



Non-isothermal crystallization kinetics of polyvinyl alcohol plasticized with glycerol and pentaerythritol

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Received: 3 September 2019 / Accepted: 9 February 2020 / Published online: 17 February 2020
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Abstract

In this work, we chose different ratios of glycerol and pentaerythritol to plasticize PVA. The solid and liquid were compounded to plasticize PVA, because pentaerythritol had a large molecular weight and a high boiling point, which can solve the glycerol's migration problem and make it beneficial for long-term plasticization. The interaction of the hydroxyl group of a large molecular weight plasticizer with the PVA hydroxyl group has not been observed for the influence of the PVA molecular chain into the crystal lattice. So, this work investigated the crystallization behaviors in detail. The results showed that the addition of plasticizer can change the regular structure of PVA. It made it difficult to discharge the molecular chain into the crystal lattice and hindered the crystallization of PVA. After the addition of plasticizer, the crystallization energy required increased. The XRD indicates that the plasticizers of different molecular weights can effectively destroy the original crystal structure of PVA, and the plasticizer interacted with PVA to form stronger hydrogen bonds to replace the intermolecular phase of PVA itself intramolecular interactions.

Keywords Polyvinyl alcohol · Crystallization behaviors · Plasticizer · Differential scanning calorimetry

Introduction

Polyvinyl alcohol (PVA) is a kind of water-soluble polymer. It possesses good biogradability, water solubility and barrier properties [1]. Therefore, people are seeing PVA as environment friendly polymeric material [2, 3]. However, there exists strong inter- and intra-molecular hydrogen bonding between PVA and a high structural regularity of the –OH groups on the backbone of PVA, leading to a high crystallinity and melting

point, which is near or higher than its decomposing temperature [4, 5]. Therefore, the melting processing of PVA is the main challenge for the production of PVA products, such as films, foams, etc. [6]. So the melting processing of PVA products attracts wide attention in the world.

Incorporating small molecular plasticizers with polar groups, such as polyols [7–9], amides [10, 11], is one of the most effective methods of improving the processability of PVA. The introduction of plasticizers would reduce the original molecular interaction between PVA [12, 13], leading to a decrease in crystallinity and melting point of PVA. Therefore, the processing window would be enlarged and the melt processing ability of PVA would be easily achieved [12].

Glycerol is often used in PVA plasticization as a traditional plasticizer, because it has hydroxyl groups in polyols [14]. But the plasticizing efficiency is limited and liquid plasticizer easily precipitates [15]. Pentaerythritol has higher stability due to its special structure and is usually used as plasticizer [16]. Solid plasticizer have the disadvantage of poor mixing. Therefore, a solid plasticizer and a liquid plasticizer can be mixed to achieve a better plasticizing effect of PVA.

The crystallization behaviors are similar to non-isothermal crystallization behaviors during the processing of PVA. The crystallization behaviors of PVA would influence its

Electronic supplementary material The online version of this article (<https://doi.org/10.1007/s10965-020-2038-4>) contains supplementary material, which is available to authorized users.

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processability as well as the product quality [17, 18]. Polymer crystallization from melting usually executes through two consecutive processes. First, homogeneous or heterogeneous nucleation of crystallites, and second, the growth of those nucleated crystallites [19]. Among these, nucleation is the process that affects significantly the structure and polymorphism of the polymers. In addition, the mechanical properties of crystalline polymers depend on partial crystallinity and crystal microstructure, so the study of crystallization kinetics is very important. Researchers often control the aggregation structure of PVA by adding additives, restricting crystallization to lower the melting point and increasing its thermal stability [20, 21]. In previous investigations, less research has been done on the action of liquid plasticizers and solid plasticizers on PVA. And few have studied the kinetic parameters of both in detail.

In our previous studies [22], the effect of compound plasticizers on the plasticizing properties of PVA had been extensively studied and we found liquid plasticizers have a good plasticizing effect on PVA. However, the plasticizer had migration and oiling phenomenon. Therefore, incorporation of solid plasticizer with higher molecular weight would improve the long-term plasticizing effect compared to liquid plasticizers. In this work, the solid and liquid was compounded to plasticize PVA and the crystallization behaviors were investigated in detail.

