The Interaction Between Poly(vinyl alcohol) and Low-Molar-Mass Poly(ethylene oxide)

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ABSTRACT: The interaction between poly(vinyl alcohol) (PVA) and low-molar-weight poly(ethylene oxide) (PEG) was studied. The thermal stability, glass transition temperature (T_g), crystallization, and melting behaviors were characterized as functions of content and molar mass of PEG. Dynamic mechanical thermal analysis revealed that PEG was compatible with PVA and provided plasticization effect to the latter. However, the plasticization was countered by the formation of hydrogen bonds between PEG molecules and PVA segments, which depressed the movement of PVA segments. At moderate contents of PEG, the hydrogen bonds were responsible for the increase in T_g, increase in crystallization heat, and decrease in crystallization rate. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 000: 000–000, 2012

Key words: polymer blend; plastic; dynamic; crystallization; differential scanning calorimetry; thermo gravimetric analysis

INTRODUCTION

The amount of research involving the production and characterization of biodegradable films has increased substantially, mainly due to interest in minimizing the ecological impact caused by using synthetic packaging. A significant proportion of this research on films has been made using a polar, water soluble, biodegradable polymer, poly(vinyl alcohol) (PVA). With multi-lateral hydroxyl groups, strong hydrogen bonding may be formed both intra- and intermolecular, which endows PVA high tensile strength, excellent adhesive properties, abrasion resistance, antialkaline resistance, and gas barrier properties.[1,2] PVA has played a significant role in many industrial applications such as fibers, films, adhesives, textile sizing, emulsifiers, paper coating, and so on.

However, PVA possesses a melt processing problem since it shows little thermoplasticity at its melting temperature where decomposition occurs quickly. To improve the thermoprocess capability of PVA, various plasticizers[3–10] were adopted to reduce the melting temperature and enhance the flowability.

The selection of a plasticizer for a specified system is normally based on the compatibility and permanence of the plasticizer, the amount necessary for plasticization, and the desired physical properties of the films.[11]

Because of the diversity of the chemical structure and molecular weight, the plasticizers show different plasticization effect on PVA, and the plasticization has become a hot topic of research. Hodge et al.[12] studied the plasticization of water for PVA, and measured the morphological, free volume, and mobility-related parameters as a function of water content by positron annihilation lifetime spectroscopy, solid state ^{13}C nuclear magnetic resonance, and dynamic mechanical analysis (DMA). The techniques were combined to elucidate the effects of water on the macro- and microstructure. Mohsin et al.[13] studied the thermal and mechanical properties of films based on blends of PVA with different weight percent of sorbitol. It was found that the thermal properties of PVA blends showed a decrease proportional to the sorbitol concentrations. The plasticization of glycerol was explored by Rahman et al.[14] using differential scanning calorimetry (DSC) to determine the changes of enthalpy of melting (ΔH_m), which was taken as a measure of intermolecular interactions among the blending components.

In this work, the plasticization of low-molecular-weight poly(ethylene glycol) (PEG) for PVA was studied in the thermal properties of their blends. Among other measures, the research was carried out

from a different point of view, i.e., from crystallization kinetics of PVA. Since, during the crystallization, the PEG species would be eliminated from the lattice of PVA. This meant that the interaction between PVA and PEG should be destroyed first and the crystallization could occur. For this reason, it was expected that the interaction between PVA and PEG would delay the process of crystallization, in other words the kinetics of crystallization could be taken as a characteristic of the interraction between PVA and PEG.

It should be mentioned that in the melt, PEG may be uniformly dispersed in PVA; while in solid state, the PEG molecules themselves did not inhabit intact crystallites, and plasticization occurs in the amorphous region only. For this reason, the quoted PEG content was only correct for the melt state and should be modified according to crystallinity of the samples. However, for the purpose of comparison, the content correction seemed unnecessary and the loaded PEG content was used throughout this study.

EXPERIMENTAL

Materials

PVA, degree of Alcoholysis 99%, degree of polymerization 1700, purchased from Kurerey Company, Japan. Polyethylene glycol, molar mass 200, 400, and 600 (denoted as PEG200, PEG400, and PEG600, respectively), from Sinopharm Chemical Reagent, Ethanol, analytical grade, Beijing Chemical Plant.

