, and T_α peak appeared at 120°C, though crystallization could not occur until 120°C by DSC results. It is estimated that DMTA was measured at 4°C/min whose rate was enough to crystallize over α_a . Especially, T_α of the IBC film was larger than that of the IAC film, which reconfirmed the fact that the crystallization of the IBC film contained the PVA original crystal factor but was relaxed.

The rapid increase in $\tan \delta$ for the IAC film was estimated to be related to the melting of the crystal, from the DSC results indicated in the first part of this study.¹⁶

Structure of IBC film after deiodination

Figures 6 and 7 show the X-ray diffraction scans and

DSC thermograms of the IBC film after deiodination. All the films indicated the peaks as being characteristic of the original crystalline of the PVA, which means that the crystalline structure of the PVA was restored through deiodination, irrespective of the crystalline structure in the iodinated state. But, the crystal structure of the larger quantity of I_2/KI was relaxed because the DSC peaks of films appeared somewhat broad.

CONCLUSIONS

IBC films were prepared by casting aqueous solutions of 10 wt % PVA containing selected quantities of I_2/KI . The quantity of I_2/KI was controlled to obtain 15.2, 39.8, 83.2, 117.0, and 140.1%. The structure of the films before and after deiodination was investigated by TG, XRD analysis, DSC, and DMTA.

The TG curves of the IBC film exhibited three distinct zones of weight loss corresponding to the evaporation of H_2O and I_2 molecules (zone I), evaporation of I_2 and partial decomposition of side groups ($-OH$) (zone II), degradation of the remaining side groups and partial degradation of the main chain (zone III-1), and degradation of the remaining main chain (zone III-2) and the char zone corresponding to KI , which is similar to those of the IAC film. But the weight loss of zone I is lower and the percent of char is higher, compared with those of the IAC film.

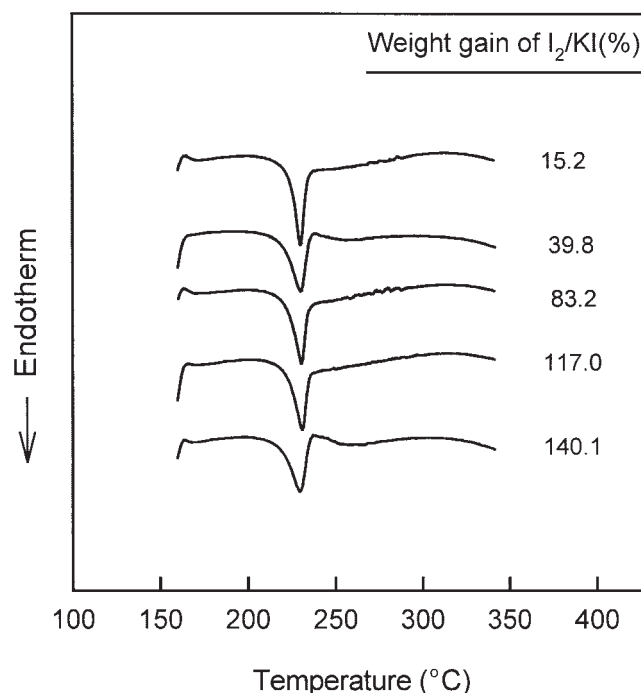


Figure 7 The DSC thermograms of films obtained by deiodination of IBC films.

The crystalline structure of the film with the weight gain of 15.2%, almost the same as that of the pure PVA, and the structure of the film of the weight gain of 39.8–117.0% gradually become similar to that of the IAC film with increasing weight gain, but the film with the weight gain of 140% was almost amorphous.

The DSC thermograms of the IBC film with the weight gain of 15.2 and 39.8% indicated endothermic single or double peaks at around 180°C, corresponding to the crystal melting and degradation of side groups; those with weight gains 83.2% and above indicated exothermic peaks at around 170°C, corresponding to crystallization, and broad endothermic peak at around 180–200°C, corresponding to the crystal melting and degradation of side groups.

The dynamic mechanical α_n transition of the IBC film with the weight gain of 140.1% appeared at around 20°C.

XRD and DSC analysis of deiodinated films show that the crystal structure on deiodination of all the IBC films, regardless of crystallinity, returned to that of the pure PVA.

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