Thermal properties in strong hydrogen bonding systems composed of poly(vinyl alcohol), polyethyleneimine, and graphene oxide

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Abstract

Blends of poly(vinyl alcohol) (PVA), polyethyleneimine (PEI), and graphene oxide (GO) were prepared by solution casting method. Calorimetric thermal properties of the blends were investigated. The T_g s of PVA/PEI blends were higher than the T_g s of either of the component polymers at low concentrations of PEI. These abnormal increases of T_g s may be due to the negative entropy of mixing which is associated with strong hydrogen bonding between PVA and PEI. The degree of depression of T_{ms}^0 was not reduced by the negative entropy of mixing, since strong hydrogen bonding also causes an increase in the magnitude of negative χ between PVA and PEI. The T_g of PVA was increased significantly by adding 0.7 wt.% GO into PVA. The magnitude of negative χ was increased by adding GO into the blends of PVA and PEI.

Key words: poly(vinyl alcohol), polyethyleneimine, graphene oxide, calorimetric thermal properties, strong hydrogen bonding

1. Introduction

Poly(vinyl alcohol) (PVA) and its blend with polyethyleneimine (PEI) have attracted great interest due to their potential application in functional membranes as well as for fibers [1-8]. The blends are also a good model system for miscible polymer blends with strong hydrogen bonding. Graphene oxide (GO) is a chemically exfoliated graphite, which is a precursor for graphene (or reduced GO) sheets [9-11]. Graphene has emerged as an ingredient for polymer nanocomposites due to its exceptional electron transport [12-14], mechanical and rheological properties [15-17], and gas barrier properties [15,18,19]. Molecular level dispersion of GO has been reported in the PVA/GO system, which may be ascribed to the hydrogen bonding interaction between the components [18,20].

Hydrogen bonding in polymer blends has been of interest to polymer scientists for several decades [21-39]. One major characteristic in such systems is the large positive deviation of glass transition temperature (T_g) from conventional mixing rules [22,23,26,35]. It is well known that miscible binary blends exhibit a single T_g between the T_g s of their individual component polymers. Many expressions have been proposed for evaluating the T_g s of miscible binary blends, such as Fox [40], Gordon and Taylor [41], Couchman and Karasz [42], and Kwei [43] equation. Most of these expressions predict a single T_g located in between the T_g s of the component polymers. However, the T_g s of blends of polyvinylphenol (PVPh) and polyvinylpyridine (PVPy) are higher than those of both components due to the strong hydrogen bonding [37]. Two different views on the abnormal increase of T_g have been reported. Painter and coworkers [37] claimed that the abnormal increase of T_g can be ascribed to the positive enthalpy of mixing (endothermic) by strong hydrogen bonding, while the hydrogen

bonding itself is exothermic. Pinal [22] have extended the classical thermodynamic approach of Couchman and Karasz [42] to the hydrogen bonding system, and reached the conclusion that the abnormal increase of T_g is due to the negative entropy of mixing. Either case, the negative entropy of mixing or endothermic enthalpy of mixing is certainly abnormal behavior induced by strong hydrogen bonding.

At equilibrium melting temperature, the chemical potential of the crystalline phase is equal to that of the liquid phase [44,45]. If the crystalline phase sustains the pure state, a new equilibrium condition arises where the chemical potential of the crystalline phase is equal to the reduced-chemical potential of the mixed-liquid phase, which leads to the depression of equilibrium melting temperature [45]. Therefore, either the negative entropy of mixing or the positive enthalpy of mixing by strong hydrogen bonding may weaken the depression of melting temperature. Unfortunately, the melting point depressions could not be examined in the amorphous blends of PVPh and PVPy by Painter and coworkers [37]. Subsequently, Painter and coworkers [46] reported the effect of hydrogen bonding on the melting point depression in polymer blends where one component crystallizes. However, the abnormal increase of T_g was not investigated in the latter case.

