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Plasticizer effect on the melting and crystallization behavior of polyvinyl alcohol

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Abstract

The melting and crystallization behavior of polyvinyl alcohol (PVA) were examined as a function of plasticizer amount. The melting temperature (T_m) of PVA decreased with increasing the amount of glycerin. The effect of a plasticizer rapidly diminished when the phase separation of glycerin in PVA occurred. In addition, the crystallization peak temperature (T_c) of a fully hydrolysed PVA was reduced, and the maximum crystallization rate (K_{max}) was retarded, and the crystallite size distribution ($\omega_{1/2}$) was widened. However, the crystallization behavior (T_c, K_{max}, $\omega_{1/2}$) of a partially hydrolysed PVA could be disregarded compared with a fully hydrolysed PVA. The thermal history did not affect the crystallization behavior of a fully hydrolysed PVA, but largely affected that of a partially hydrolysed PVA. In a fully hydrolysed PVA / a partially hydrolysed PVA blend system, two T_m peaks appeared, and the concurrent crystallization occurred.

Keywords: Polyvinyl alcohol; Plasticizer; Melting and crystallization behavior

1. Introduction

Polyvinyl alcohol (PVA) has been attractive in different areas of science and technology, for example, textile sizing and finishing agent, emulsifier, photosensitive coating, and adhesives for paper, wood, textiles, leather [1,2].

In addition, PVA has excellent gas barrier properties due to small, dense and closely packed 'Monoclinic' crystallite [1,2]. PVA also offers flexibility, transparency, toughness as well as the lower cost than the other barrier polymer. Therefore, PVA has been developed as a barrier film for food packaging application [3–6]. However, it is difficult to produce the film because the T_m and decomposition temperature of PVA are closed. It is a limit for expanding into the market of food packaging application due to high manufacturing cost. Therefore, it is necessary to improve the thermal characteristic of PVA in order to apply for the facile packaging film formation.

The aim of this study is, therefore, to develop novel methodology of PVA extrusion by conventional extruder without modification by means of improving the thermal characteristic of PVA. In addition, the melting and crystallization behavior of PVA were also examined according to the amount of a plasticizer, thermal history and PVA blend.

2. Experimental

2.1. Materials

In this experiment, four commercial grades of polyvinyl alcohol were adapted and obtained from Dupont (USA) and Oriental Chemical Industries (Korea) in granule form: Elvanol 71-30 (viscosity (mPa S, 4% aqueous solution at 20 °C) = 27–33, hydrolysis (mol%, dry basis) = 99.0–99.8), Polinol F17 (viscosity = 27–30, hydrolysis = 98.0–99.5), Polinol P17 (viscosity = 21–24, hydrolysis = 85.0–88.5), Polinol P05 (viscosity = 5.0–5.6, hydrolysis = 85.5–87.5). PVA is classified by the degree of hydrolysis and polymerization. The mainly used PVA is classified into the fully hydrolysed grades (97.5–99.8% degree of hydrolysis) and the partially hydrolysed grades (87–89% hydrolysis) [1,2].

The extra pure glycerin grade was used as a plasticizer and supplied by Junsei corporation (Japan).

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2.2. Sample preparation

Glycerin was impregnated into PVA and then dried in a vacuum oven at 80 °C for 1.0 h. The dried PVA was used in granule form, and the PVA blend was used in pellet form through using C.W. Brabender Plasticorder—3/4 inch single screw extruder ($L/D = 25$). The operating temperature of extruder was 210 °C.

2.3. Thermal measurement

Thermal analysis was performed from 30 to 250 °C at a rate 20 °C/min under nitrogen atmosphere by the model TA-7 differential scanning calorimeter (Perkin–Elmer company). In order to erase the thermal history, the temperature was kept for 3 min in the molten state and decreased to room temperature at a cooling rate of 20 °C/min.

3. Results and discussion

3.1. Effect of plasticizer on melting behavior

Most of the plasticizers used in PVA are capable of reducing the melting point of a PVA, and provide the flexibility to a final product. The most generally used plascitizer is triethylene glycol and glycerin [1,2,7–10]. To have higher boiling point and lower the dissolving temperature of PVA, glycerin is an optimum plasticizer.

In general, when the degree of hydrolysis of a PVA is higher, the T_m and glass transition temperature (T_g) are also higher too [1,2]. The relationship between T_g of PVA and plasticizer has been estimated by Kelly–Bueche equation [7,10]. Similar to T_g, there is a relationship between T_m and the amount of a plasticizer.

Fig. 1 shows the DSC heating thermograms and melting peak temperature according to the amount of glycerin in case of the fully hydrolysed PVA. As the amount of glycerin increased, the T_m of PVA diminished. It can be interpreted that glycerin increases the segmental mobility of PVA and decreases the crystallite region of a PVA.

