

UNIQUE EVOLUTION OF SPATIAL AND DYNAMIC HETEROGENEITIES ON THE GLASS TRANSITION BEHAVIOR OF PVPh/PEO BLENDS*

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Abstract Glass transition behavior of hydrogen bonded polymer blends of poly(vinyl phenol) (PVPh) and poly(ethylene oxide) (PEO) is systematically investigated using normal differential scanning calorimetry (DSC) and recently developed multifrequency temperature-modulated DSC (TOPEM), in combination with Fourier transform infrared spectroscopy (FTIR) and nuclear magnetic resonance (NMR) techniques, focusing on the effect of the PEO molecular weight on the spatial and dynamic heterogeneity. It is found, for the first time, that both the glass transition temperature (T_g) and activity energy (E_a) of the blends strongly depend on PEO molecular weight, and a common turning point, which separates the rapid and slow increasing regions, can be found. The interchain hydrogen bonding interactions, both determined by FTIR measurements and obtained from the Kwei equation, decrease with increasing PEO molecular weight, indicating a decrease of the componential miscibility. A series of parameters related to the microscopic spatial and dynamic heterogeneity, such as the activity energy, fragility, nonexponential factor and the size of cooperatively rearranging regions, are calculated from frequency dependency complex heat capacity measured using TOPEM. It is found that each of these parameters monotonically changes with increasing the PEO molecular weight during the glass transition process, demonstrating that hydrogen bonding interaction is the key factor in controlling the spatial and dynamic heterogeneity, thus the glass transition. NMR relaxation results reveal the existence of obvious phase separation large than 5 nm, implying that the cooperatively rearranging regions should be closely related to the interphase region between the two components. The above obtained origin and evolution of spatial and dynamic heterogeneity provide a new insight into the glass transition behavior of polymer blends.

Keywords: Glass transition; Polymer blend; DSC; FTIR; Solid-state NMR.

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INTRODUCTION

The theory relating the nature of glass and glass transition is proposed as the deepest and the most interesting unsolved problem in solid-state theory^[1]. People have studied glass transition from experimental and theoretical aspects for a long time and proposed many models, like the free volume theory^[2], the Adam-Gibbs theory^[3], the mode couple theory^[4] and so on. However, there is still no theory that could explain all the phenomena associated with the glass transition process so far. Nowadays, It is widely accepted that the glass transition is regarded as a process simultaneously controlled by thermodynamics and dynamics^[1], and closely related to the spatial and dynamic heterogeneities^[5]. For most glass-forming systems, The heterogeneity results in highly

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nonexponential relaxation^[6]. Recently, the dynamic heterogeneity on microscopic scales has been studied by a number of novel experimental techniques^[7,8] and molecular simulations^[9,10]. However, the question of how the spatial and dynamic heterogeneities connecting with microscopic interactions remains^[11]. For a polymer system, if we can systematically manipulate its spatial and dynamic heterogeneities and then detect the corresponding responds on glass transition behavior, it will be very helpful to understand the nature of glass transition at a molecular level and establish the structure-property relationship^[11]. However, few suchlike studies have been reported in homopolymers, because only a few methods can be used to manipulate the structure and dynamics in these systems, such as the controlling of the interchains proximity^[12,13] and the thickness of ultrathin films^[14,15].

Compared to homopolymer, there are many convenient approaches to manipulate the structure and dynamics of miscible polymer blends by adjusting the composition, component molecular weight or concentration, which enable us to obtain systematic response of their influence on glass transition behavior^[16,17]. This property attracts very large interest of researchers. During the past decades, the spatial and dynamic heterogeneity in miscible polymer blends without special interchain interactions has been extensively studied using many techniques, including dielectric spectroscopy^[18,19], NMR^[18,20], quasielastic neutron scattering^[18,19,21] and so on. In explanation of the glass transition behavior in polymer blends, theories were developed on the basis of the idea that the effective T_g is determined by a local region with a composition that varies from the bulk blend composition^[16]. Depending on what is considered as the main origin of the biased local composition, two different models have been developed over the past ten years including the Lodge-Mcleish theory^[22] and the thermal concentration fluctuations models^[23]. These two models have successfully explained many experimental observations. On the other hand, it is notable that special interchain interaction, such as hydrogen bonding, can effectively suppress the concentration fluctuations and increase the segmental cooperative dynamics between components^[24] at the molecular level, and typically result in a single T_g . This property of interchain interaction in blends makes it correlate well to the structure and dynamics. Therefore, hydrogen bonded polymer blends with well controlled hydrogen bonding interaction by properly adjusting the componential parameters are expected to be a unique system to study the nature of glass transition behavior. Furthermore, systematic studies on polymer blends can also provide new insight into the nature of glass transition in homopolymers. In addition, these studies are also very important to the design and preparation of high performance polymer alloys in the industry field.

The effect of polymer molecular weight on T_g has been widely studied, including homopolymers, copolymers and polymer blend systems^[25,26]. Based on the free volume theory, a formula proposed by Fox and Flory^[27] provided a connection between the molecular weight and T_g in homopolymers. Such a relation was also confirmed by molecular dynamics simulations^[28,29]. Flory and Huggins^[30] found that the molecular weight had a strong effect on the miscibility of polymer blends, and the low molecular weight for one component was found to be useful to achieve good miscibility in many reported polymer blends^[31]. However, for hydrogen bonded polymer blends, it is still not clear that how the component molecular weight affects the intermolecular hydrogen bonding and thus the glass transition behavior, detailed study on this topic needs to be further elucidated.

Poly(vinyl phenol) (PVPh) can form miscible blends with many of the polyesters, polyamides and cellulose esters due to the intermolecular hydrogen bonding interaction between the hydroxyl groups of PVPh and the other component^[32]. It was reported that blends of semicrystalline poly(ethylene oxide) (PEO) with amorphous PVPh exhibited a single T_g over the entire composition range, and blends containing less than 50 wt% PEO were completely amorphous^[33–35]. Furthermore, FTIR experiments showed that the good miscibility comes from the strong interchain hydrogen bonding interaction between the phenol side group of PVPh and the ether bond of PEO. The experiments of ¹H-NMR relaxation times in the rotational frame ($T_{1\rho}$) revealed that the PVPh-rich blends are intimately mixed over distances less than 2–3 nm in PVPh/PEO blends. However, till now, few studies have reported the influence of PEO molecular weight on the glass transition behavior of PVPh/PEO blends, and thus the relationship between the spatial heterogeneity dynamics and the hydrogen bonding interaction needs to be further elucidated.