Experimental

Materials

PVA (117) with the molecular weight of 83,000 and alcoholysis degree of 98–99% was purchased from Kuraray Co., Ltd. (Japan). Pentaerythritol and glycerol were provided by Sinopharm Chemical Reagent Co. Ltd., China. All the materials were used as received without further treatment.

Melting processing of PVA

The pentaerythritol and glycerol were mixed to obtain the compound plasticizer. The compositions of the plasticizers were shown in Table 1. PVA and the compound plasticizers were charged into a mixer and further mixed at 210 °C for

10 min with a stirrer speed of 1800 rpm. The plasticized PVA were obtained by compression molding on a plate vulcanizing machine (XLB-400, Huaqing Industry Group, Qingdao, China). The molding temperature, pressure and time were 110 °C, 5 tons, and 5 min respectively. All the films were dried at 105 °C and placed in desiccators (P₂O₅ as desiccant) before tested.

Characterization

Non-isothermal crystallization behaviors were investigated by differential scanning calorimetry analyzer (DSC Q100, TA Instruments, USA) under N₂ atmosphere. Samples of 4–5 g were maintained at 240 °C for 3 min to eliminate thermal history. Then the samples were quenched to 50 °C with a cooling rate of 5, 10, 20 and 40 °C / min to investigate the influence of cooling rate on crystallization behaviors. X-ray diffraction (XRD) patterns of the samples were recorded on a XRD instrument (XRD-6000, SHIMADZU Co., Japan) with Cu K_α radiation ($\lambda = 0.154$ nm) at 40 kV and 30 mA. X-ray diffraction data were collected from $2\theta = 5^\circ$ to 45° at a scanning rate of 4° /min.

Results and discussion

Non-isothermal crystallization analysis

The non-isothermal crystallization curves of pure PVA and plasticized PVA were shown in Fig. 1 and the related kinetic parameters were listed in Supporting Information, Table S1. With the increase of cooling rate, the peak temperature of crystallization (T_p) and onset temperature of crystallization (T_{onset}) both shifted to lower temperature. The T_{onset} of neat PVA changed from 197 °C to 190 °C as the cooling rate decreased, and the crystallinity also decreased. PVA molecular segment had enough time to motion at a lower cooling rate, so the sample could crystallize at a higher temperature. But the relaxation time of the molecular chain could not adapt to the cooling rates, so the crystallinity was relatively low.

As can be seen from Fig. 1, the DSC data plots of the five samples changed the same. After adding plasticizers, the T_{onset} and T_p were reduced at the same cooling rate because the plasticizers reduced the force between molecular chains and increased the plasticity of polymerization. And when the content of glycerol increased, the T_{onset} and T_p reduced more notably (from 191 °C to 188 °C; 185 °C to 183 °C). This was because the liquid plasticizer had a good plasticizing effect on PVA, and incorporation of solid plasticizer reduced the phenomenon of plasticizer migration.

The absolute crystallinity was the ratio of the crystallization enthalpy of the sample to 100% crystalline PVA, which can be calculated by Eq. (1).

Table 1 Sample formulation

Sample	Glycerol(%)	Pentaerythritol(%)
Neat PVA	0	0
P/G = 5/15	5	15
P/G = 10/10	10	10
P/G = 15/5	15	5
P/G = 20/0	20	0