The heat of fusion of the fully hydrolysed PVA with respect to the amount of glycerin was represented in Fig. 2. The heat of fusion of PVA significantly decreased as the amount of glycerin increased. This phenomenon indicates that the crystallinity of PVA is reduced according to the amount of glycerin.

Fig. 3 shows the variation of T_m as a function of the amount of glycerin in the partially hydrolysed PVA. The T_m also decreased with increasing the amount of glycerin. However, as shown in Figs. 1 and 3, the diminished magnitude of T_m was reduced gradually. It is interpreted that the effect of a plasticizer diminishes gradually as the amount of glycerin increases.

In order to clarify this phenomenon, the diminished magnitude of melting point (ΔT_m) is divided by the

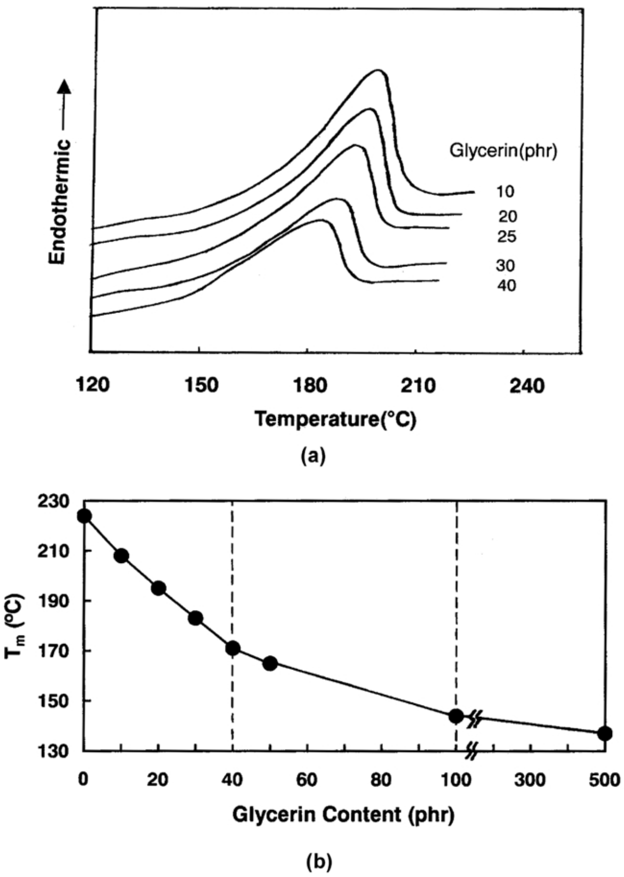


Fig. 1. DSC heating thermograms and melting peak temperatures (T_m) of Elvanol 71-30 having various amount of glycerin (heating rate = 20 °C/min): (a) DSC heating thermograms; (b) melting peak temperature (T_m).

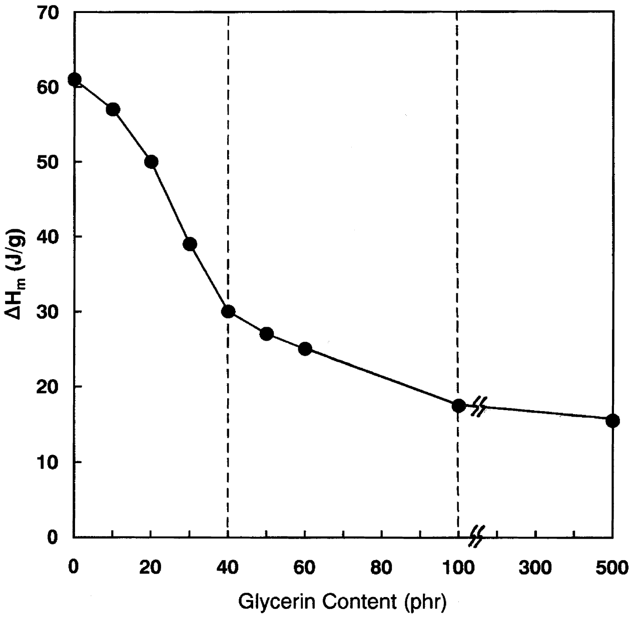
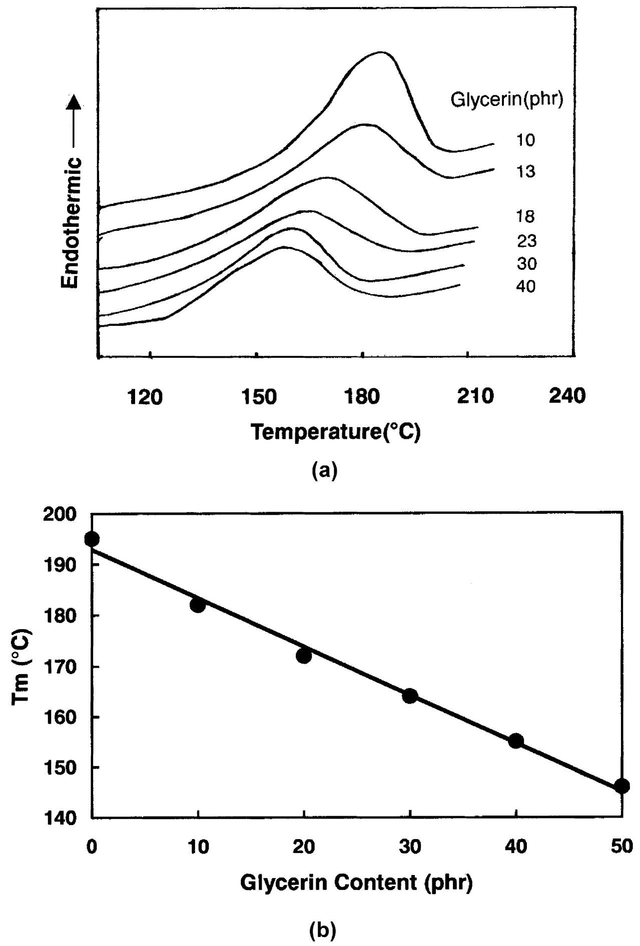