Differential scanning calorimetry (DSC) has been proved to be a powerful technique and widely used to

investigate the glass transition phenomena in polymeric systems^[36, 37]. With the advent of temperature-modulated calorimetry (TMDSC), it becomes possible to measure the isothermal frequency response to gain rich information associated with the glass transition^[38]. Recently, a new multifrequency TMDSC technique, TOPEM, has been developed by Schawe *et al.*^[39]. In principle, the sample can show thermal relaxation processes due to the lag in heat transfer from the fast external to slow internal. Thermal relaxation is related to degree of freedom of internal structure dynamics. Therefore, when a thermo stimuli is given, the heat capacity measured by TMDSC becomes frequency dependent and also structure relaxation time dependent. Compared with traditional TMDSC which imposes a sinusoidal modulation of heating rate, TOPEM includes a stochastic modulation for temperature. This technique allows the evaluation of the “quasi-static” heat capacity ($C_{p,0}$) and the separation of the total heat flow in two components including the reversing and non-reversing heat flows. The major advantage of TOPEM over TMDSC is that the complex heat capacity for a wide range of frequencies can be determined in a single experiment using just one sample, and experimental errors can be remarkably reduced. Thus TOPEM is particularly suitable to study the kinetics of frequency-dependent phenomena such as the α relaxation related to glass transition. A single value of apparent activation energy (E_a) can be determined from the dependence of T_g on frequencies. Besides, based on the Donth’s equation^[40], the size of cooperatively rearranging region can be estimated from the data on the quasi-static heat capacity. The $C_{p,0}$ is obtained from the TOPEM measurements as the reversing heat capacity corresponding to the zero frequency. These parameters obtained from TOPEM measurements can directly reflect the spatial and dynamic heterogeneities which influence T_g , this makes TOPEM become a powerful tool to study the glass transition phenomena. This novel technique has been widely applied in studying of glass transition of polystyrene^[41, 42], polystyrene/clay^[42], maltitol^[43], lignin^[44] and so on. However, few studies were reported on polymer blends.

In this paper, we aim to investigate the influence of PEO molecular weight of wide range on the interchain hydrogen bonding interaction and the glass transition behavior of PVPh/PEO blends using normal DSC and TOPEM in combination with FTIR and NMR techniques. Based on these studies, we obtain the origin and evolution of the spatial and dynamic heterogeneities near the glass transition temperature. The PEO molecular weight dependence of T_g for PVPh/PEO blends is determined for the first time. Through fitting the Kwei equation from the connection between T_g and PEO fraction for blends with different PEO molecular weights, the parameter q , reflecting the strength of interchain hydrogen bonding interaction, is obtained. Furthermore, The FTIR experiments are performed to detect different types of hydrogen bonding in the blends. Proton NMR relaxation experiments are utilized to determine the extent of microphase separation. TOPEM technique is further used to study the glass transition dynamics of the blends, and the activity energy (E_a) is determined from the frequency dependent complex heat capacity. Besides, the fragility parameter m and nonexponential factor β_{KWW} reflecting the dynamic heterogeneity are calculated by fitting the Vogel-Fulcher-Tammann (VFT) equation. Finally, the size of cooperatively rearranging regions (CRRs) associated with spatial heterogeneity is determined from the Donth’s equation. On the basis of these studies, the relation between the PEO molecular weight dependent glass transition behavior and the spatial and dynamic heterogeneities of PVPh/PEO blends is well established.

EXPERIMENTAL

Materials and Preparation of Samples

Poly(vinyl phenol) (PVPh) with $M_n = 20 \times 10^3$ was obtained from Polymer Source Inc. Poly (ethylene glycol) (PEG) with $M_n = 1.0 \times 10^3$, 1.5×10^3 , 3.4×10^3 and poly(ethylene oxide) (PEO) with $M_n = 20 \times 10^3$, 100×10^3 , 300×10^3 were purchased from Aldrich Chemical Co. Poly(ethylene glycol) dimethyl ether (PEG2Me) with $M_n = 1 \times 10^3$ and polydispersity index = 1.05 was purchased from Polymer Source Inc. Its structure is similar to PEG except that both the end groups are methyls rather than hydroxyls. Though the synthesis methods and molecular weights for PEG and PEO are different, they have the same molecular structure. Here we use PEO to represent both of these polymers. PVPh/PEO blends were prepared by solution blending in tetrahydrofuran with

the polymer concentration of 10 g/L at 55°C and stirred for 3 h. The blends were obtained in the form of a film by evaporating the solvent at 60°C for 3 days in dry flowing nitrogen and then dried under vacuum at 20°C above T_g for 2 days. Finally, the samples were allowed to cool to room temperature for study. The details were described in a previous publication^[35]. PVPh/PEO1k represents the PEO molecular weight is 1×10^3 in the blends, other samples were abbreviated as PVPh/PEO1.5k, PVPh/PEO3.4k, and so on. PVPh/PEO2Me1k represents the methyl end-capped PEO with a molecular weight of 1×10^3 in the blend.

Differential Scanning Calorimetry (DSC) Measurements

All the DSC measurements were performed on a Mettler-Toledo DSC1 STAR system with a FRS5 sensor under a dry nitrogen atmosphere (N_2 flow of 50 mL/min). The instrument was calibrated with indium and zinc standards. In conventional DSC experiments, all samples of about 8 mg were first heated from room temperature to 220°C (about 50°C above the T_g of PVPh) at a rate of 20 K/min, and kept at that temperature for 10 min to eliminate the thermal history; subsequently, they were cooled to -90°C at a rate of -10 K/min and kept at that temperature for 5 min. Following the cooling scan, a second heating scan was conducted to 220°C with a rate of 10 K/min. The midpoint of the slope change of the heat capacity plot was taken as the glass transition temperature (T_g).

In principle, the TOPEM technique is overlaying a series of stochastic temperature pulses of different durations with a temperature ramp at a constant underlying rate. One single TOPEM run allows for determining the frequency dependence of the complex heat capacity that can be conveniently used to characterize the glass transition dynamics. Samples used in TOPEM experiments were first heated from room temperature to the temperature of ($T_g + 50$) K for 5 min to erase the thermal history, subsequently, they were cooled to ($T_g - 50$) K at a rate of 10 K/min and kept at that temperature for 5 min. Then TOPEM measurements were conducted on the second heating scan at an underlying heating rate of 1 K/min with a scanning temperature ranging from ($T_g - 50$) K to ($T_g + 50$) K. The amplitude was fixed at ± 1 K and the period of pulses was ranging from 25 s to 60 s for all the TOPEM experiments. No correction of the heat flow by an empty run is needed in TOPEM experiments, because the weight of both reference and sample crucibles is entered into the method.