Membrane preparation

The solid-state PVA/PEG polymer membranes (various PEG contents) were prepared by solution casting method. PVA and PEG were dissolved in distilled water with a concentration of 10 wt % forming a homogeneous solution, which was then poured onto a PTFE plate to obtain a film. For comparison, film of neat PVA was prepared with above procedures.

Thermo gravimetric analysis

TGA analysis of PVA/PEG membranes were performed using a Thermogravimetric Analyzer Q5000IR (TA Instruments, US). The samples ($\sim$ 10 mg) after weighted in a pan were placed inside a tube furnace, which was heated up to 600°C at a rate of 20°C/min under nitrogen or air atmosphere.

Differential scanning calorimetry

DSC analysis of polymeric membranes were performed using a DSC Q100 (TA Instruments, US). The sample was first heated from room temperature to 240°C, holding 8 min to erase the thermal history. Subsequently, the sample was cooled to (70°C at a preset rate, and then heated at 20°C/min to 240°C. All the scanning was carried out under nitrogen atmosphere.

The data was analyzed with Jeziorny method[15] using the equation:

$$1 - \alpha(T) = \exp[-Z_t t^n] \tag{1}$$

The rate constant Z_t. should be modified to accommodate the cooling rate:

$$\log Z_c = \frac{\log Z_t}{\beta} \tag{2}$$

The half-time was calculated as

$$t_{1/2} = \left(\frac{\ln 2}{Z_c}\right)^{1/n} \tag{3}$$

Dynamic mechanical thermal analysis

DMTA measurements with tensile mode were performed using a DMA 242C instrument (NETZSCH, Germany). The tests were run in a temperature range from (50 to 150°C with a frequency of 10 Hz and a heating rate of 3°C/min. To prevent sample buckling during heating, the 'force track' option was activated and set at 120% with an initial preload of 0.5N. All rectangular samples (15 $\times$ 5 $\times$ 0.3 mm^3) were taken from central part of the film.

RESULTS AND DISCUSSION

Water evaporation of PVA/PEG film

After a PVA/PEG blend film was cast, it was subjected to drying at 80°C in a vacuum oven and with its weight registered as a function of time. Figure 1 compared the weight loss rate of the samples containing 20 wt % PEG200, 400, or 600. In spite of the difference in the molar mass of the PEGs, the weight loss rates before 5 h for the three samples were comparable; this was obviously because of the evaporation of water. After 5 h, the PEG200 system continued to loss weight with a certain rate, while the weight of other two samples basically maintained constant. The stable reservation of PEG400 and PEG600 was mainly originated from the formation of hydrogen bonds between the terminate hydroxyl groups on PEG and the lateral hydroxyl groups of PVA. Of course, PEG200 may also form hydrogen-bonds with PVA segments; however, its molar mass was too small to be stable reserved. Based on the
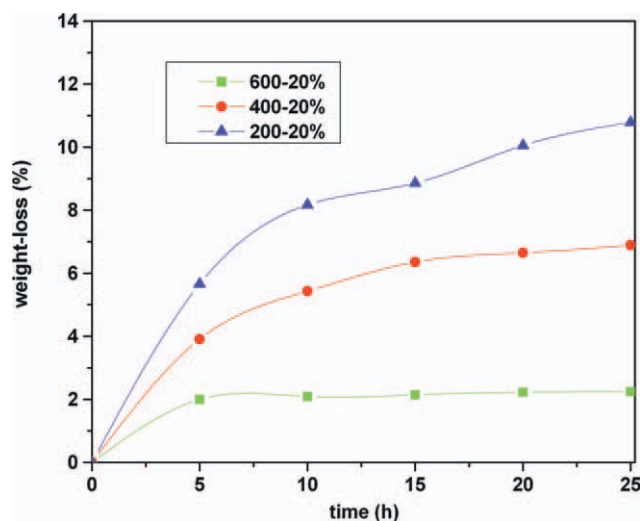
Figure 1 Weight loss of PVA/PEG films during drying. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com]

time of water removal, the films after 5 h drying were used in other determinations.

Because of the hydrophilic nature of the polymer, some water species may be still present in the system after 5 h drying; on other hand, some PEG species may be evaporated before 5 h. To be simple, the water content after 5 h drying was considered constant and its effect was ignored in later discussions. For the same reason, the PEG loss during the first 5 h drying was also ignored.