Fig. 2. Heat of fusion (ΔH_m) versus glycerin content for Elvanol 71-30.



(a)

(b)

Fig. 3. DSC heating thermograms and melting peak temperatures (T_m) of Polinol P17 having various amount of glycerin (heating rate = 20 °C/min): (a) DSC heating thermograms; (b) melting peak temperature (T_m).

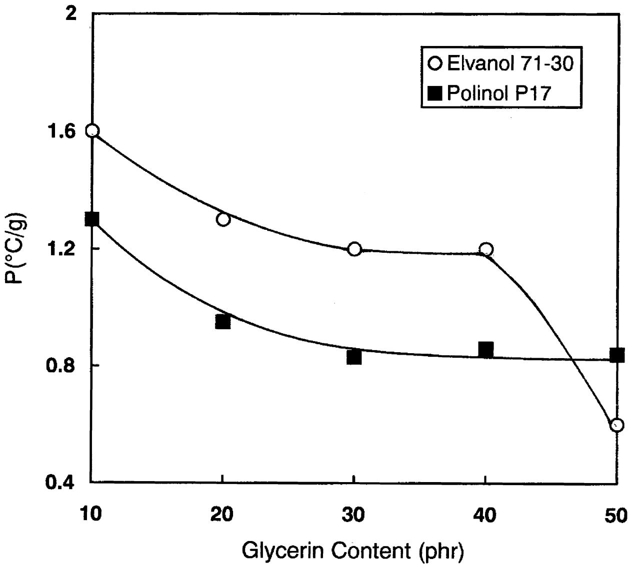


Fig. 4. Effect of plasticizer (P) for Elvanol 71-30 and Polinol P17 as a function of the content of glycerin.

concentration of added glycerin (ΔC), and it is defined as '*P*' (the effect of a plasticizer).

$$P = \frac{T_1 - T_2}{C_2 - C_1} \tag{1}$$

where T_1, T_2 represent the melting point before and after glycerin addition, and C_1, C_2 represent the concentration before and after glycerin addition.

Fig. 4 shows '*P*' according to the concentration of glycerin by applying the data of Figs. 1 and 3 to Eq. (1). As shown therein, the *P* generally decreased with increasing the amount of glycerin. In case of the fully hydrolysed PVA, the effect of a plasticizer was maintained up to 40 phr of glycerin, but it was drastically reduced beyond 40 phr. It has good agreement with the phenomenon as shown in Fig. 2. In other words, the heat of fusion sharply diminishes, but the diminishing rate of the heat of fusion largely reduces beyond 40 phr of glycerin. However, in case of the partially hydrolysed PVA, the effect of a plasticizer slowly decreased and then sharply reduced beyond 65 phr of glycerin. This phenomenon is due to the occurrence of the phase separation of glycerin in PVA. In case of the fully hydrolysed PVA, the phase separation of glycerin occurred beyond 40 phr, and the perfect phase separation was existent at ca. 100 phr. The T_m and heat of fusion of PVA did not almost change beyond 100 phr of glycerin, as shown in Figs. 1 and 2. In case of the partially hydrolysed PVA, the phase separation occurred beyond 65 phr. It is coincided with the reported data by P. Sakellariou et al. [7,8]. In Fig. 4, the fully hydrolysed PVA has a larger '*P*' compared with that of the partially hydrolysed PVA until the phase separation of glycerin occurred. It can be explained by the different activity that takes part in polar and hydrogen-bonding interaction between PVA and glycerin for obtaining the effect of a plasticizer. As a result, the effect of a plasticizer with respect to the fully hydrolysed PVA is larger than the partially hydrolysed PVA below 40 phr of glycerin. As the amount of glycerin increases, the activity of a PVA gradually diminishes, and the hydrogen-bonding interaction between the glycerin also increases. Therefore, the effect of a plasticizer is reduced gradually and the phase separation of glycerin in PVA occurs at last stage.