Fourier Transition Infrared Spectroscopy (FTIR)

All the FTIR measurements were performed on a Bio-Rad FTS6000 FTIR spectrometer, the resolution was 0.075 cm^{-1} and the average scan number was 16. Samples were fixed in two glass slides and heated from room temperature to the temperature of ($T_g + 50$) K at a rate of 10 K/min and kept at that temperature for 5 min to form a thin film; subsequently, they were cooled to room temperature at a rate of -10 K/min and kept at that temperature for 5 min. Following the cooling scan, FTIR measurements were performed on the region from 750 cm^{-1} to 4000 cm^{-1} at room temperature.

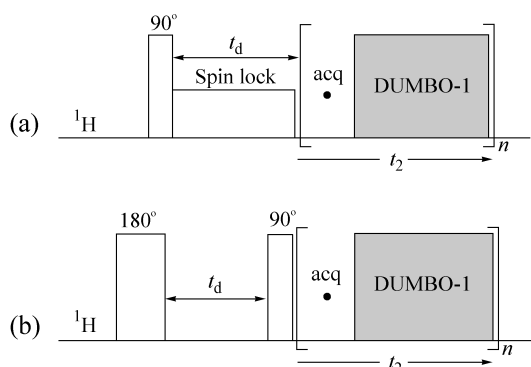


Fig. 1 Pulse sequences for ^1H relaxation NMR experiments recorded with DUMBO-1 homonuclear decoupling during t_2 : (a) the $T_{1\rho}^H$ experiment and (b) the T_1^H experiment (t_d is the relaxation delay time.)

Nuclear Magnetic Resonance (NMR) Experiments

Solid-state NMR experiments were performed on a Varian Infinityplus-400 wide-bore (89 mm) NMR spectrometer operating at a proton frequency of 399.7 MHz. A conventional 4 mm double-resonance HX CP/MAS NMR probe was used, and samples were placed in a 4 mm zirconia PENCIL rotor with 52 μL sample volume. The magic angle spinning (MAS) was automatically controlled at 9.8 kHz within ± 2 Hz with a MAS speed controller for all NMR experiments. ^1H T_1 and $T_{1\rho}$ relaxation experiments are utilized to estimate the extent of microphase-separation in blends, and the pulse sequences shown in Fig. 1 are based on the continuous phase modulation technique for ^1H - ^1H homonuclear dipolar decoupling (DUMBO-1) proposed by Emsley *et al.*^[45,46]. The DUMBO-1 decoupling cycle time was set to 32 μs divided in 64 discrete phase steps of 500 ns duration each, and the ^1H decoupling RF field strength of DUMBO-1 was set to 100 kHz in both dimensions. The recycle delay was set to 8 s.

RESULTS AND DISCUSSION

Influence of PEO Molecular Weight on the Glass Transition Temperature and Interchain Hydrogen Bonding Interaction

Conventional DSC is used to characterize the glass transition temperatures, T_g , of PVPh/PEO blends with different PEO molecular weights, and the weight fraction of PEO is chosen as 30%. In a previous work, Rinderknecht *et al.*^[47] found that when the weight fraction of PEO was 30%, the mole ratio of phenol groups of PVPh and ether bonds of PEO was about 1:1 and the intermolecular hydrogen bonding between the two different components also reached a maximum. Figure 2 shows the DSC traces of the second heating scan for PVPh/PEO blends with different PEO molecular weights. No melting peak is detected for these blends, indicating the formation of PEO crystalline domains in these blends is inhibited. A single T_g is clearly observed for each blend, suggesting that the two components are miscible at a scale less than the scale of DSC measurements.

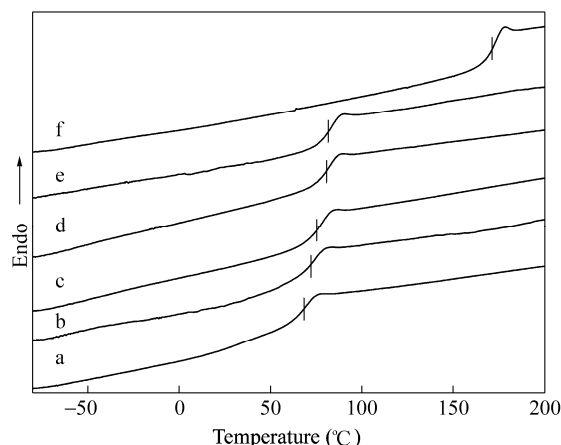


Fig. 2 DSC traces in the second heating scan of pure PVPh (f) and PVPh/PEO blends with different PEO molecular weights of (a) 1.5×10^3 , (b) 3.4×10^3 , (c) 20×10^3 , (d) 100×10^3 , (e) 300×10^3 , respectively

Figure 3 plots the PEO molecular weight dependence of T_g . It is noteworthy that T_g increases with increasing the PEO molecular weight, and a turning point (dotted line) can be found at the PEO molecular weight of about 10×10^3 , where the T_g increases rapidly when the PEO molecular weight is less than this value and it increases slowly above this value. To our knowledge, this is the first study of the PEO molecular weight dependent glass transition behavior in PVPh/PEO blends.

Over the past years, a number of theories have been proposed to describe the relationship between T_g and the composition of miscible polymer blends or copolymers, including the linear rule and the Fox, Gordon-Taylor, Couchman-Karas, Kwei, and Braun-Kovacs equations^[24]. The Kwei function^[48] considered the

intermolecular special interactions and was usually used to study polymer blends consisting of hydrogen bonds. The Kwei equation can be written as^[48]:

$$T_g = \frac{W_1 T_{g1} + k W_2 T_{g2}}{W_1 + k W_2} + q W_1 W_2 \quad (1)$$

where W_1 and W_2 denote weight fractions of the two compositions, respectively, T_{g1} and T_{g2} represent the corresponding glass transition temperatures, and k and q are fitting parameters. Here, the parameter q associates with the strength of hydrogen bonding in the blend, which should be considered as a balance between the breaking of the self-association hydrogen bonding and the forming of the inter-association. The value of q depends on the change of entropy corresponding to the change of the number of hydrogen bonds in the blend^[48]. The absolute value of q is large when the number of intermolecular hydrogen bonds is large. On the other hand, based on the hypothesis that the terminal segments have a greater free volume than intermediate segments, the relationship between T_g and molecular weight of a homopolymer can be written as the Fox and Flory's equation^[27]:

$$T_g = T_g(\infty) - \frac{C}{M_n} \quad (2)$$

where $T_g(\infty)$ is the T_g when the polymer's molecular weight is infinite and C is the characteristic constant. By combining Eq. (1) and Eq. (2), we can obtain a new relation between T_g and componential molecular weight for polymer blends:

$$T_g = \frac{W_1 T_{g1} + k W_2 (T_g(\infty) - \frac{C}{M_n})}{W_1 + k W_2} + q W_1 W_2 \quad (3)$$