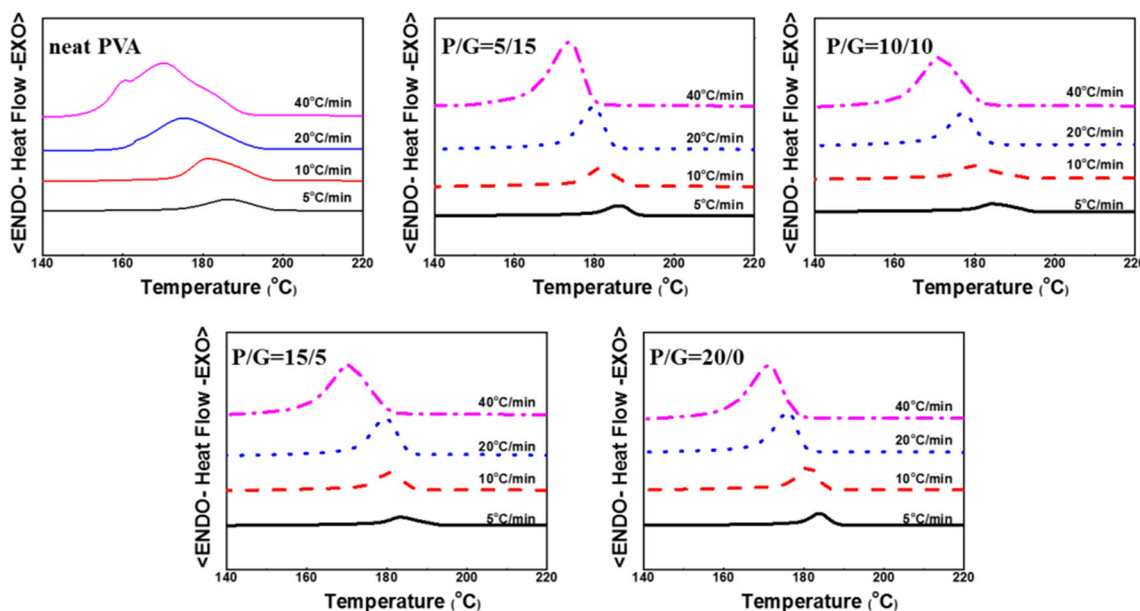


Fig. 1 DSC crystallization curves of PVA and Modified PVA (MPVA) at different cooling rates

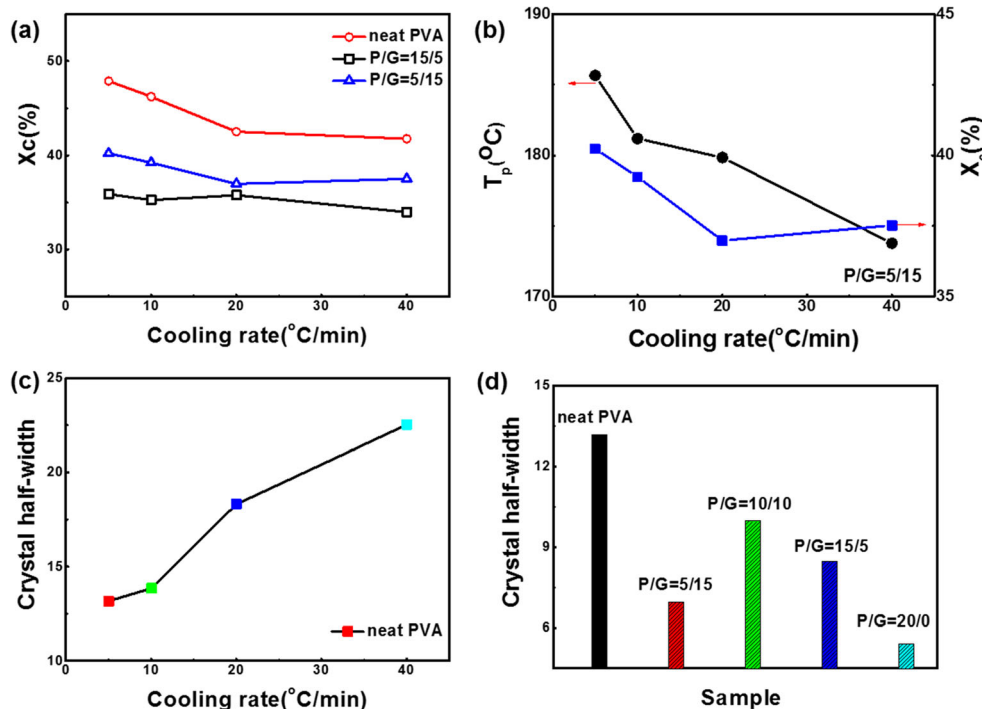
$$X_c = \frac{\Delta H_f}{\Delta H_f^0} \tag{1}$$

Where X_c was the absolute crystallinity, ΔH_f and ΔH_f^0 were the crystallization enthalpy of the sample and 100% crystalline PVA, respectively. The 100% crystalline of PVA was 138.6 J/g.

The values of X_c for plasticized PVA were lower than that of pure PVA as shown in Fig. 2(a), indicating that the adding of plasticizers in PVA could lower crystallinity.