3.2. Effect of plasticizer on crystallization behavior

Fig. 5 shows the DSC cooling thermograms and crystallization peak temperature (T_c) of Elvanol 71-30 and Polinol P17 according to the amount of glycerin. As the amount of a plasticizer increased, the peak temperature of an exotherm of two grades continuously decreased irrespective of the degree of hydrolysis. Since the glycerin is strong polar and hydrogen bonded with PVA, it act as like polymer diluent and reduces the T_c of a PVA. This result is similar to the experimented result by Moon et al. [11]. They reported that the T_c of blend decreased by the combining Nylon 6 with compatibilizer in PP/Nylon 6 blends. In addition, the diminished magnitude of T_c (the slope of Fig. 5(b)) was

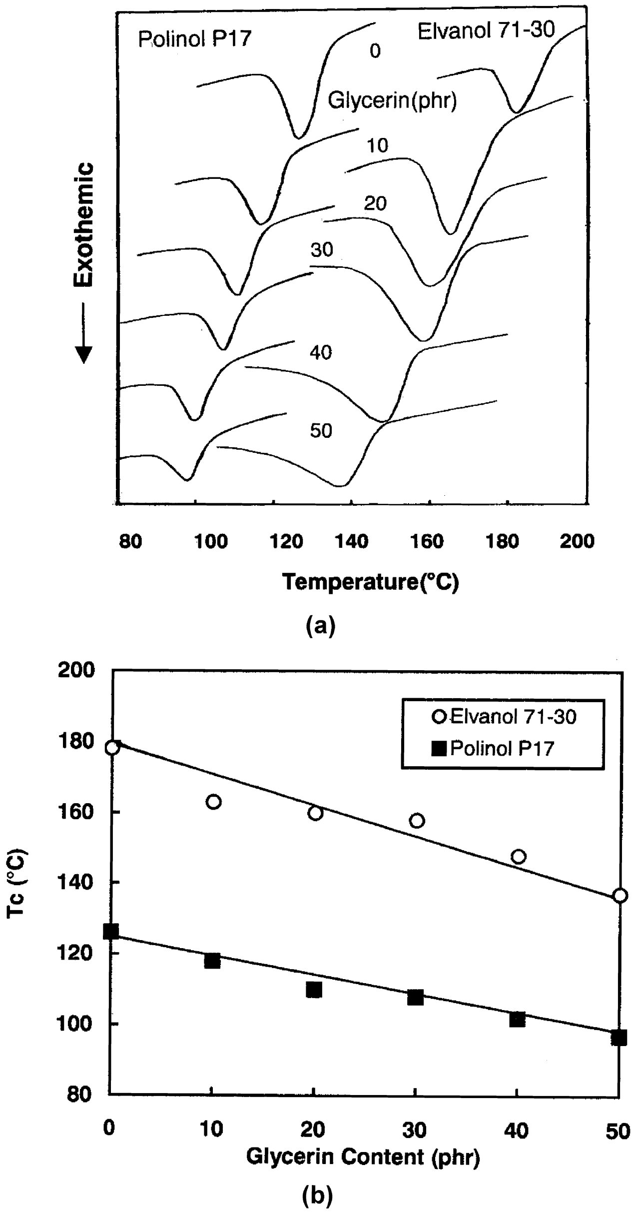


Fig. 5. DSC cooling thermograms and crystallization peak temperatures (T_c) of Elvanol 71-30 and Polinol P17 according to glycerin content (cooling rate = −20 °C/min): (a) DSC cooling thermograms; (b) crystallization peak temperature (T_c).