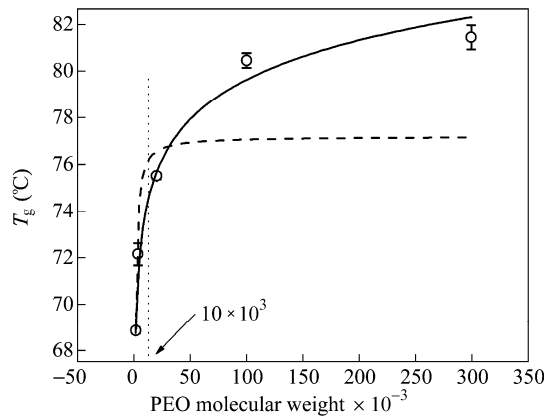


Fig. 3 PEO molecular weight dependence of T_g in PVPh/PEO blends
The dashed line represents the fit curve using Eq. (3); The dotted line represents the turning point.

Figure 3 also displays the fitting curve from Eq. (3) (dashed line) using a constant value of q , where it is clearly noted that the theoretical curve obviously differs from the experiment results, especially when the PEO molecular weight is above a critical value. As Eq. (2) is based on the hypothesis that the terminal segments have a greater free volume than intermediate segments, whereas in the large PEO molecular weight case, the terminal segment effect becomes less pronounced. Hence, Eq. (3) predicts that the variation of T_g is small in the large PEO molecular weight region. The difference between the predicted result and the observed one implies that the terminal segmental free volume is not the main reason of the increase of T_g with the PEO molecular weight in

the large PEO molecular weight region. Therefore, we consider that the intermolecular hydrogen bonding interaction parameter q in Eq. (3) should not be a constant. Furthermore, we can reasonably infer that the changes of PEO molecular weights induce the changes of interchain hydrogen bonds and finally influence the T_g of blends. To get a better understanding of the effect of PEO molecular weight on the interchain hydrogen bonding, PVPh/PEO blends with various PEO weight fractions and molecular weights are investigated using DSC, where a quantitative analysis of the q value associated with hydrogen bonding can be achieved. Figure 4 shows the PEO fraction dependence of the T_g of PVPh/PEO blends with three different PEO molecular weights measured by DSC. Table 1 lists the calculated q values for blends with 30 wt% PEO through fitting the experimental data in Fig. 4 with Eq. (1). In previous studies, it was found that blends with high strength of interchain hydrogen bonding interaction always have high absolute value of q , e.g., $q = 140$ in PVPh/PVP blends^[49] and $q = 130$ in PHPMA/PVP blends^[50]. Thus, the absolute value of q is larger than 100 for all the three blends listed in Table 1, implying a strong interchain hydrogen bonding between PEO and PVPh. It is noteworthy that as PEO molecular weight increases, the absolute value of q decreases, indicating a decrease of the interchain hydrogen bonding interaction in these blends.

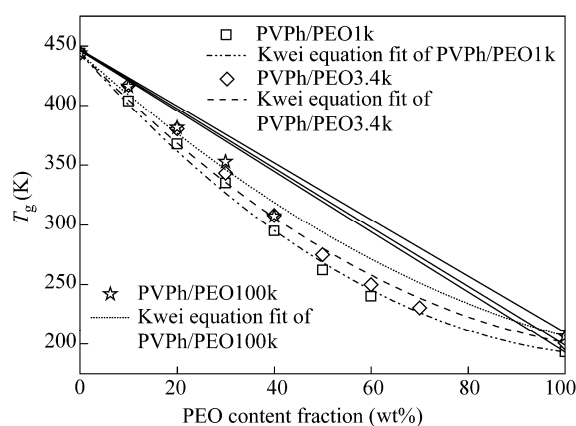


Fig. 4 PEO weight fraction dependence of T_g in PVPh/PEO blends

The dashed and dotted curves are fits to the Kwei function. The solid lines represent linear superposition T_g s²⁴ of PVPh (170°C) and PEO (−67°C, −72°C, −80°C for PEO100k, PEO3.4k and PEO1k, respectively).

Table 1. Fitting parameters in Kwei function for the interchain hydrogen bonding interaction in PVPh/PEO blends with 30 wt% PEO

Samples	$K (\pm 0.01)$	$q (\pm 10)$
PVPh/PEO1k	1.0	−200
PVPh/PEO3.4k	1.0	−167
PVPh/PEO100k	1.0	−124

FTIR spectroscopy is a powerful technique to provide important information about the special interactions between polymers^[24]. In a previous report on PVPh/EVA blends^[51], it was found that lots of phenolic groups of PVPh participate in intrachain hydrogen bonds when the PVPh's fraction is more than 50 wt%. From FTIR measurements, it is also noted that the miscibility in PVPh/PEO blends is driven from the strong hydrogen bonding between the phenol side group of PVPh and the ether bond of PEO^[33, 34]. Cai *et al.*^[52] found that there are free, intra- and inter-associated hydroxyl groups in these blends, and the fraction of free phenol groups obviously decreases with increasing PEO fraction, while the intra-associated interaction remains almost constant. However, till now, few studies were reported concerning the effect of PEO molecular weight on the interchain hydrogen bonding interaction in PVPh/PEO blends. Figure 5 shows the FTIR spectra of the phenolic hydroxyl stretching measured at room temperature with wave number ranging from 3100 cm^{−1} to 3800 cm^{−1} for PVPh

homopolymer and PVPh/PEO blends. To avoid the influence of the terminal hydroxyl groups of PEO with low molecular weight on the FTIR spectrum at the range of 3500 cm^{-1} to 3600 cm^{-1} , dimethyl terminated PEO (PEO2Me) was used to prepare PVPh/PEO2Me1k sample. On the basis of previous FTIR results on PVPh/PEO blends^[33], the absorption at 3525 cm^{-1} in Fig. 5 should be assigned to the free phenolic hydroxyl group; and the broad absorption at 3360 cm^{-1} should be assigned to wide distribution of intrachain hydrogen bonded hydroxyl groups (dimers or multimers) among phenol groups in PVPh. In a previous study, the absorption at 3320 cm^{-1} in blend with 80 wt% PEO was assigned to interchain hydrogen bonds between PVPh hydroxyl groups and PEO ether oxygens^[33]. It is noted that the free phenolic hydroxyl absorption decreases rapidly in blends in Fig. 5. The hydrogen bonded phenolic hydroxyl absorption becomes narrow compared to that of the PVPh homopolymers, indicating that the hydrogen bonds undergo a new distribution in blends. In addition, the peak of phenolic hydrogen bonds shifts to low wave number as PEO molecular weight decreases, indicating an increase of the interchain hydrogen bonds. This result is consistent with that obtained from DSC.