The addition of the plasticizer blocked the molecular chain into the crystal lattice like impurities. Among them, when the plasticizer P/G = 15/5, the crystallinity decreased most notable. This was due to the plasticizing effect of liquid plasticizer and solid plasticizer is the best under this ratio. With the increase of the cooling rate, the crystallinity of PVA and Modified PVA (MPVA) generally showed a downward trend in Fig. 2(b). When the cooling rate increased, the molecular chain motion of PVA could not keep up with the temperature change, and the

Fig. 2 Kinetic parameters of non-isothermal crystallization for various samples. (a) X_c . (b) T_p and X_c of P/G = 5/15. (c) Crystal half-width of neat PVA at different cooling rate. (d) Crystal half-width.



movement become slow, so it could only form imperfect crystals. The half-peak width was related to the crystal size of crystalline polymer. When the half-peak width value was small, that meant the crystal size was uniform, the crystallization was more complete. In Fig. 2(c), the half-peak width of the crystallization peak of pure PVA increased with the increase of the cooling rate, crystallization ability was deteriorated. Figure 2(d) displayed the crystal half-width of different samples. After adding the plasticizer, the half-width of the crystal was smaller than neat PVA, but there was no change with the proportion of the plasticizer. The results were consistent with the above analysis.

In order to clearly find the variation of crystallization peak temperature, the relationship between the T_p and the cooling rate was plotted in Fig. 3. The T_p decreased as the cooling rate increased, because it hardly crystallized in such short time. The T_p reached the maximum at different cooling rates when the plasticizer ratio was P/G = 5/15.

The relationship of relative crystallinity with temperature was shown in Eq. (2):

$$X_t = \frac{\int_{T_0}^T (dH/dT)/dT}{\int_{T_0}^{T_\infty} (dH/dT)/dT} \quad (2)$$

Where the first integral was the heat generated at temperature T and the second one was the total heat when the crystallization is complete. The relationship between the relative crystallinity and the cooling rate was shown in Fig. 4. As the cooling rate increased, the crystallization temperature decreased when the same degree of crystallinity was reached. The reason was that the chain movement of PVA molecular was easier at lower cooling rate, and it was easier to arrange neatly at high temperatures.

Analysis of Jeziorny equation

Generally, isothermal crystallization of polymers could be described by the Avrami equation, which assumes that the

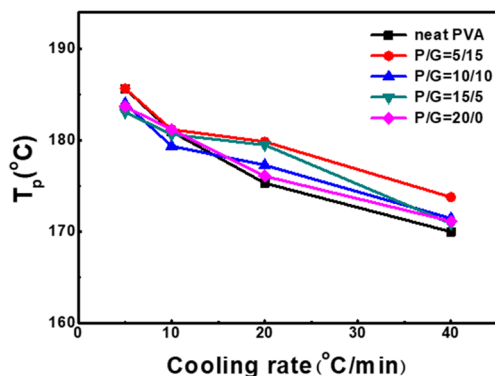


Fig. 3 Relation between T_p and cooling rate

relative degree of crystallinity develops with crystallization time t . The crystallization temperature can be converted to crystallization time t , by Eq. (3) during non-isothermal crystallization processes:

$$t = \frac{(T_0 - T)}{\phi} \quad (3)$$

Where t was the crystallization time, T was the crystallization temperature, T_0 was the initial temperature when crystallization begins ($t = 0$), and ϕ was the cooling rate.

At this time, assuming that the crystallization temperature was constant, the Avrami equation could be used to describe the entire non-isothermal crystallization process. According to the Avrami equation Eq. (4) [23].

$$1 - X(t) = \exp(-Z_t t^n) \quad (4)$$

Take the logarithm of both sides to get Eq. (5):

$$\lg\{-\ln[1 - X(t)]\} = \lg Z_t + n \lg t \quad (5)$$

Where Z_t was the parameter of the reaction non-isothermal crystallization rate, n was the crystallization nucleation mode and parameters of the growth process. Considering the non-isothermal processing characteristics, Jeziorny equation was based on the assumption of isothermal kinetics, indicating that the rate parameter Z should be corrected.

Using $\lg\{-\ln[1 - X(t)]\}$ and $\lg t$ plotting, as shown in Supporting Information, Fig. S1, the slope and intercept of the obtained line were n and $\lg Z_t$, respectively. Mandelkern believed that only the pre-crystallization process conforms to the Avrami equation [24]. Jeziorny corrected the parameter Z_t in the non-isothermal crystallization process to obtain the parameter Z_c (Eq. (6)) [25] related to the cooling rate:

$$\ln Z_c = \frac{\ln Z_t}{\phi} \quad (6)$$

Where Z_c reflected the resulting rate parameter with a cooling rate correction.