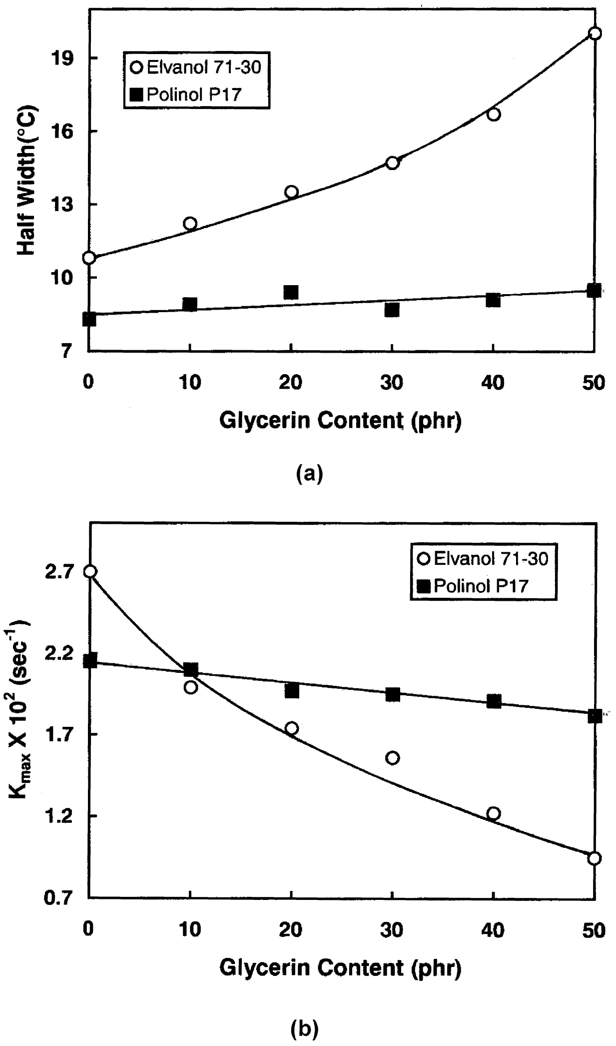


Fig. 6. Half width ($\omega_{1/2}$) and maximum crystallization rate (K_{max}) versus glycerin content for Elvanol 71-30 and Polinol P17 (cooling rate = −20 °C/min): (a) half width of crystallization exotherms; (b) maximum crystallization rate.

different due to the degree of hydrolysis between Elvanol 71-30 and Polinol P17. The slope of Polinol P17 is gentler because the activity of polar and hydrogen bonding interaction and the crystallite region are reduced significantly. This is mainly due to the irregular molecular chain like acetate group in the backbone of Polinol P17.

Fig. 6 shows the half width ($\omega_{1/2}$) and maximum crystallization rate (K_{max}) of PVA as a function of the concentration of glycerin. The half width ($\omega_{1/2}$) was calculated by the width of the crystallization exotherms at half height and is a measure of crystallite size distribution [12]. In case of Polinol P17, the $\omega_{1/2}$ value was not drastically changed with increasing the concentration of glycerin, but the $\omega_{1/2}$ value of Elvanol 71-30 significantly increased. It can be predicted that glycerin takes part in the crystallization behavior of a fully hydrolysed PVA and widens the distribution of the PVA crystallite. Although the $\omega_{1/2}$ value of the partially hydrolysed PVA slightly increased, it can be disregarded compared with the fully hydrolysed PVA. This means that the glycerin does not affect largely the crystallite size distribution of a partially hydrolysed PVA. This phenomenon comes from the difference of the crystallite region and affinity with respect to glycerin. The crystallization peak temperature (T_c) represents the typical value of a semi-crystalline polymer and is measured by cooling from the molten state. During the sample cooling, T_c reflects overall crystallization rate due to the combined effects of nucleation and growth. Several studies have been carried out with respect to the non-isothermal crystallization kinetics and mainly described the crystallization behavior according to the structural regularity of the co-polymer chain in detail [14–19]. Ziabicki [13,14] suggested that maximum value of the rate constant corresponding to crystallization peak temperature, K_{max}, could be calculated by the following equation.

$$\mathrm{K}_{\max} = \frac{C_{\mathrm{K}}}{\mathrm{t}_{\max}} \tag{2}$$

Where t_{max} is the time from the start of crystallization to reach of the maximum rate of reaction, and C_K is the ratio of crystallinity before and after t_{max}. The larger value of K_{max} indicates that polymer crystallizes more rapidly.

Non-isothermal crystallization exotherms were observed on DSC cooling thermograms at a cooling rate of 20 °C/min and was shown in Fig. 6(b). Although the crystallization rate of Polinol P17 gradually decreased, the crystallization rate of Elvanol 71-30 was reduced dramatically according to the increment of glycerin concentration. This result has a good agreement with the results of Figs. 5(b) and 6(a). In case of a fully hydrolysed PVA, the glycerin lowers the T_c and retards the crystallization rate and widens the crystallite size distribution. This result means that a plasticizer is bonded with a fully hydrolysed PVA for thereby diminishing the regularity of molecular chain and increasing the active energy of homogenous nucleation, so that retarding the crystallization rate of PVA.