Thermogravimetry

Figure 2 presented TG and DTG thermograms of neat PVA and PEGs. The PEGs exhibited a single temperature peak whereas PVA exhibited two peaks at 280 and 440°C, in agreement with Mohsin et al.[13] The first step region around 250–370°C was due to the degradation of PVA chains; the second step around 380–500°C was due to the carbonation of polymer matrix followed by a final decomposition of the polymer that began around 500°C.

The first weight loss of neat PVA around 250–350°C provided a processing window between 180 and 250°C. For the PEGs, it was obvious that, the higher the molar mass, higher the decomposition temperature range. Owing to the low-molar-mass, the decomposition of PEG200 occurred between 150 and 300°C, which eliminate its usage as a plasticizer for the melt-processing of PVA. The decomposition temperature ranges for PEG400 and 600 were 250–350°C and 300–400°C, respectively, both higher than the conventional processing window of PVA and were thus suitable to be used as plasticizers for PVA. For this reason, the research work in this article was mainly focused on the blends of PVA and these two PEGs.

The TG and DTG curves of PVA/PEG400 blends were presented in Figure 3, with neat PVA as a reference. One may find that the weight loss curves of the blends were not a simple superposition of those of neat PVA and PEG400: the temperature of maximum weight loss rate of the blend decreased with increasing content of PEG400, and was a few degrees lower than that of neat PVA. When PEG400 was dispersed in the PVA matrix, the molecules of PEG400 form hydrogen bonds with PVA segments with the price of the disassociation of the hydrogen bonds in the previous neat PEG400. The mobility of nonhydrogen bonded PEG400 molecules was thus increased. On the other side, the inclusion of PEG species into PVA enlarged the intersegment spacing and the mobility of PVA segments was also enhanced. For this reason, PEG400 and the blends were decomposed at a lower temperature than neat PVA, as seen in Figure 3.
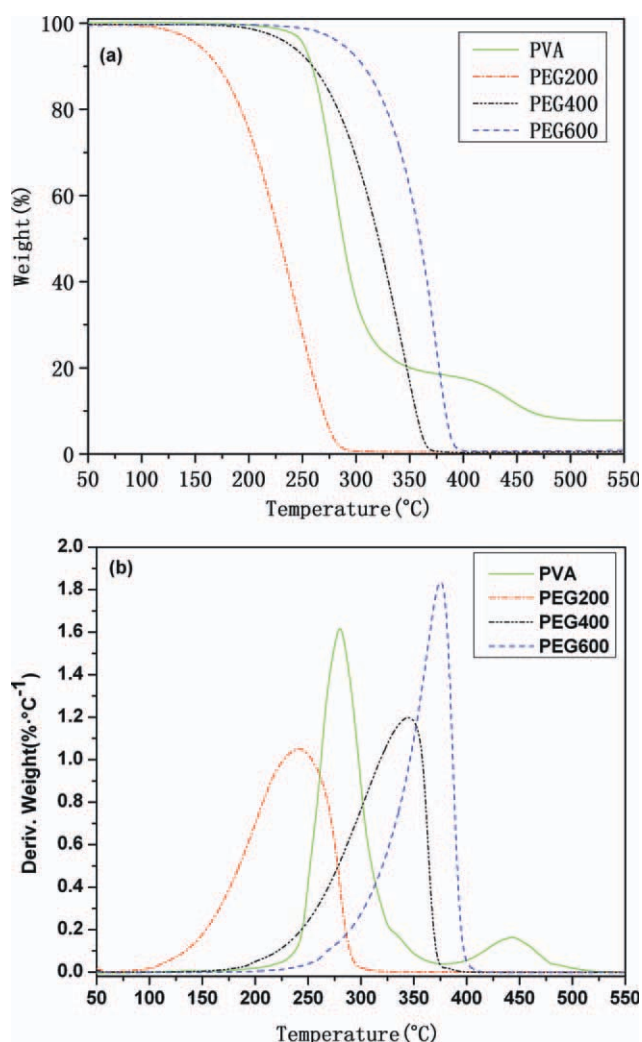