The data was linearly fitted to get the Supporting Information, Table S2.

Figure 5 plotted the crystallization parameters of each sample after fitting. According to Eq. (3), the value of the X-axis in Fig. 5 could be transformed into crystallization time t .

It can be seen from Fig. 5(b) that $t_{1/2}$ decreased with the increase of the cooling rate. And at the same cooling rate, the $t_{1/2}$ of the MPVA did not change much compare with the neat PVA. The overall appearance except $t_{1/2}$ increased in Fig. 5(a) and 5(c), indicating that the addition of plasticizers hindered crystallization. And comparing with neat PVA, the X_c was obviously decreased under a different ratio of P/G. Overall, the smallest crystallinity was P/G = 15/5. The result was consistent with the above analysis.

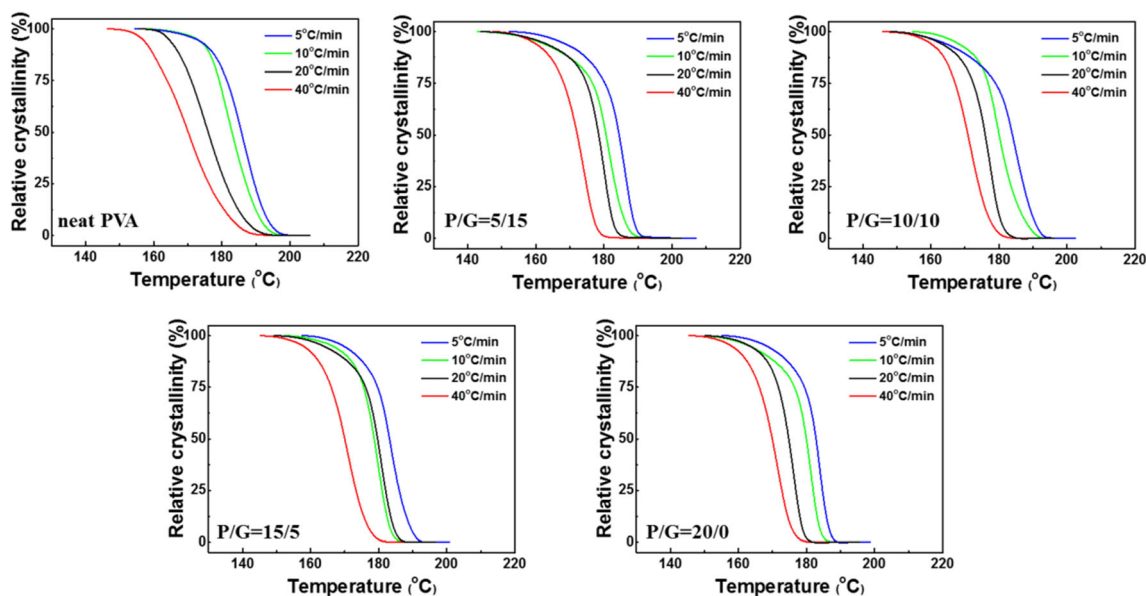


Fig. 4 Plots of X_t versus Temperature for crystallization of neat PVA and MPVA

The parameter of “n” had relationship with nucleation method, Table S2. The data of “n” showed that PVA added with plasticizer is higher than pure PVA. Indicating that the addition of plasticizer changed the nucleation and crystal growth mode, and the crystal nucleation point increased. This also proved that the plasticizer had heterogeneous nucleation, but the change of cooling rate has no obvious effect on crystal growth. The n value of neat PVA changed from 4.09 to 5.26, which was a homogeneous nucleation mode. The n value of MPVA reached 12.61, which was ascribed to heterogeneous nucleation growth. Therefore, the conclusion could be drawn that the plasticizer can change the crystal structure of PVA and hinder the growth of PVA crystals. In addition, it can be seen from crystallization enthalpy that as the cooling rate increased, the crystallization enthalpy gradually decreased. The absolute crystallinity was small at high cooling rate. At the same cooling rate, the crystal enthalpy after adding plasticizer was lower than the neat PVA, indicating that the addition of plasticizer hindered the crystal growth, and many fine and small crystals were formed,

processing products was easier which improved the performance of PVA products.