3.3. Effect of thermal history on crystallization behavior

Fig. 7 shows the DSC cooling thermograms and crystallization peak temperature (T_c) of two partially hydrolysed grades without glycerin according to the number of heating–cooling operation. Fig. 8 represents the half width and maximum crystallization rate of two partially hydrolysed PVA. The one unit of heating–cooling operation was performed from 30 to 250 °C at a rate 20 °C/min, and was kept for 3 min in the molten state and was cooled to room temperature at a rate of 20 °C/min. In case of a fully hydrolysed PVA, it was conformed that the T_c, $\omega_{1/2}$ and K_{max} were not changed according to the repeated heating–cooling operation. When the heating–cooling operation was repeatedly performed after adding the plasticizer and reducing T_c, there was no variation. The T_c and K_{max} of a

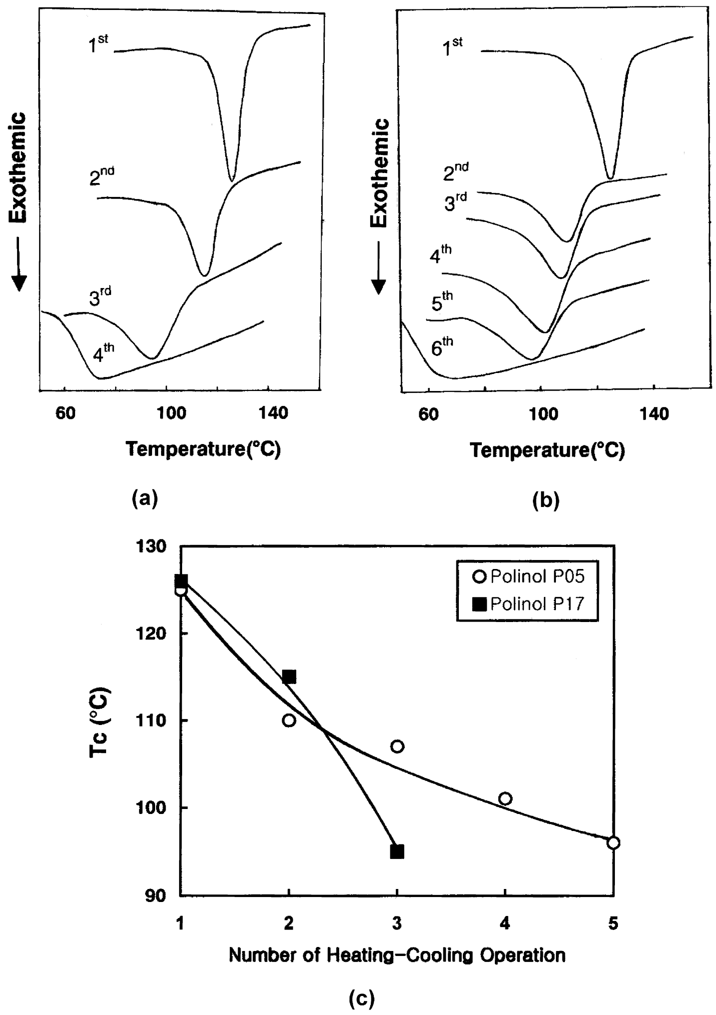


Fig. 7. DSC cooling thermograms and crystallization peak temperatures (T_c) versus the number of heating–cooling operation for two partially hydrolysed grades without glycerin: (a) DSC cooling thermograms of Polinol P17; (b) DSC cooling thermograms of Polinol P05; (c) crystallization peak temperature (T_c).

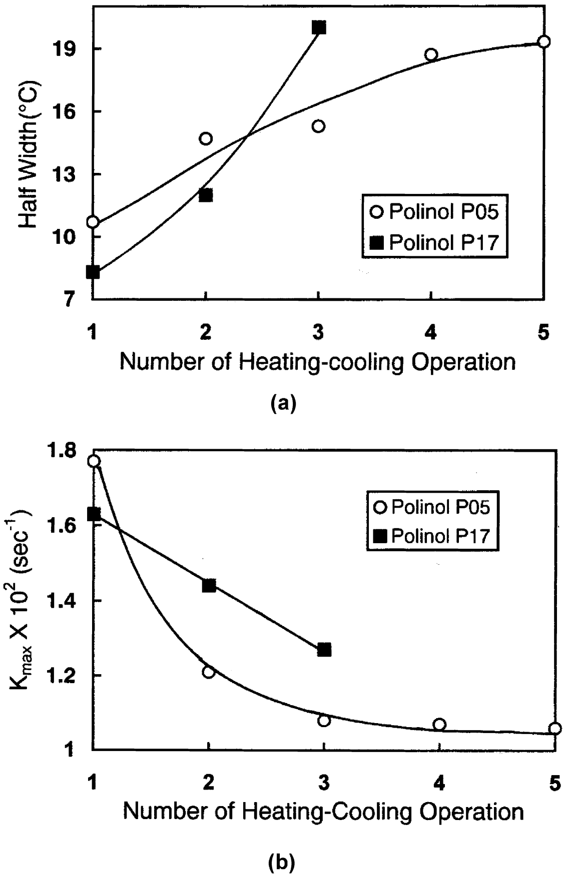


Fig. 8. Half width ($\omega_{1/2}$) and maximum crystallization rate (K_{max}) versus the number of heating–cooling operation for Polinol P17 and Polinol P05 without glycerin: (a) half width of crystallization exotherms; (b) maximum crystallization rate.