Blends of PVA/PEI may be a good alternative model system for investigating both melting behaviors and glass transition temperatures, since PVA is a semi-crystalline polymer. PEI is a multifunctional aliphatic amine with strong cationic characteristics, whereas PVA is a water-soluble poly hydroxyl polymer. Amino groups in the PEI chain could also form strong hydrogen bonds with hydroxyl groups in the PVA chain.

In this work, we have explored the thermal properties of PVA/PEI/GO blend systems. In particular, we investigated the glass transition temperatures and the equilibrium melting temperatures. We evaluated the configurational entropy of mixing from the glass transition temperatures in the strong hydrogen bonding systems. The effect of strong hydrogen bonding on the degree of depression of equilibrium melting points was also investigated. We also examined the effect of GO on the thermal behaviors of PVA/PEI blends.

2. Experimental Section

2.1. Materials

PVA was purchased from Sigma Aldrich (99 mol% hydrolyzed, $M_w = 89\,000\text{--}98\,000$ g). PEI, 50 wt% aqueous solution with the low molecular weight of 2000 including amino groups (ratio of primary/secondary/tertiary amino groups was roughly 1/2/1), was purchased from Sigma Aldrich. Flake graphite powder (19 μm nominal particle size) was supplied from Asbury Carbon. GO was synthesized from purified conventional flake graphite by modified Hummers method [9] as reported in our earlier work [17,18].

2.2. PVA/PEI/GO blend preparation

PVA solution was prepared by dissolving pure PVA powder with distilled water at 363 K for 1 h and stirring at the same time. Then, the PVA solution was cooled to room temperature

and mixed with PEI aqueous solution at a designated mixing ratio by stirring for 1 h. A homogenized solution was prepared in a bubble-free state. A colloidal solution of GO was added to the PVA/PEI solution with a designated mixing ratio and the PVA/PEI/GO solution was milled for 0.5 h at 298 K. Then, the solution was cast on glass plate at 373 K and dried in a convection oven at 373 K for 3 h followed by drying in a vacuum oven at 393 K for 3 h to ensure the removal of moisture.

2.3. Characterization of PVA/PEI blends

The morphology of the blends was characterized with field emission scanning electron microscopy (FE-SEM; JEOL JSM-6700F) by observation of the cryogenically fractured surface of samples. High-resolution transmission electron microscopy (HRTEM) was performed with a Hitachi HF-2000 operated at 200 kV. Samples were applied onto a 400 mesh Cu grid with lacey carbon film and dried in air before TEM imaging. X-ray photoelectron spectroscopy (XPS) was performed in a MultiLab2000 with a Mg-K X-ray source using a power source of 300 W. The atomic fractions of the different elements in the 10 nm upper layer were probed by XPS and calculated from the survey spectra. X-ray diffraction (XRD) analyses were performed directly on the hybrid samples using a Rigaku (Japan)-Ultima IV (XRD; 40 kV, 40 mA) with Cu irradiation at a scanning rate of 0.02/s in the 2θ range of 2–40. The non-isothermal melting temperatures and glass transition temperatures were measured by differential scanning calorimetry (TA-DSC) from 203 to 523 K during a 2nd run with a heating rate of 20 K/min. To investigate isothermal crystallization and melting, samples were heated to 523 K, held there for 5 min, and cooled rapidly (–80 K/min) to the designated crystallization temperature. When the isothermal crystallization procedure was finished (as monitored by exothermic peaks during isothermal crystallization), the samples were heated again to 523 K with a heating rate of 20 K/min.