Figure 2 TG curves of PVA and PEGs (a) TG; (b) DTG. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com]
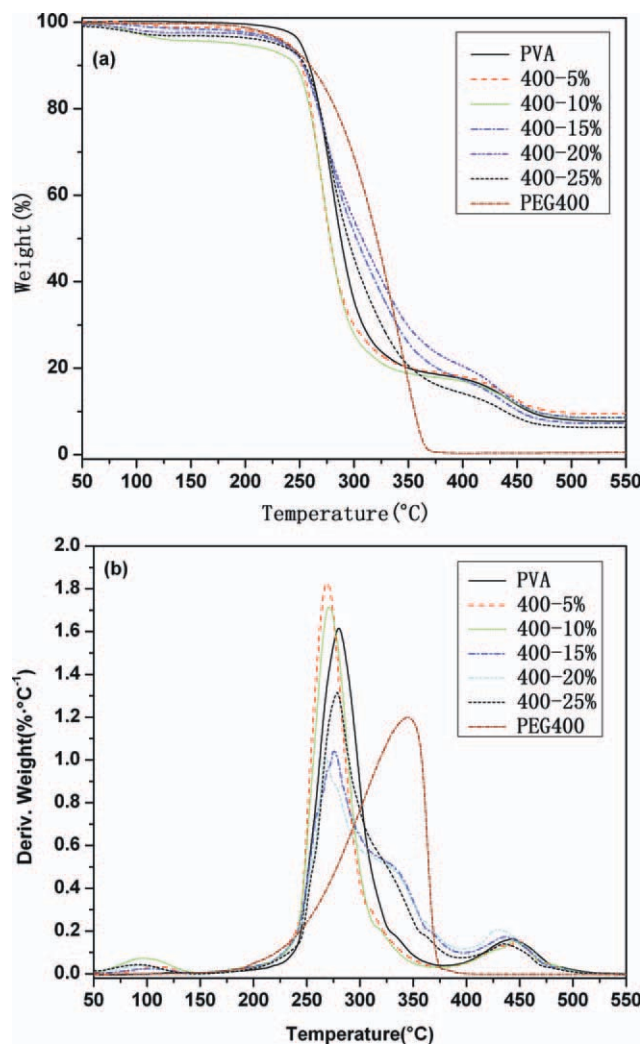
Figure 3 TG curves for PVA/PEG400 blend films (a) TG; (b) DTG. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com]

The maximum weight loss rate provided more information, which was presented in Table I. In the PEG400 loading between 5 and 20 wt %, a systematic change in maximum weight loss rate was observed: the higher the content of PEG400, the higher the maximum weight loss rate. When the loading of PEG400 was lower or equal to 10 wt %, the hydrogen bonding was not sufficient to stabilize the PVA segments. And, because of its low-molar-mass, PEG400 molecules themselves were subjected to decompose at this

TABLE I
Maximum Weight Loss Rates of Various PVA/PEG Blends

	Maximum weight loss rate (wt %/°C)				
Neat PVA	1.62				
PEG content (wt %)	5	10	15	20	25
PEG400	1.83	1.74	1.04	0.96	1.33
PEG600	1.41	1.55	1.52	0.97	1.22

temperature region (one may recognize this from Fig. 3), as a result, the maximum weight loss rate of the blends was higher than neat PVA. When a sufficient amount of PEG molecules was introduced (higher than 10 wt %), the hydrogen bonding became strong enough to stabilize the PVA segments and molecules of PEG400, the maximum weight loss rate was lower than that of neat PVA. However, when the loading of PEG400 was too high, some of the PEG400 molecules became self-aggregated, the spacing effect was enhanced, and the maximum weight loss rate was somewhat increased.