In addition, the frequency difference ($\Delta\nu$) between the free hydroxyl absorbance and the absorbance of studied hydrogen bonded species is a measure of the average strength of interchain interactions. From previous FTIR results, the frequency difference reflecting the average strength of the interchain hydrogen bonding interaction between PEO and PVPh is about 325 cm^{-1} ^[33], which is stronger than the frequency difference ($\Delta\nu = 3525 - 3364 = 161\text{ cm}^{-1}$) reflecting the intrachain hydrogen bonding interaction in PVPh as shown in Fig. 5. Therefore, according to previous work by Kuo^[24], we should observe a positive deviation of the experimentally observed T_g compared to the linear superposition T_g calculated from the T_g of pure PVPh (170°C) and PEO (-67°C , -72°C , -80°C for PEO100k, PEO3.4k and PEO1k, respectively), and vice versa. However, it is interesting to note that a negative deviation is observed in Fig. 4. According to previous work by Wu *et al.*^[53], this negative deviation should be attributed to the entropy change. As many multimer hydrogen bonds and π - π stacking interactions exist among phenol and phenyl groups, respectively^[24, 54], therefore, when PVPh blends with PEO, the increase of entropy in blends resulted from the disassociation of intrachain interaction among phenol groups in PVPh should be larger than the decrease of entropy resulted from the formation of interchain hydrogen bonds between PVPh and PEO. Thus, this net increased entropy results in the observed negative deviation in these blends as shown in Fig. 4.

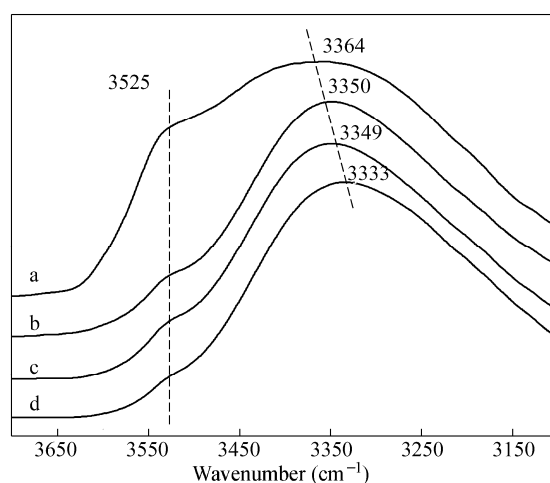


Fig. 5 FTIR results for the PVPh/PEO blends with 30 wt% PEO at room temperature: (a) pure PVPh, (b) PVPh/PEO300k, (c) PVPh/PEO20k and (d) PVPh/PEO2Me1k

There are two factors that may result in the decrease of the interchain hydrogen bonding interaction with increasing the PEO molecular weight. The first factor that may influence the PEO molecular weight dependence of T_g is the PEO hydroxyl end groups. Since the hydroxyl value of PEO reduces quickly with the increase PEO

molecular weight, it is expected that for blends with lower PEO molecular weight, more interchain hydrogen bonds should be formed and thus should result in a significant decrease in T_g . In order to investigate this effect, we also prepared a blend consisting of the methyl end-capped PEO. Figure 6 shows the DSC curves of the second heating scan of PVPh/PEO1k and PVPh/PEO2Me1k blends containing PEO with hydroxyl and methyl end groups, respectively. It is noteworthy that each curve exhibits a single T_g and the two curves are almost identical, indicating that with or without PEO end groups does not influence the T_g .

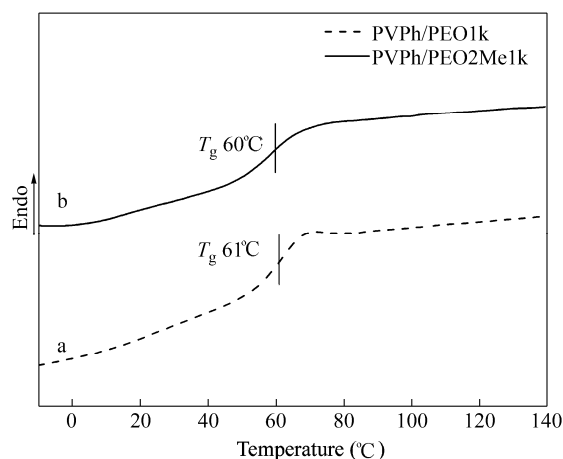


Fig. 6 DSC traces in the second heating scan of PVPh/PEO blends with 30 wt% PEO and different PEO terminal groups: (a) PVPh/PEO1k and (b) PVPh/PEO2Me1k

The other factor that may influence the PEO molecular weight dependence of T_g is the miscibility between PEO and PVPh. Component molecular weight can influence the miscibility from two aspects: thermodynamics and kinetics. From the viewpoint of thermodynamics, two polymer components must meet the condition that their mixing Gibbs free energy (ΔG_{mix}) is less than zero and the spinodal equation $\partial^2(\Delta G_{\text{mix}}/RT)/\partial\Phi_B^2 = 0$ to get miscible, where Φ_B is the self-association component. We use the Painter-Coleman model^[55] to describe the mixing Gibbs free energy ΔG_{mix} :

$$\frac{\Delta G_{\text{mix}}}{RT} = \frac{\Phi_A}{N_A} \ln \Phi_A + \frac{\Phi_B}{N_B} \ln \Phi_B + \Phi_A \Phi_B \chi_{AB} + \frac{\Delta G_H}{RT} \quad (4)$$