3. Results and Discussion

3.1. Glass transition temperatures (T_g s) of PVA/PEI blends

DSC thermograms for PVA/PEI blends are seen in Fig. 1. The glass transition temperatures (T_g s), onset points (T_i s) and end points (T_e s) of glass transitions are listed in were obtained by DSC thermograms. The composition dependency of T_g s of the PVA/PEI binary blend is presented in Fig. 2a. The calculation results by Couchman-Karasz equation are compared to the experimental data in Fig. 2a. The Couchman and Karasz equation [42] is

$$\ln T_{CK} = \frac{x_1 \Delta C_{p1} \ln T_{g1} + x_2 \Delta C_{p2} \ln T_{g2}}{x_1 \Delta C_{p1} + x_2 \Delta C_{p2}} \quad (1)$$

where T_{CK} , T_{g1} , and T_{g2} is the glass transition temperature of the mixture, PEI, and PVA, respectively. x_1 and x_2 are the mole fractions of PEI and PVA, respectively. ΔC_{pi} is the difference in the heat capacity of the liquid and the heat capacity of the glass forms of component i . Molar volumes of the repeating unit of PEI ($V_{iu} = 36.11$ cm³/mol) and PVA ($V_{iu} = 32.28$ cm³/mol) were

Fig. 1. Differential scanning calorimetry thermograms for the glass transition temperatures of the blends of poly(vinyl alcohol) (PVA) and polyethyleneimine (PEI).

used to estimate mole fractions x_i .

A large positive deviation from the calculated values can be observed in Fig. 2a. Specifically, the T_g s of the PVA/PEI blends are higher than either of the component T_g s at low concentrations of PEI in Fig. 2a. These abnormal increases of T_g s may be due to the strong hydrogen bonding between PVA and PEI, which is a rarely observed behavior in polymer blend systems.

According to Gibbs and DiMarzio [47], the glass transition temperature may be defined as the point where the configurational entropy becomes zero when a polymer in melt state is cooled down to a glassy state. OH--N bonding may be formed in PVA/PEI blends, as seen in Fig. 2b, which may be stronger than OH--O bonding in PVA itself or than NH--N bonding in PEI. So, the strengthened hydrogen bonding produced by mixing may induce a decrease of the configurational entropy in the blend at melt state. This may lead to the abnormal increase of T_g s. Pinal [22] has extended the classical thermodynamic approach of Couchman-Karasz to a hydrogen bonding system and has obtained following expression.

$$T_{gm} = T_{CK} \exp\left(-\frac{\Delta S_{mix}^c}{x_1 \Delta C_{p1} + x_2 \Delta C_{p2}}\right) \quad (2)$$

where T_{gm} is the glass transition temperature of the mixture obtained experimentally, T_{CK} is defined in Eq. 1, and ΔS_{mix}^c is the

Fig. 2. Composition dependency of the glass transition temperatures of the blends of poly(vinyl alcohol) (PVA) and polyethyleneimine (PEI); (a) the T_g s with respect to the weight fraction of PEI, (b) schematic illustration for the hydrogen bondings in the blends of PVA and PEI.

configurational part of the entropy of mixing. We determined ΔS_{mix}^c by applying Eq. (2) to the experimental data in Fig. 2a. The estimated ΔS_{mix}^c has a negative sign as seen in Fig. 3a. The abnormal increases of T_g s in Fig. 2a are ascribed to the negative configurational entropy of mixing, which may be caused by the formation of strong hydrogen bonding between PVA and PEI.

The entropy change of the PVA/PEI blends in the glass transition region can be obtained by Fig. 3b according to the definition of entropy by Clausius [44].

$$\Delta S_g = \int_{T_1}^{T_2} \frac{\Delta C_p}{T} dT = \Delta C_p \ln\left(\frac{T_2}{T_1}\right) \quad (3)$$

ΔS_g was evaluated from the experimental data in Table 1 and Fig. 2a. The ΔS_g shows an S-shaped curve, as seen in Fig. 3b. The ΔS_g is initially decreased by adding PEI into PVA, up to a 0.2 weight fraction. ΔS_g reaches maximum value around the mid-composition range, then is decreased by the further increase of PEI weight fraction, in Fig. 4. The abnormal increase of T_g s in Fig. 2a may also be consistent with the decrease of ΔS_g at low concentration range in Fig. 3b, where the weight fraction of PEI is less than 0.2.

Fig. 3. Entropy of mixing of the blends of poly(vinyl alcohol) and poly(ethyleneimine) (PEI); (a) configurational entropy of mixing, (b) entropy in the glass transition region.