Figure 4 showed the weight loss behavior for PVA/PEG600 systems. Because of the similarity, the above discussion for PVA/PEG400 systems could well be applied with the only exception regarding the change of maximum weight loss rate with the loading of PEG600. One may see that even at low content of PEG600, the maximum weight loss rate of the blend
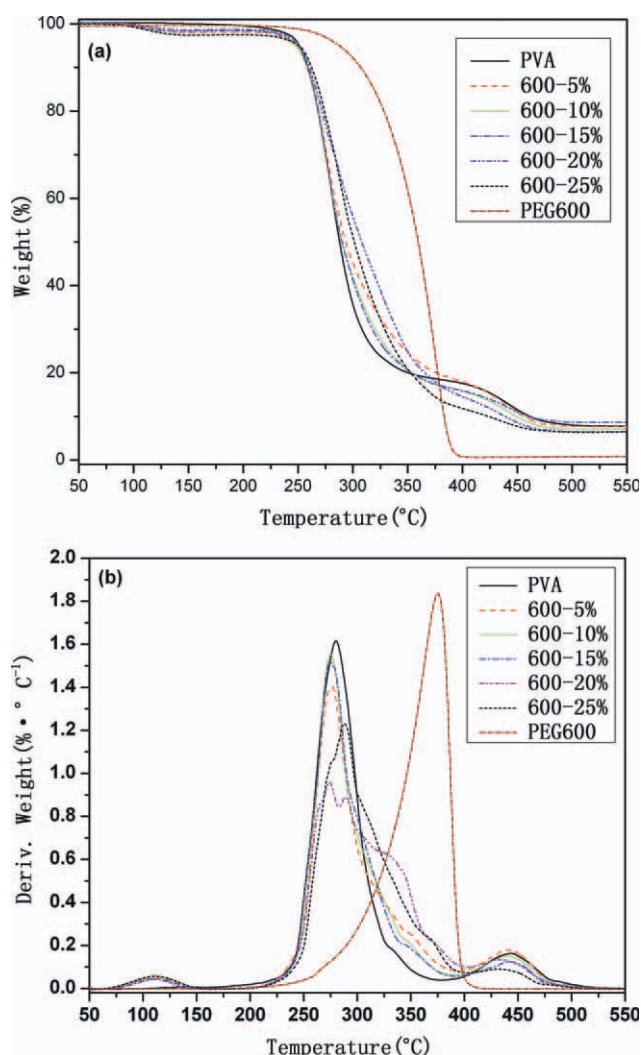

Figure 4 TG curves for PVA/PEG600 blend films (a) TG; (b) DTG. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com]
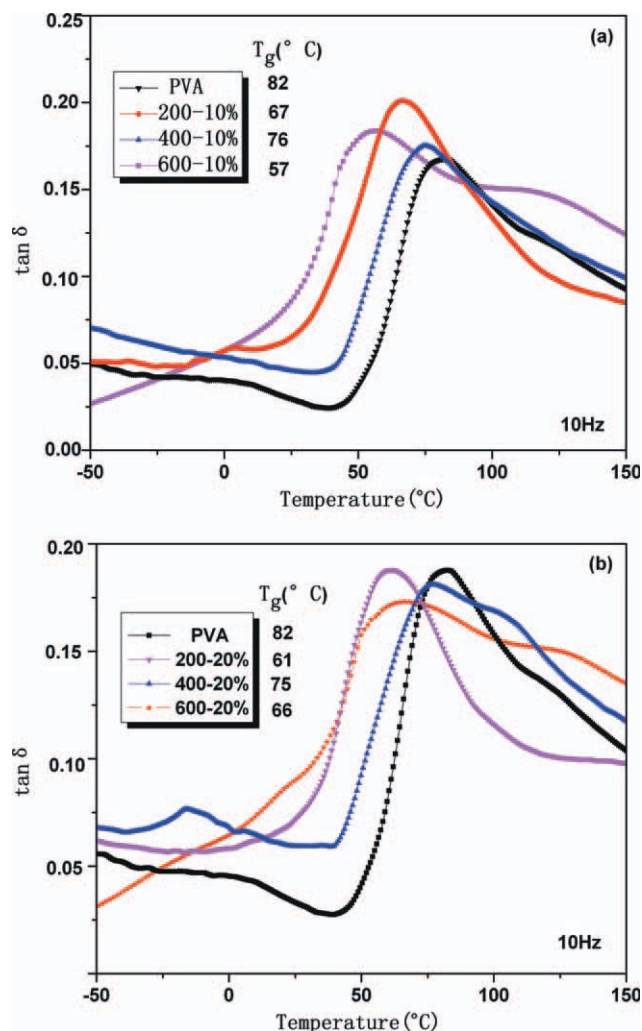
Figure 5 Tan δ-temperature plots via DTMA for PVA and PVA/PEG blends PEG content (a) 10 wt %, (b) 20 wt %. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com]

was lower than neat PVA. This was resulted from its higher-molar-mass of PEG600. From Figure 4 one could see that at the temperature region of maximum weight loss rate, PEG600 was not yet substantially decomposed, all the PEG600 introduced may be readily hydrogen bonded with PVA segments, and thus decreased the maximum weight loss rate.