partially hydrolysed PVA diminished and the $\omega_{1/2}$ value increased as the heating–cooling operation was repeatedly performed. A partially hydrolysed PVA has ca. 11–14 mol% of acetate group. Therefore, a partially hydrolysed PVA provides the free volume capable of increasing the segmental mobility and has the T_c, $\omega_{1/2}$ and K_{max} variations. In particular, Fig. 8(b) shows that Polinol P17 had a faster crystallization rate than that of Polinol P05. The fast crystallization rate makes to reduce fast T_c and to widen fast the crystallite size distribution. This result is caused by the different chain mobility of two grades. Since Polinol P05 has the lower degree of polymerization, it has the high potential of the chain mobility compared with that of Polinol P17. Therefore, at initial stage, the decreasing rate of the T_c and the crystallization rate were very large, and the crystallite distribution was wide. It may be interpreted that a lot quantity of Polinol P05 molecules form to crystallites at initial stage, and then only the small quantity of remaining molecules is crystallized gradually under the repeated heating–cooling operation. However, in case of Polinol P17, the fixed quantity of molecules is continuously crystallized. Therefore, the rate of T_c, $\omega_{1/2}$ and K_{max} of Polinol P17 were in a first proportion to the number of heating–cooling operation.

The T_c of Polinol P05 approached to 96 °C and it was similar to that of Polinol 17, in Fig. 7(c). In addition, the final $\omega_{1/2}$ values of two grades existed at the near $\omega_{1/2} =$ 20 °C, as shown in Fig. 8(a). It can be explained that the final values of T_c and $\omega_{1/2}$ are nearly same due to same degree of hydrolysis of the two grades (almost same quantity of acetate group).

Therefore, the crystallization behavior of a partially hydrolysed grade is largely affected with respect to the heat history and has different behaviors according to the degree of polymerization.

3.4. Effect of PVA blend on thermal behavior

Fig. 9 shows the DSC heating and cooling thermograms of the Polinol F17/P17 blend according to blending ratio.

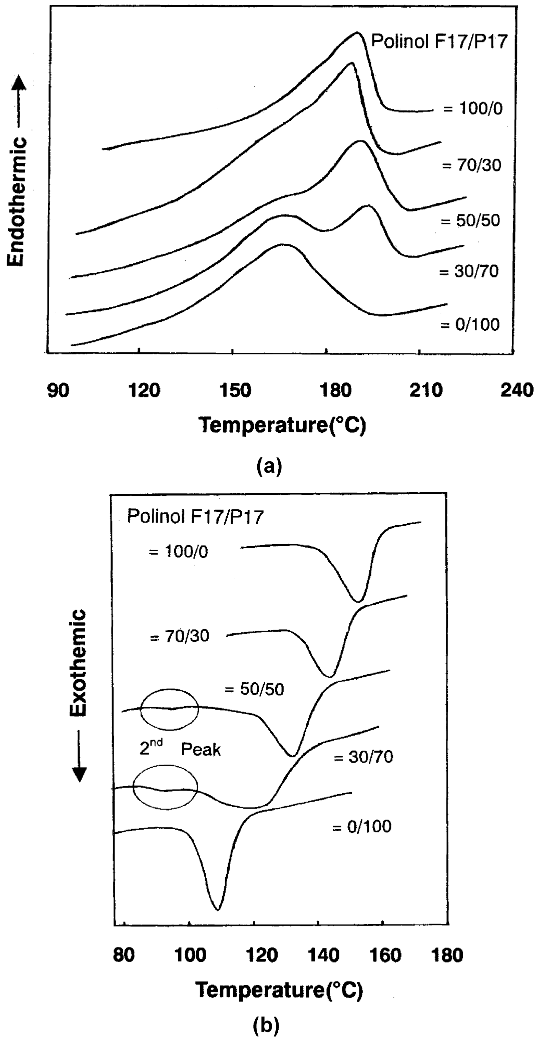


Fig. 9. DSC heating and cooling thermograms of Polinol F17/P17 blend impregnated with glycerin 30 phr as a function of blending ratio: (a) DSC heating thermograms (heating rate = 20 °C/min); (b) DSC cooling thermograms (cooling rate = −20 °C/min).