Fig. 4. Differential scanning calorimetry thermograms for the melting temperatures of poly(vinyl alcohol) (PVA) in the blends of PVA and poly(ethyleneimine) (PEI).

Fig. 5. Non-isothermal properties of poly(vinyl alcohol) (PVA) in the blends of PVA and poly(ethyleneimine) (PEI) with the heating or cooling rate of 20 K/min in differential scanning calorimetry; (a) melting temperatures, (b) crystallization temperatures, (c) crystallinities.

3.2. Melting behaviors of PVA/PEI blends

DSC thermograms for melting peaks of PVA in PVA/PEI blends are presented in Fig. 4. The non-isothermal melting temperatures (T_m s) were measured from the 2nd heating with a heating rate of 20 K/min. The crystalline temperatures (T_c s) were measured with the cooling rate of 20 K/min. Crystallinity (X_c) of the blends was evaluated with the equation below.

$$X_c = \frac{\Delta H_f}{\Delta H_f^0} \quad (4)$$

where X_c is the crystallinity, ΔH_f is the heat of fusion of the blends and ΔH_f^0 is the heat of fusion of 100% crystalline polymer, PVA

Fig. 6. Equilibrium melting temperatures of poly(vinyl alcohol) (PVA) in the blends of PVA and polyethyleneimine (PEI); (a) Hoffman-Weeks plot, (b) composition dependency of equilibrium melting temperatures of PVA.

(138.6 J/g) [31]. In Fig. 5a-c, the T_m s, T_c s, and X_c s are remarkably decreased by the addition of PEI up to 0.2 weight fraction, and are changed slightly by the further addition of PEI into PVA. When the weight fraction of PEI was higher than 0.8, melting peaks were not observed by DSC in the PVA/PEI blends. The composition range associated with the large decreases of T_m s, T_c s, and X_c s in Fig. 5 is consistent with the composition range associated with the abnormal increases of T_g s in Fig. 2a.

Fig. 6a is a Hoffman-Week's plot [48] for the estimation of equilibrium melting temperature (T_m) of PVA in blends of PVA and PEI. The composition dependency of T_m is plotted in Fig. 6b. At equilibrium melting temperature, the chemical potential of crystalline PVA (μ_c) is equal to those of PVA melt (μ_l). The μ_l may be reduced to μ_i by adding PEI into PVA, since PVA may be mixed with PEI spontaneously. Then, one can obtain the following equilibrium condition [45].

$$\mu_c - \mu_l = \mu_l^* - \mu_l \quad (5)$$

The left hand side of Eq. (5) is the molar free energy of fusion ($\Delta F_f = -\Delta H_f(1 - T_m/T_m^0)$) and the right hand side is the partial molar free energy of mixing with respect to the crystalline component (ΔF_m). In the case of a hydrogen-bonding system, the free energy of mixing can be divided into two terms, as in Eq. (6) [37].

$$\tilde{\Delta F}_m = \tilde{\Delta F}_m^P + \tilde{\Delta F}_m^H \quad (6)$$

where $\tilde{\Delta F}_m^H$ and $\tilde{\Delta F}_m^P$ is the partial molar free energy of mixing contributed by the hydrogen bonding force and by all other

forces, respectively. Usually, $\tilde{\Delta F}_m^P$ is given by the Flory-Huggins equation. Eq. (6) can be re-written as Eq. (7).

$$\tilde{\Delta F}_m = \frac{\partial F_{mix}}{\partial n_2} = (\tilde{\Delta H}_m^P + \tilde{\Delta H}_m^H) - T\tilde{\Delta S}_m \quad (7)$$

where n_2 is the number of moles of the repeating unit of PVA. According to Nish and Wang [49], the enthalpy of mixing can be given by Eqs. (8) and (9) by neglecting the effect of ϕ_2 in the Flory-Huggins equation.