where Φ_i ($i = A, B$) is the volume fraction of the i -th component, N_i is the number of repeat units in the i -th component; χ_{AB} is the Flory-Huggins interaction parameter which can be calculated from the formula $\chi = (\delta_A - \delta_B)^2/RT$ containing Hildebrand's solubility parameters δ_A and δ_B . ΔG_H is the Gibbs free energy change due to hydrogen bonding interaction. If we know these parameters, the mole volume of repeat units V_B and V_A , the intrachain and interchain hydrogen bonding interaction equilibrium constant K_B and K_A , as well as the relevant interaction enthalpy h_B and h_A , we can obtain the molecular weight dependence of spinodal equation. The calculated curves (see Supporting Information for more details) show that when the fraction of PEO is 30% and the molecular weight of PVPh is 20×10^3 , the blends transform from immiscibility to miscibility with the decrease of temperature. The order of the calculated critical transition temperature for three blends is as follows: $T_{\text{PVPh/PEO1k}} (138^\circ\text{C}) > T_{\text{PVPh/PEO3.4k}} (136^\circ\text{C}) > T_{\text{PVPh/PEO100k}} (135^\circ\text{C})$. We can conclude that all the three blends are thermodynamically miscible near the glass transition temperatures which are lower than 135°C .

It is well-known that the miscibility of blends is also controlled by kinetics. The experiments of Composto *et al.*^[56] show that the diffusion coefficient of polymer blends depends on the “fast” component, and the component molecular weight has a great effect on diffusion coefficient^[56]. The smaller the component molecular weight is, the faster the diffusion and thus the better the miscibility are. Since the remarkable large difference of the T_g s for PVPh and PEO, thus the miscibility between PVPh and PEO in blends should depends

on PEO which has the lower T_g and relatively fast segment motion. As the PEO molecular weight increases, the diffusion ability of the PEO chain weakens, thus the miscibility between PEO and PVPh decreases. As discussed above, we can conclude that the PEO molecular weight should have a significant influence on its diffusion dynamics, which causes the miscibility changes as well as the change of interchain hydrogen bonding interaction.

The presence of microphase separation in all blends is further confirmed by ^1H T_1 and $T_{1\rho}$ relaxation solid-state NMR experiments. Table 2 summarizes the ^1H T_1 and $T_{1\rho}$ values of PVPh/PEO1.5k and PVPh/PEO300k. From Table 2 we can see that a single ^1H T_1 value is observed for each blend, implying that the domain sizes of the two blends are all less than several tenth nanometers^[57]. Two ^1H $T_{1\rho}$ values including fast and slow components are observed for both the blends, clearly indicating that the existence of microphase separation on the scale of larger than 5 nm in these blends^[57].

Table 2. ^1H T_1 and $T_{1\rho}$ values of PVPh/PEO1.5k and PVPh/PEO300k at 298 K

Samples	^1H T_1 (s)	^1H $T_{1\rho}$ (ms)
PVPh/PEO1.5k	1.74	5.04
		0.50
PVPh/PEO300k	1.69	3.82
		0.37

Influence of PEO Molecular Weight on the Glass Transition Dynamics

Spatial and dynamic heterogeneities play an important role in glass transition behavior of blends. In order to understand the microscopic mechanism of PEO molecular weight dependence of glass transition behavior in PVPh/PEO blends, the new multi-frequency TMDSC technique (TOPEM) is utilized to measure a series of parameters related to the microscopic spatial and dynamic heterogeneities, such as the activity energy E_a , fragility m , nonexponential factor β_{KWW} and the size of cooperatively rearranging regions ξ_{cr} . The so-called fragility can be used to express the degree of curvature of the Arrhenius curve, or in other words the degree of variation of the activation energy with temperature. Nonexponential factor β_{KWW} comes from the Kohlrausch-Williams-Watts (KWW) equation and reflects the dynamic heterogeneity in glass-formers. Activation energy can be gained from frequency dependence of complex heat capacity. The multifrequency TMDSC technique measures the glass transition at different frequencies as a stepwise change in the heat capacity, the midpoint of which can serve as an estimate of T_g . The resulting value of T_g increases with the frequency, f . Due to the reciprocal relation between f and τ , Eq. (5) allows one to calculate the activation energy of the glass transition:

$$E = -R \frac{d \ln f}{d T_g^{-1}} \quad (5)$$

The advantage of the TOPEM technique is that the evaluation of the activation energy can be accomplished in a single experiment, eliminating run-to-run experimental errors unavoidable in using a series of single-frequency or single heating rate runs in regular TMDSC^[58].

Figure 7 shows an example of TOPEM experimental result of the PVPh/PEO3.4k. The real part of the complex heat capacity is determined at the frequencies ranging from 5 mHz to 20 mHz, and $C_{p,0}$ is the quasi-static heat capacity at zero frequency. It is found that the T_g increases with increasing frequency. The activation energy of glass transition can thus be determined from the frequency dependence of T_g as shown in Fig. 8. According to Eq. (5), the slope of $\ln f$ versus $1/T_g$ yields an average value of the glass transition activity energy. Figure 9 shows the calculated activation energy of the blends as a function of PEO molecular weight. It is interesting to note that activation energy increases with increasing PEO molecular weight, and again, a turning point (dotted line) can be obtained at the PEO molecular weight value of about 10×10^3 where the increase is rapid when the PEO molecular weight is less than this value and the increase is slow above this value. The variation trend of the activation energy is similar to that obtained for the PEO molecular weight dependence of T_g shown in Fig. 3.

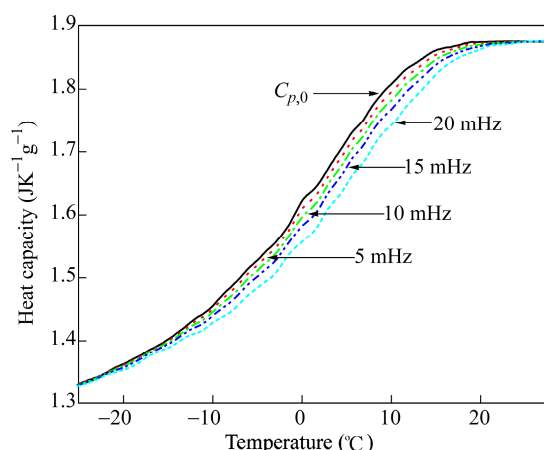


Fig. 7 Frequency dependence of the heat capacity of PVPh/PEO3.4k measured by TOPEM