Glass transition temperature

The glass transition temperature (T_g) of the samples was determined via dynamic mechanical thermal analysis (DMTA) and was taken as the location of maximum loss tangent (tan δ). This was shown in Figure 5, where the dependence of T_g on the molar mass was presented. One could conclude that all the PEGs displayed plasticization effect on PVA, since their inclusion indeed caused decrease in T_g. As aforementioned, the introduction of PEG resulted in two changes:

(i) Forming hydrogen bond with PVA segments, which increased T_g of PVA, and (ii) enlarging the intersegment distance, which lowered T_g. However, since the hydrogen bonding could only occur at two ends of each PEG molecules, the spacing effect could be strengthened by increasing the molar mass of PEG. Indeed, as seen in Figure 5, the plasticization provided by PEG600 was much effective than the counterpart of PEG400. As for PEG200, an even low T_g of 61°C was exhibited, which could also be attributed to the spacing effect. At the same weight loading, the molecule number introduced for PEG200 was a half of that for PEG400 or one-third for PEG600. Such a large number of molecules could not be accommodated with hydrogen bonds, and a large fraction of the molecules was self-aggregated, resulting in a lower T_g. However, as aforementioned, the PEG200 was not stable in the system; its plasticization effect was only temporarily.

Figure 6a showed the effect of PEG400 content on the glass transition temperature. At low loadings, the T_g of the blends kept increased with increasing content of PEG. When the content of PEG400 was 25 wt %, the T_g of the blend increased to the level of neat PVA. This meant that the plasticization for PVA was only effective at low PEG400 contents. When the PEG400 content was too high, the spacing effect was fully offset by the hydrogen bonding, therefore an antiplasticization was observed. Figure 6(b) was the counterpart of Figure 6(a), for PEG600. The same change trend in T_g with PEG content was observed, as a result, above discussion for PEG400 system could be well applied to the PEG600 system. However, one may notice that the T_g of the PEG600 system was well lower than its PEG400 counterpart, which once again demonstrated the effect of intersegment spacing.

Crystallization kinetics of PVA

The crystallization kinetics of PVA was studied through nonisothermal crystallization and the data was analyzed with Jeziorny method. All the calculated parameters for PEG400 and PEG600 were presented in Tables II and III, and typical DSC curves for PVA/PEG400 systems were shown in Figure 7. Two crystallization events could be observed from the curves. Cooled from melt, PVA species crystallized at about 204°C, and the PEG species remained in liquid state until its much lower crystallization temperature was reached. Since the crystallization temperatures of PVA and PEG were separated by a distance about 200°C, the crystallization of PEG had no effect on the crystallization behavior of PVA and thus was ignored in the following discussions. Among the numerous parameters, the half-time of crystallization or half-conversion time, $t_{1/2}$, was considered a characteristic of the crystallization rate and it constituted the main concern in this article.
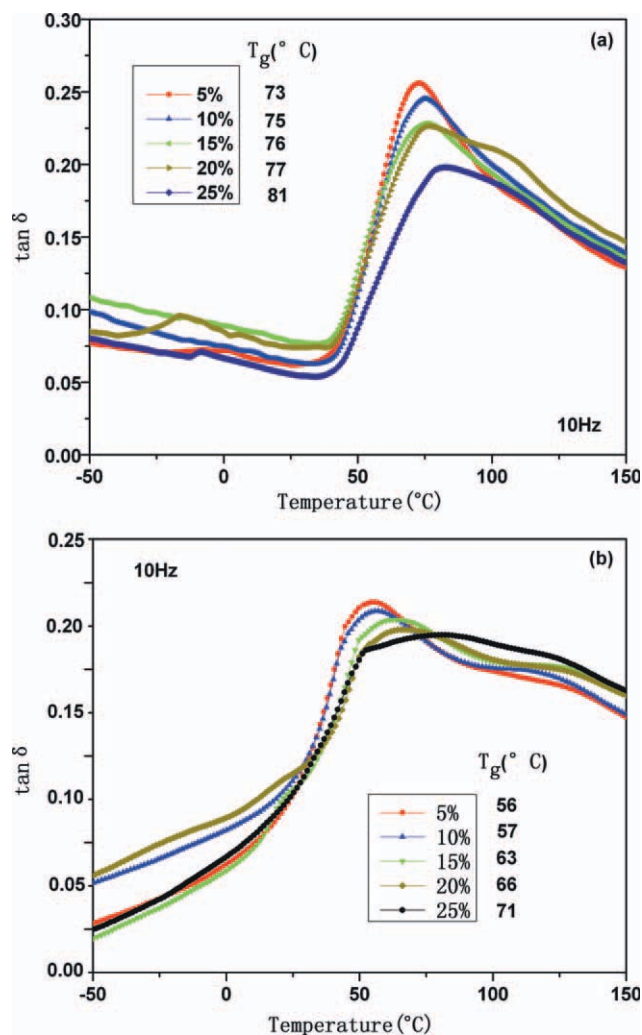
Figure 6 Effect of PEG content on the glass transition temperature (a) PEG400, (b) PEG600. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com]