$$\tilde{\Delta H}_m = \frac{\partial H_{mix}}{\partial n_2} = \left(\frac{V_{2u}}{V_{1u}}\right)RT\phi_1^2(\chi^P + \chi^H) = \left(\frac{V_{2u}}{V_{1u}}\right)RT\phi_1^2\chi \quad (8)$$

$$\chi = \frac{BV_{1u}}{RT} \quad (9)$$

where B is the interaction energy density characteristic of the polymer pair. The following expression can be obtained by inserting Eq. (8) into Eq. (7).

$$\frac{\tilde{\Delta F}_m}{RT} = -\frac{\tilde{\Delta S}_m}{R} + \phi_1^2\left(\frac{V_{2u}}{V_{1u}}\right)(\chi^P + \chi^H) = -\frac{\tilde{\Delta S}_m}{R} + \phi_1^2\left(\frac{V_{2u}}{V_{1u}}\right)\chi \quad (10)$$

By setting $\tilde{\Delta F}_m$ equal to the molar free energy of fusion ($\Delta F_f = -\Delta H_f(1 - T_m/T_m^0)$) and inserting Eq. (9) into Eq. (10), the following expressions can be obtained

$$\frac{1}{\phi_1}\left(\frac{1}{T_m} - \frac{1}{T_m^0}\right) - \left(\frac{\tilde{\Delta S}_m}{\phi_1} \frac{1}{\Delta H_f}\right) = -\frac{\phi_1 BV_{2u}}{T_m \Delta H_f} \quad (11)$$

where $\tilde{\Delta S}_m$ is athermal in the liquid state. We refer to the left hand side of Eq. (11) as Q as follows.

$$Q = \frac{1}{\phi_1}\left(\frac{1}{T_m} - \frac{1}{T_m^0}\right) - \left(\frac{\tilde{\Delta S}_m}{\phi_1} \frac{1}{\Delta H_f}\right) \quad (12)$$

We can refer the first term in Eq. (12) to be the degree of the depression of melting point (D_m).

$$D_m = \frac{1}{\phi_1}\left(\frac{1}{T_m} - \frac{1}{T_m^0}\right) = Q + \left(\frac{\tilde{\Delta S}_m}{\phi_1} \frac{1}{\Delta H_f}\right)$$

The D_m is expected to be reduced in the case where the entropy of mixing has a negative sign. We obtained the empirical equation for $\Delta S_{mix}^c/n_T$ in Fig. 3a with the unit (cal/mol K) as follows.

$$\frac{\Delta S_{mix}^c}{n_T} = -A\phi_1\phi_2 \quad (13)$$

where n_T is the total number of moles; $n_T = n_1 + n_2$, n_1 and n_2 is the number of moles of PEI and PVA, respectively. A is determined to be 2.3 for PVA/PEI blends. A similar value of A is determined for PVA/PEI/GO systems. Then, the molar entropy of mixing is obtained as the following.

$$\tilde{\Delta S}_m = \frac{\partial \Delta S_{mix}^c}{\partial n_2} = A\phi_1^2 \quad (14)$$

Since the entropy of mixing of the blends of PEI and PVA has a negative sign, it can be supposed that the D_m would be reduced by the strong hydrogen bonding. However, large depressions of

Fig. 7. Morphology of graphene oxide (GO) and the poly(vinyl alcohol) (PVA)/polyethyleneimine (PEI)/GO blends; (a) transmission electron microscopy image of graphene oxide, (b) scanning electron microscopy (SEM) image of the surface of the PVA/PEI (90/10) blends, (c) SEM image of the surface of the PVA/PEI (90/10) blends with 0.7 wt% GO.

melting points are observed for the blends of PEI and PVA as seen in Fig. 6b. This result points to the fact that the effect of negative entropy may be compensated by the strong enthalpic interaction, as seen in Fig. 7. In Fig. 7, the melting temperatures in Fig. 6b and the entropy of mixing in Fig. 3a are re-plotted using Q and ϕ_i/T_m as variables. From the slope in Fig. 7, B is determined to be $-37 \text{ cal} (\text{cm}^3 \text{ of PEI})$ and χ is -1.34 at 500 K . Eq. (11) reduces to the Nish-Wang equation [49], if the entropy of mixing is neglected. The χ by Nish-Wang's plot is -0.10 at 500 K . So, the magnitude of negative χ becomes much larger when we consider the entropy term in Eq. (11). Here, it is concluded that the D_m in the strong hydrogen bonding system is not reduced by the negative ΔS_m , because the magnitude of negative χ is also increased by the strong hydrogen bonding.