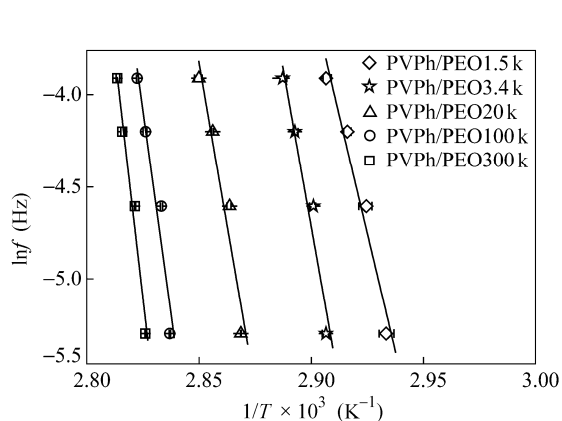


Fig. 8 Log(frequency) versus reverse of glass transition temperature for PVPh/PEO blends in TOPEM experiments

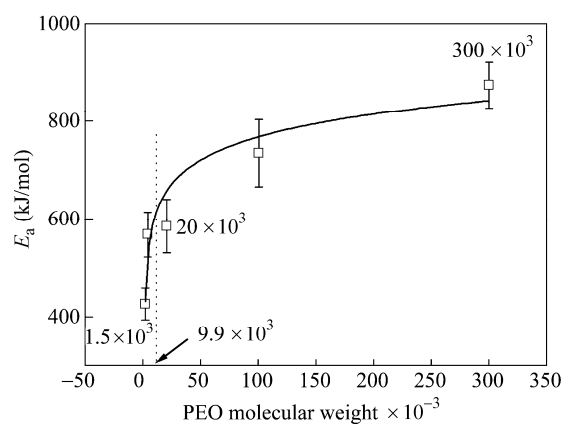


Fig. 9 PEO molecular weight dependence of glass transition activity energy of PVPh/PEO blends with 30 wt% PEO

The dotted line represents the turning point.

For PVPh/PEO blends with PEO weight fraction of 30%, the ΔT_g of PEO and PVPh is as high as about 240 K, indicating that the segment dynamics in each homopolymers is remarkably different. In previous reports about blends with high T_g component and large ΔT_g , e.g. PS/PVME, PMMA/PEO and PVAc/PEO, the segmental dynamics of the high T_g component is frozen during the glass transition process of the blend, while the segmental dynamics of the low T_g component still presents the Arrhenius relaxation^[16]. This implies that the glass transition in PVPh/PEO blends needs to overcome the energy barrier mainly from PVPh segments. Compared to PVPh/PEO blends, the E_a (ca. 1255 kJ mol⁻¹) and T_g (ca. 170°C) of pure PVPh have the highest value, indicating the energy barrier of PVPh segments is remarkably stronger than that in PVPh/PEO blends. From the foregoing discussion on FTIR results, we know that the average strength of intrachain hydrogen bonding between PVPh chains is weaker than that of the interchain hydrogen bonding between PEO and PVPh, therefore, the energy barrier for PVPh segment relaxation is not only from the intrachain hydrogen bonds, but also from the π - π interaction among phenol groups. The interchain hydrogen bonding interaction between PVPh and PEO disrupts the multimer hydrogen bonds and π - π interaction among phenol groups in PVPh, thus leads to the PVPh segments gaining high mobility and entropy in blends. This also implies that the more phenol groups participating in the interchain hydrogen bonds between PEO and PVPh, the lower the energy barrier needed to be overcome during the glass transition process. Therefore, a decrease of the activity energy in these blends with decreasing PEO molecular weight can be expected.

As we mentioned above, the temperature dependence of relaxation time can be described by the VTF function^[1] rather than the Arrhenius function near the glass transition. By replacing the relaxation time with frequency, the VTF function can be written as^[59]

$$f = A \exp\left(-\frac{B}{T - T_v}\right) \quad (6)$$

where A is the exponential prefactor, T_v is the Vogel temperature, it is corresponding to the temperature when the relaxation begins to divide. B is related to the fragility of the system. The fragility of a glass-former is defined as^[60]

$$m = \left. \frac{\partial(\lg x)}{\partial(T_g/T)} \right|_{T=T_g} = \frac{BT_g}{\ln 10 \times (T_g - T_v)^2} \quad (7)$$

here x is a dynamic variable such as viscosity or relaxation time. A “fragile” glass-former (high value of m) is one with a great deviation from the Arrhenius behavior^[60]. Figure 10 shows the frequency dependence of T_g for PVPh/PEO1.5k, where the dashed line represents the fitting curve by the Arrhenius function and the solid line represents the fitting curve by the VTF function. It is clear that the VTF function fits the data much better than the Arrhenius function. The fragilities of polymer blends are then calculated using Eqs. (6) and (7) and the results are listed in Table 3. We find that the fragility usually increases with increasing the PEO molecular weight.

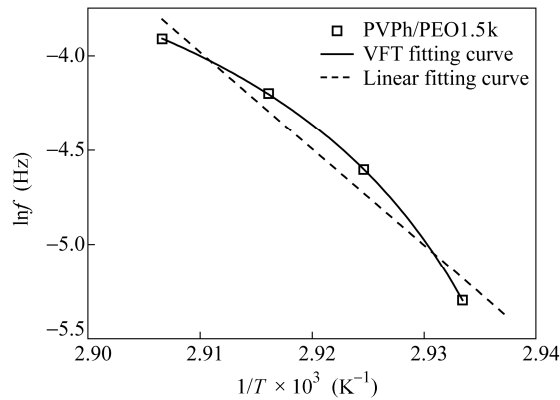


Fig. 10 $\lg(\text{frequency})$ versus reciprocal glass transition temperature for PVPh/PEO1.5k with 30 wt% PEO in TOPEM experiments

Adam and Gibbs^[3], as well as Stukalin *et al.*^[61], reported that the fragility was related to the configurational entropy (S_c). From the foregoing discussion, we know that as the degree of interchain coupling increases, the energy barrier decreases. Therefore, it is expected that the configurational entropy should increase, and the blend with the greatest fraction of interchain coupled segments should have the lowest fragility. As shown in Table 3, the calculated fragility usually increases with increasing of PEO molecular weight, and this result is consistent with that obtained from the glass transition activity energy analysis. In a previous study, Zhang *et al.*^[62] found that the fragility increases with the increase of inter associated segments in the rich-PVME/PVPh blends. Masser *et al.*^[63] studied the PolyHFS/PVME blends and observed the similar phenomena. It can be easily understood since the entire energy barrier in their system is only from hydrogen bonds. However, for our PVPh/PEO blends with 30 wt% PEO, the entire energy barrier is not only from the intermolecular hydrogen bonds, but also from the π - π stacking among phenol groups. Because the intermolecular hydrogen bonds disrupt the original multimer hydrogen bonds and the π - π stacking among phenol groups, they decrease the energy barrier. Therefore, the fragility decreases with increasing of the intermolecular hydrogen bonds in the studied blends.