Mo method

In order to better described the entire non-isothermal crystallization process, there were many new methods to date, in which the Mo method combined the Avrami equation and the Ozawa equation to study the kinetic equation of non-isothermal crystallization. Under a certain relative crystallinity, there was a relationship represented by Eq. (7) [20]:

$$\ln\phi = \ln F(T) - \alpha \ln t \tag{7}$$

Where $F(T)$ was the cooling rate required to reach a certain degree of crystallinity in a unit crystallization time, it can reflect the difficulty of the sample reaching a certain crystallinity within a certain t . α was the ratio of the Avrami index to the Ozawa index.

The relative crystallinity of 20%, 40%, 60%, and 80% were selected, and the results were shown in Supporting

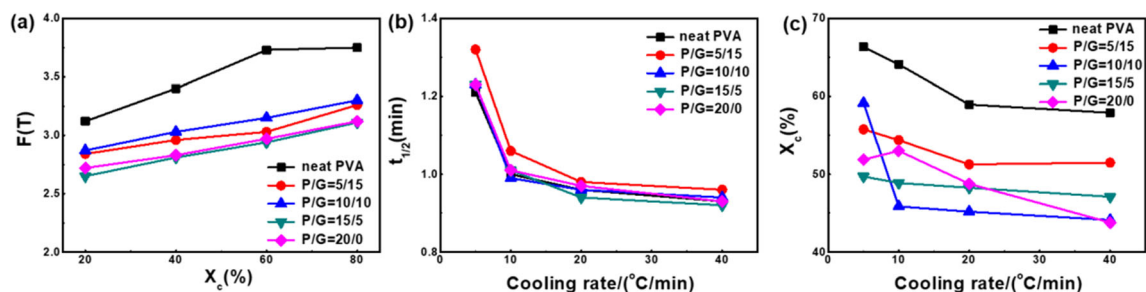


Fig. 5 (a) Relation between Z_c and cooling rate. (b) Relation between $t_{1/2}$ and cooling rate. (c) Relation between X_c and cooling rate

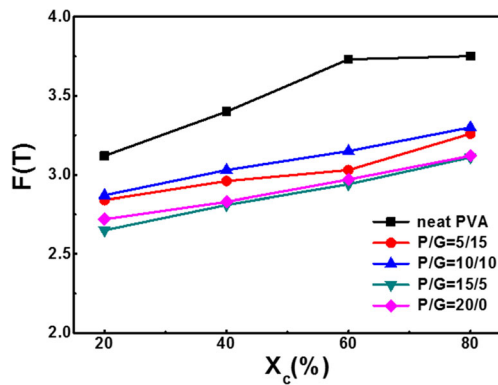


Fig. 6 Relation between $F(T)$ and X_c in different samples

Information, Fig. S2 and Table S3. The crystallization parameters can be calculated from the intercept and slope in the figure, and the results were showed in Fig. 6.

It could be seen from the data in the Fig. 6, that $F(T)$ increased with the increase of relative crystallinity, indicating that a higher temperature cooling rate was required to achieve greater crystallinity per unit crystallization time. The $F(T)$ of MPVA was smaller than neat PVA, indicating that the addition of the plasticizer slowed down the rate of cooling required to reach a certain degree of crystallinity per unit time. It meant that the crystallization was difficult. When the ratio of P/G is 15/5, $F(T)$ reached the minimum at different cooling rates, and α did not change much with the change of cooling rate from Table S3.

Crystal activation energy

The Kissinger formula calculated the crystallization activation energy, which was expressed by Eq. (8) [26]:

$$\frac{d[\ln(\phi/T_p^2)]}{d(1/T_p)} = -\frac{\Delta E}{R} \quad (8)$$

Where ΔE was crystallization activation energy; ϕ was cooling rate; T_p was peak temperature and R was gas constant.

The crystallization activation energy can be calculated by plotting $\ln(\phi/T_p^2)$ and $1/T_p$, and the results were shown in Fig. 7.