3.3. Effect of GO on the thermal behaviors of PVA/PEI blends

GO was prepared from purified conventional flake graphite ($19 \mu\text{m}$ nominal particle size, Asbury Carbon) by the modified Hummers method [9,17,18]. The TEM image of the reduced GO sheets suspended on a carbon grid are presented in Fig. 7a,

Fig. 8. Effects of graphene oxide on the glass transition temperature and the equilibrium melting temperature of the blends of poly(vinyl alcohol) (PVA) and polyethyleneimine (PEI).

showing the typical image of graphene with electron transparency. We investigated the degree of oxidation of the GO by XPS. The carbon to oxygen atomic ratio of GO was determined to be 1.8 from the XPS spectra. We dispersed 0.7 wt% GO into the blends of PVA and PEI. The SEM images of the surface of the blend films are presented in Fig. 7b and c. The PVA/PEI blends are thermodynamically miscible to form a single phase, therefore, no appreciable domain is observed in Fig. 7b. A rough layer-like morphology is observed on the surface of the PVA/PEI/GO blends in Fig. 7c. The XRD patterns of the PVA/PEI/GO blends show no GO characteristic peak at $2\theta = 9.5^\circ$, indicating GO is fully exfoliated in the blends [18].

The T_g s and T_m^0 s of PVA/PEI/GO blends are compared to those of PVA/PEI blends in Fig. 8a and b. The T_g of PVA is increased about 5 K by adding GO into PVA. In our previous report [18], the T_g of PVA was not changed by adding GO into PVA. We used 86-89 mol% hydrolyzed PVA in the previous work [18] and 99 mol% hydrolyzed PVA in this work. Therefore, the hydrogen bonding interaction between PVA and GO may be stronger in this work compared to those in our previous work. This may be evidenced by the increase of the T_g s of PVA/PEI blends after adding 0.7 wt% GO in Fig. 8a. The depressions of T_m^0 s are more pronounced after adding GO into PVA/PEI blends, as shown in Fig. 9. The results in Figs. 8a and 9 indicate that the hydrogen bonding in PVA/PEI/GO blend systems are pronounced compared to those in the PVA/PEI blend system. We plotted Q versus ϕ_i/T_m for the PVA/PEI/GO blends in Fig. 9. It is reasonable that the mixtures of PEI and GO are treated as diluents for the crystallization of PVA in the PVA/PEI/GO blend systems. So,

Fig. 9. A plot of quantity Q versus ϕ_1/T_m according to Eq. (11). PVA: poly(vinyl alcohol), PEI: polyethyleneimine.

the χ in the PVA/PEI/GO blend systems stands for the enthalpic interaction between PVA and the PEI/GO mixture. The χ in the PVA/PEI/GO ternary blend system was determined to be -1.53, which is larger than in the PVA/PEI binary blends. The increase of the magnitude of negative χ by GO may be ascribed to the increase of hydrogen bonding interaction (χ^H).

4. Conclusions

The T_g s of PVA/PEI blends were higher than the T_g s of either of the component polymers at low concentrations of PEI. These abnormal increases of T_g s may be due to the negative entropy of mixing, which is associated with the strong hydrogen bonding between PVA and PEI. The degree of depression of T_m^0 s was not reduced by the negative entropy of mixing, since strong hydrogen bonding also causes an increase in the magnitude of negative χ between PVA and PEI. The T_g of PVA was increased significantly by adding 0.7 wt% GO into PVA. The magnitude of negative χ was increased by adding GO into the blends of PVA and PEI.

Acknowledgments

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