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 $T_g$s was not reduced by the negative entropy of mixing, since strong hydrogen bonding also causes an increase in the magnitude of negative $\chi$ between PVA and PEI. The $T_g$ of PVA was increased significantly by adding 0.7 wt.% GO into PVA. The magnitude of negative $\chi$ 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 (PVP) 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
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2. Experimental Section

2.1. Materials

PVA was purchased from Sigma Aldrich (99 mol% hydrolyzed, Mw = 89 000-98 000 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 (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 (Tgs) of PVA/PEI blends

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

\[
\ln T_{ck} = \frac{x_1 \Delta C_p1 \ln T_{g1} + x_2 \Delta C_p2 \ln T_{g2}}{x_1 \Delta C_p1 + x_2 \Delta C_p2}
\]

where \(T_{g1}, T_{g2}\) is the glass transition temperature of the mixture, PEI, and PVA, respectively. \(x_1, x_2\) are the mole fractions of PEI and PVA, respectively. \(\Delta C_p\) 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 (Vw = 36.11 cm3/mol) and PVA (Vw = 32.28 cm3/mol) were

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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 $T_g$. Pinal [22] has extended the classical thermodynamic approach of Couchman-Karasz to a hydrogen bonding system and has obtained following expression.

$$T_{gm} = T_{CK} \exp \left( \frac{\Delta S_{mix}^c}{x_1\Delta C_p^{PVA} + x_2\Delta C_p^{PEI}} \right)$$

(2)

where $T_{gm}$ is the glass transition temperature of the mixture obtained experimentally, $T_{CK}$ is defined in Eq. 1, and $\Delta S_{mix}^c$ is the configurational part of the entropy of mixing. We determined $\Delta S_{mix}^c$ by applying Eq. (2) to the experimental data in Fig. 2a. The estimated $\Delta S_{mix}^c$ 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].

$$\Delta S_g = \int \frac{\Delta C_p}{T} dT = \Delta C_p \ln \left( \frac{T_2}{T_1} \right)$$

(3)

$\Delta S_g$ was evaluated from the experimental data in Table 1 and Fig. 2a. The $\Delta S_g$ shows an S-shaped curve, as seen in Fig. 3b. The $\Delta S_g$ is initially decreased by adding PEI into PVA, up to a 0.2 weight fraction. $\Delta S_g$ 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 $T_g$ in Fig. 2a may also be consistent with the decrease of $\Delta S_g$ at low concentration range in Fig. 3b, where the weight fraction of PEI is less than 0.2.

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

Fig. 2. Composition dependency of the glass transition glass transition temperatures of the blends of poly(vinyl alcohol) (PVA) and polyethyleneimine (PEI); (a) the $T_g$ with respect to the weight fraction of PEI, (b) schematic illustration for the hydrogen bondings in the blends of PVA and PEI.
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 ($T_m$) were measured from the 2nd heating with a heating rate of 20 K/min. The crystalline temperatures ($T_c$) were measured with the cooling rate of 20 K/min. Crystallinity ($X_c$) of the blends was evaluated with the equation below.

$$X_c = \frac{\Delta H_f}{\Delta H_f^0}$$  \hspace{1cm} (4)

where $X_c$ is the crystallinity, $\Delta H_f$ is the heat of fusion of the blends and $\Delta H_f^0$ is the heat of fusion of 100% crystalline polymer, PVA.

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Fig. 3. Entropy of mixing of the blends of poly(vinyl alcohol) and polyethyleneimine (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 polyethyleneimine (PEI).

Fig. 5. Non-isothermal properties of poly(vinyl alcohol) (PVA) in the blends of PVA and polyethyleneimine (PEI) with the heating or cooling rate of 20 K/min in differential scanning calorimetry; (a) melting temperatures, (b) crystallization temperatures, (c) crystallinities.
forces, respectively. Usually, $\Delta F_m^p$ is given by the Flory-Huggins equation. Eq. (6) can be re-written as Eq. (7).

$$\Delta F_m^p = \frac{\partial F_m^{nl}}{\partial n_2} = (\Delta H_m^p + \Delta H_m^p) - T\Delta S_m$$

(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 $\phi_2$ in the Flory-Huggins equation.

$$\Delta H_m = \frac{\partial H_m^{mix}}{\partial n_2} = \left(\frac{V_2}{V_1}\right)RT\phi_2^p(\chi^p + \chi^p) = \left(\frac{V_2}{V_1}\right)RT\phi_1^2$$

(8)

$$\chi = \frac{BV_{11}}{RT}$$

(9)

By setting $\Delta F_m^p$ 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

$$\frac{1}{\phi_1}\left(1 - \frac{1}{T_m^0}\right) - \left(\frac{\Delta S_m}{\phi_1^2}\right) = \frac{1}{\phi_1}\left(1 - \frac{1}{T_m^0}\right) - \left(\frac{\Delta S_m}{\phi_1}\right)$$

(10)

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

$$Q = \frac{1}{\phi_1}\left(1 - \frac{1}{T_m^0}\right) - \left(\frac{\Delta S_m}{\phi_1}\right)$$

(12)

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

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

(13)

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 $\Delta S_m/n_T$ in Fig. 3a with the unit (cal/mol K) as follows.

$$\frac{\Delta S_m}{n_T} = -A\phi_1$$

(14)

where $n_T$ is the total number of moles; $n_1 = n_1 + n_2$, $n_2$ 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.
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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 $\phi_i/T_m$ as variables. From the slope in Fig. 7, B is determined to be $-37\text{cal} \ (\text{cm}^3 \text{of PEI})$ and $\chi$ is -1.34 at 500 $K$. Eq. (11) reduces to the Nish-Wang equation [49], if the entropy of mixing is neglected. The $\chi$ by Nish-Wang’s plot is -0.10 at 500 $K$. So, the magnitude of negative $\chi$ 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 $\Delta S_m$ because the magnitude of negative $\chi$ 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 $\mu$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, showing the typical image of graphene with electron transpar-
cy. 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.

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).
the $\chi$ in the PVA/PEI/GO blend systems stands for the enthalpic interaction between PVA and the PEI/GO mixture. The $\chi$ 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 $\chi$ by GO may be ascribed to the increase of hydrogen bonding interaction ($\chi''$).

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 $T_w^0$ was not reduced by the negative entropy of mixing, since strong hydrogen bonding also causes an increase in the magnitude of negative $\chi$ between PVA and PEI. The $T_g$ of PVA was increased significantly by adding 0.7 wt% GO into PVA. The magnitude of negative $\chi$ was increased by adding GO into the blends of PVA and PEI.

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References


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