This two PVA grades were impregnated with 30 phr of glycerin and has the same degree of polymerization. As the ratio of Polinol P17 increased, the melting peak temperature was divided into two parts. Namely, the melting peak temperature of Polinol P17 clearly appeared because the heat of fusion of Polinol P17 becomes larger. This is because it is not fully miscible with Polinol F17 and P17 due to the hydrophobic property of the acetate group in Polinol P17. However, the T_c of PVA blend became near to the T_c of a pure Polinol P17 with increasing the amount of the Polinol P17. In addition, the temperatures at which the crystallization starts and ends were also diminished. This result is similar with that of the lowering T_c of PVA when increasing the amount of glycerin in Fig. 5. This phenomenon is in agreement with the previous results of PP/Nylon 6 blend used the compatibilizer [11,20]. They reported that the concurrent crystallization happened due to the strong bonding between two phases.

Fig. 10 shows the T_c, $\omega_{1/2}$ and K_{max} of Polinol F17/P17 blend impregnated with glycerin 30 phr according to blending ratio. The T_c of blend was first proportion to the amount of Polinol P17. The crystallite size distribution became wider, and the crystallization rate drastically dropped. This result is the same as that of the fully hydrolysed PVA in Figs. 5(b) and 6.

Therefore, in case of crystallization behavior, it can be judged that the partially hydrolysed grade plays the role of a plasticizer when blending a partially hydrolysed grade with a fully hydrolysed grade.

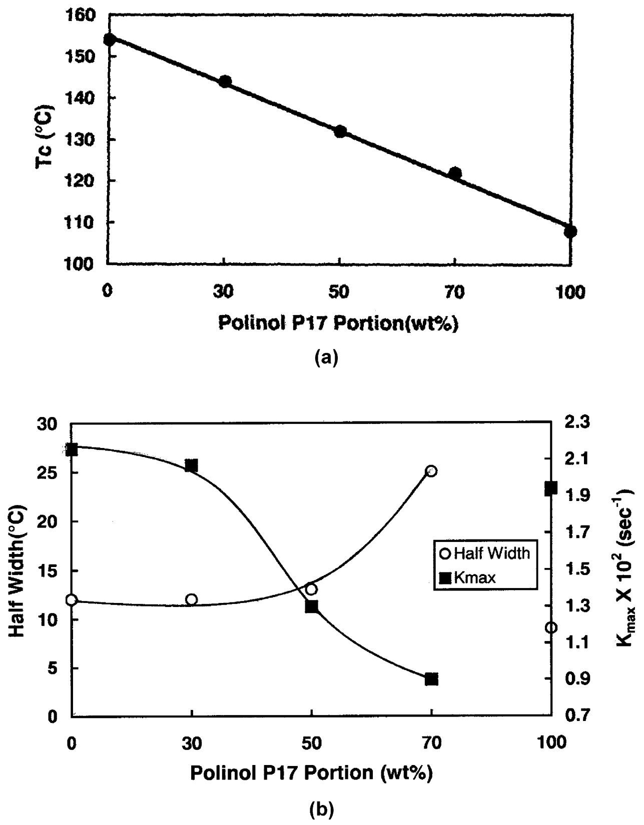


Fig. 10. Crystallization peak temperatures (T_c), half width ($\omega_{1/2}$) and maximum crystallization rate (K_{max}) of Polinol F17/P17 blend impregnated with glycerin 30 phr versus blending ratio: (a) T_c; (b) $\omega_{1/2}$ and K_{max}.

As shown in Fig. 9(b), the second T_c peak was not observed at 30 wt% of Polinol P17. However, it appeared very weakly at 95 °C in case of 50 wt% of Polinol P17, when the content of Polinol P17 approached at 70 wt%, the second T_c peak appeared clearly at 92.5 °C. In addition, the area of second peak increased with increasing the amount of a partially hydrolysed PVA. This second T_c peak is mainly attributed to a surplus partially hydrolysed PVA.

4. Conclusions

We have investigated the effects of a plasticizer, thermal history and PVA blend on the melting and crystallization behavior of PVA.

In case of melting behavior, the melting point (T_m) of PVA was reduced with increasing the amount of a plasticizer regardless of the degree of hydrolysis. However, the effect of a plasticizer was different according to the degree of hydrolysis, and decreased due to the phase separation of a plasticizer in PVA.

In case of crystallization behavior, a fully hydrolysed PVA was affected with the amount of plasticizer, and a partially hydrolysed PVA was mainly influenced by the thermal history. In addition, in case of a fully hydrolysed PVA / a partially hydrolysed PVA blend system, the crystallization behavior was changed by the amount of a partially hydrolysed PVA. When the content of a plasticizer, the number of heating–cooling operation (thermal history) as well as the amount of a partially hydrolysed PVA increased, respectively, the crystallization peak temperature (T_c) was reduced, and the crystallite size distribution ($\omega_{1/2}$) was widened. In the crystallization behavior of a partially hydrolysed PVA, the maximum crystallization rate (K_{max}) was different according to the degree of polymerization, and the final value of T_c and $\omega_{1/2}$ were almost same.

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