Fig. 7 (a) Relationship between $\ln(\phi/T_p^2)$ and $1/T_p$ in neat PVA and MPVA. (b) Crystal activation energy of neat PVA and MPVA

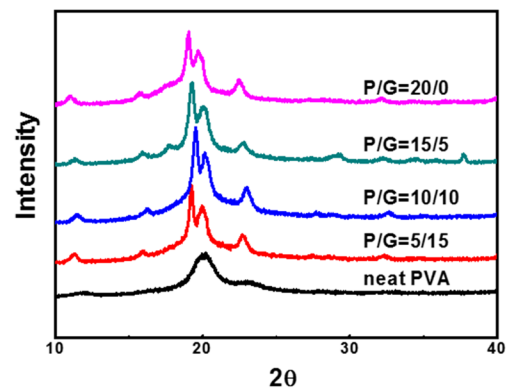
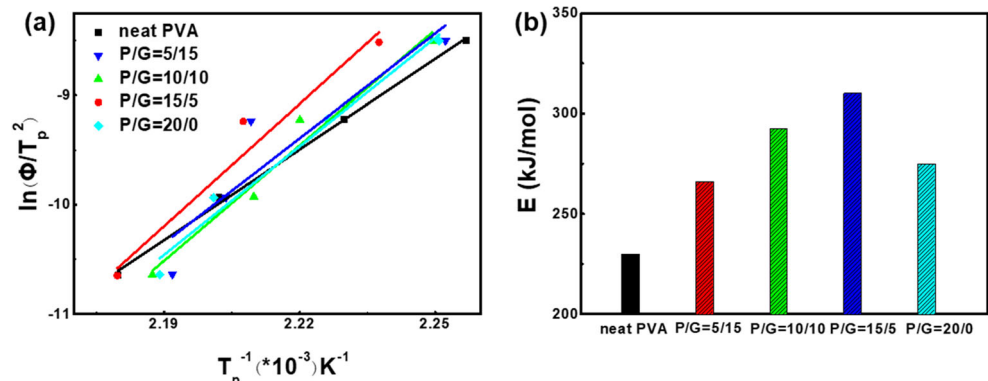


Fig. 8 XRD patterns of neat PVA and MPVA

It can be seen from Fig. 7(b) that after the addition of plasticizer, the crystallization activation energy increased compared with neat PVA, indicating that the addition of plasticizer destroyed the regular structure of PVA. That meant PVA molecular chain was difficult to discharge into the lattice, and the required energy increased, which was consistent with the results of above conclusions. The energy was largest when the P/G = 15/5, that meant crystallization was the most difficult under this plasticizer ratio. Plasticizers reduced the force between molecular chains, increased the plasticity of polymerization, and also reduced crystallinity.

XRD analysis

In the above non-isothermal crystallization analysis, the effect of plasticizer on the crystallization kinetics of PVA was investigated. In order to further analyzed the change in the crystal morphology of PVA, these samples characterized by X-ray diffraction and Fig. 8 showed XRD diffraction spectrum.

In Fig. 8, it could be seen that the strong diffraction peak 2θ of the neat PVA was located at the position of 20.17° and 22.96° . After plasticizing and modifying, the diffraction peaks of the 101-crystal plane in MPVA at the position of 20.17° were split into two crystallization peaks (19.30° and 19.98°), and 200-crystal plane at the original 22.6° position

was also enhanced. A new crystal vibration peak appeared at 2θ of 11.5° and 16.3° .

The above XRD indicated that the plasticizers of different molecular weights could effectively change the original crystal structure of PVA when plasticized. In this plasticized PVA system, the original crystalline form of PVA was hindered due to the heterogeneous nucleation of plasticizer. The new interaction between PVA molecules and plasticizer molecules formed during the melt cooling process, and induced crystal formation of different structures, resulting in a decrease in crystallinity of PVA.

Conclusions

In this work, we used the compounded solid and liquid to plasticize PVA and investigated the crystallization behaviors in detail. The results showed the addition of plasticizer changed the regular structure of PVA, made it difficult to discharge the molecular chain into the crystal lattice, and hindered the crystallization of PVA. And after the addition of the plasticizer, the energy required increased. That also proved the plasticizer hindered the crystallization. The XRD indicated that the plasticizers of different molecular weights could effectively destroy the original crystal structure of PVA, and the plasticizer interacted with PVA to form stronger hydrogen bonds to replace the intermolecular phase of PVA itself intramolecular interactions.

Acknowledgements This work was supported by Funding of Key Laboratory of Polymer Processing Engineering, South China University of Technology, Ministry of Education and National Natural Science Foundation of China (51573066).

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