Regarding the same composition cooled at different rates, one found a well known behavior: the higher the cooling rate, the shorter the half-time, i.e., the faster the crystallization. The interesting observation was the effects of the content and molar mass of PEG species. Since the crystallization behavior was similar at different cooling rates, we just took the data for

TABLE II
Kinetics Parameters of Nonisothermal Crystallization of PVA/PEG400 Blend

PEG400 content (%)	Φ (°C/min^{-1})	n	$\log Z_t$	Z_c	$t_{1/2}$ (min)
5	25	4.390	1.569	1.155	0.890
10	25	4.729	1.691	1.168	0.895
15	25	5.061	1.428	1.140	0.906
20	25	5.537	1.636	1.163	0.911
25	25	5.981	1.709	1.170	0.916

TABLE III
Kinetics Parameters of Nonisothermal Crystallization of PVA/PEG600 Blend

PEG600 content (%)	Φ (°C/min^{-1})	n	$\log Z_t$	Z_c	$t_{1/2}$ (min)
5	25	4.461	1.819	1.182	0.887
10	25	4.643	1.907	1.192	0.890
15	25	4.964	1.846	1.185	0.897
20	25	4.869	1.591	1.158	0.900
25	25	5.089	1.391	1.137	0.907

cooling rate of 25°C/min as an example in the discussion, which was summarized in Tables II and III.

As aforementioned, the PEG species in PVA matrix may form hydrogen bonds with PVA segments. When crystallization occurred, such PEG species should be removed from PVA crystallites, as a result, the crystallization would be delayed. The more the PEG species incorporated, the slower would be the crystallization. Such a behavior was reflected from the data in Tables II and III. One could see that the $t_{1/2}$ indeed increased with increasing PEG content with other parameters constant. Although, the difference in $t_{1/2}$ was minor, a systematic change was observed.

Comparing Tables II with III, one could hardly tell substantial difference in $t_{1/2}$'s between systems based on PEG400 and 600. Intuitively, the $t_{1/2}$ of PEG600 based system should be a little shorter than its counterpart of PEG400 ones because its lower density of hydrogen bonds. However, the removal of PEG species from PVA crystallites was not only an energetic process, but also a diffusion process. The compromise between diffusion and energy
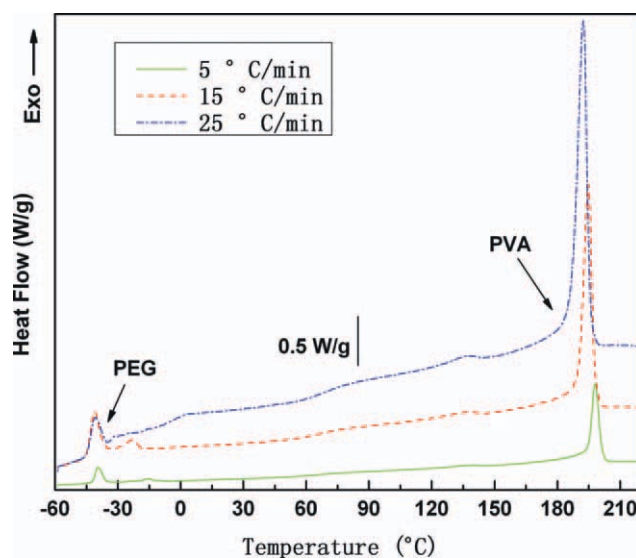

Figure 7 Typical DSC cooling spectra of PVA/PEG blends. The loading of PEG400 was 25 wt %. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com]

TABLE IV
Crystallization Heat for a Cooling Rate of 20°C/min

PEG content (wt %)	Crystallization heat (J/g)	PEG content (wt %)	Crystallization heat (J/g)
400-5	61.9	600-5	51.6
400-10	63.5	600-10	54. 8
400-15	63.5	600-15	57.6
400-20	69.5	600-20	60.7
400-25	72.4	600-25	67.0

requirement made the difference between the two systems very small.

Crystallization heat

The interaction between PVA segments and low-molar-mass PEG was also confirmed with crystallization heat, which was presented in Table IV. For simplicity, only the data from a cooling rate of 20°C/min was given here. One may notice that, higher the PEG content, the larger the crystallization heat. The PEG species influenced the crystallization heat in two competing ways: (i) the total crystallinity was reduced. In a study of plasticization of water to PVA, Hodge et al.[12] revealed that the crystallinity decreased with increasing water content. If this case could be applied to present systems, the crystallization heat would have been decreased with increasing PEG content; (ii) as the crystallization proceeded, the PEG species was driven to amorphous region, and an increasing number of hydrogen bonds were formed there, and the excess energy was released, and the crystallization heat increased with increasing content of PEG. The data in Table IV showed that the effect (ii) was prevailing, which just reflected the strong interaction between PEG species and PVA.

CONCLUSIONS

The inclusion of low molar mass poly(ethylene oxide) (PEG) into matrix of PVA changed the inter-action between the two species in two aspects: (i) PEG acted as spacers to enlarge the distance among PVA segments, and (ii) PEG formed hydrogen bonds with PVA segments, resulting in a physical network. The spacing effect decreased the glass transition temperature of PVA, resulted in plasticization; the hydrogen bonding effect influenced the crystallization behavior substantially. The higher the PEG content, the higher the crystallization heat, the slower the crystallization rate, and the higher the glass transition temperature, though still below that of neat PVA. PEG with higher molar mass formed less hydrogen bonds, and this may weakened a little the hydrogen bonding effect.

References

1. Mansur, H. S.; Sadahira, C. M.; Souza, A. N.; Mansur, A. A. P. Mater Sci Eng C: Biomim Mater Sens Syst 2008, 28, 539.
2. Sudhamani, S. R.; Prasad, M. S.; Sankar, U. K. Food Hydrocolloids 2003, 17, 245.
3. Kroschwitz, J. I. Encyclopedia of Polymer Science and Technology, Vol.8; Wiley: Hoboken, NJ, 2003.
4. Raj, B.; Siddaramaiah, S.; Somashekar, R. J Appl Polym Sci 2004, 91, 630.
5. Yoon, S. D.; Chough, S. H.; Park, H. R. J Appl Polym Sci 2007, 106, 2485.
6. Fishman, M. L.; Coffin, D. R.; Onwulata, C. I.; Willet, J. L. Carbohydr Polym 2006, 65, 421.
7. Mao, L.; Imam, S.; Gordon, S.; Cinelli, P.; Chiellini, E. J Polym Environ 2000, 8, 205.
8. Jang, J.; Lee, D. K. Polymer 2003, 44, 8139.
9. Ku, T.; Lin, C. Text Res J 2005, 75, 681.
10. Cheng, L. H.; Karim, A. A.; Seow, C. C. J Food Sci E: Food Eng Phys Properties 2006, 71, 62.
11. Shin, J. H.; Henderson, W. A.; Tizzani, C.; Passerini, S.; Jeong, S. S.; Kim, K. W. J Electrochem Soc A 2006, 153, 1649.
12. Hodge, R. M.; Bastow, T. J.; Edward, G. H.; Simon, G. P.; Hill, A. J. Macromolecules 1996, 29, 8137.
13. Mohsin, M.; Hossin, A.; Haik, Y. Mater Sci Eng A 2011, 528, 925.
14. Rahman, W. A.; Sin, L. T.; Rahmat, A. R.; Samad, A. A. Carbohydr Polym 2010, 81, 805.
15. Jeziorny, A. Polymer 1978, 19, 1142.