Table 3. Fragility (m), $\beta_{\text{KWW}}(T_g)$ and size of CRRs (ξ_{crr}) for PVPh/PEO blends

Samples	$V_{\text{crr}} (\text{nm}^3)$	$\xi_{\text{crr}} (\text{nm})$	$M (\pm 1)$	$\beta_{\text{KWW}}(T_g) (\pm 0.09)$
PVPh/PEO1.5k	3.4	1.5	72	0.56
PVPh/PEO3.4k	4.1	1.6	67	0.57
PVPh/PEO20k	6.9	1.9	122	0.40
PVPh/PEO100k	9.3	2.1	134	0.36
PVPh/PEO300k	6.9	1.9	124	0.40
PVPh	15.6	2.5	176	0.23

The glass transition dynamics has a dynamic heterogeneous nature. The most direct evidence proving the existence of heterogeneous dynamics comes from the observation of nonexponential relaxation processes. Often these relaxation functions are fitted to the Kohlrausch-Williams-Watts (KWW) or stretched exponential equation^[1]:

$$\Phi(t) = \exp[-(t / \tau_{\text{KWW}})^{\beta_{\text{KWW}}}] \quad (8)$$

where $\Phi(t)$ is the relaxation function, τ_{KWW} is the relaxation time and β_{KWW} the nonexponential factor. An empirical equation for the fragility m and β_{KWW} was proposed by Böhmer^[64]:

$$m = 250(\pm 30) - 320\beta_{\text{KWW}} \quad (9)$$

This empirical equation is suitable for many glass-formers, such as covalent glass, ion melt, small molecular supercooled systems and most of the polymers. The calculated $\beta_{\text{KWW}}(T_g)$ values of PVPh/PEO blends from Eq. (9) are listed in Table 3. It was previously reported that $\beta_{\text{KWW}}(T_g)$ depended on the length of segment, polydispersity and segment motions. Generally speaking, the more rigid the polymer segment is or the stronger the interaction between segments is, the smaller $\beta_{\text{KWW}}(T_g)$ is^[65]. As shown in Table 3, $\beta_{\text{KWW}}(T_g)$ decreases with the increase of the PEO molecular weight. As the β_{KWW} parameter is known to correlate with heterogeneous dynamics, this leads to the conclusion that blends with low PEO molecular weight are more homogeneous than those with high PEO molecular weight.

Another important parameter related to glass transition is the size of cooperatively rearranging regions (CRRs) suggested by Adam and Gibbs^[3]. It corresponds to the characteristic length of glass transition, and this parameter is usually regarded as an indication for spatial and dynamic heterogeneities^[40]. The relationship between the size of CRRs and the configurational entropy can be described as $\xi_{\text{crr}} = \alpha \Delta S_c^{-1/3}$ ^[66], where α is the proportional constant. From the foregoing discussion, it is concluded that with increasing the PEO molecular weight, the configurational entropy decreases in PVPh/PEO blends. Thus, an increase of the size of CRRs can be expected. Donth *et al.* assumed that the volume of CRRs can be written as $V_{\text{crr}} = \xi_{\text{crr}}^3$ and V_{crr} can be calculated using the following equation^[40]

$$V_{\text{crr}} = \frac{k_B T_g^2 \Delta(C_v^{-1})}{\rho(\delta T)^2} \quad (10)$$

where k_B is Boltzmann constant, T_g is the glass transition temperature, ρ is density, C_v is the isovolumetric heat capacity, and δT represents average temperature fluctuation. More details see Ref. [40]. This method was recently modified by Schröter^[36]. However, for polymers with low β_{KWW} value, the results obtained from the origin and modified methods are very similar. Thus, we still use the Donth's method to calculate the size of CRRs in the following discussion. The calculated sizes of CRRs of PVPh/PEO blends are also listed in Table 3. It is noteworthy that the size of CRRs obviously increases with increasing the PEO molecular weight, and it is obviously less than the scale of microphase separation in these blends. According to the foregoing discussion, with the increase of PEO molecular weight, the number of the interchain hydrogen bonds between PEO and PVPh decreases, while the intrachain interactions among phenol side groups increase. Because the change of interchain hydrogen bonding interaction can only occurs in the interphase, and the size of CRRs defines a special

volume where the chain dynamics does not disturb those in neighbor area, therefore, we can reasonably infer that the cooperatively rearranging regions, reflecting the spatial and dynamic heterogeneities, should be closely related to the interphase region between the two components. On the other hand, it is interesting to note that the size of CRRs in pure PVPh is the biggest one compared with that in blends as shown in Table 3, indicating a larger spatial heterogeneity exists in this homopolymer. In previous work, it was found that spatial and dynamic heterogeneities resulted from local phase separation generally exist in homopolymers^[67, 68], FTIR revealed that a portion of free phenols in pure PVPh undergoes fast motion, and other groups are rigid due to strong intrachain interaction including hydrogen bonding and π - π interaction. Therefore, much large spatial and dynamic heterogeneities can be expected from the calculated size of CRRs of PVPh. A similar result was also observed in the PS/Clay system^[42]. In this nanocomposite, exfoliated clay confines the PS dynamics and leads to the increase of the size of CRRs and T_g . Because clay molecules are rigid compared with PS and PEO chains, so that the effect of the clay on T_g in the clay/PS system is opposite with the effect of PEO on T_g in PVPh/PEO blends.

On the basis of the foregoing discussion, a physical picture of the relationship between the PEO molecular weight dependent glass transition behavior and the corresponding evolution of the microscopic spatial and dynamic heterogeneities, as well as the mutual interactions in PVPh/PEO blends could be achieved as shown in Figure 11. Through improving the miscibility between PEO and PVPh by decreasing PEO molecular weight, interchain hydrogen bonds between PVPh and PEO reflecting the segmental cooperative motion increase in number and disrupt the multimer hydrogen bonds and π - π interaction among phenol groups of PVPh segments. This leads to a portion of PVPh segments gaining high mobility and further leads to the spatial heterogeneous dynamics in blends. This spatial and dynamic heterogeneities change the energy barrier in CRRs needed to be overcome during glass transition process and thus determines the glass transition temperature.

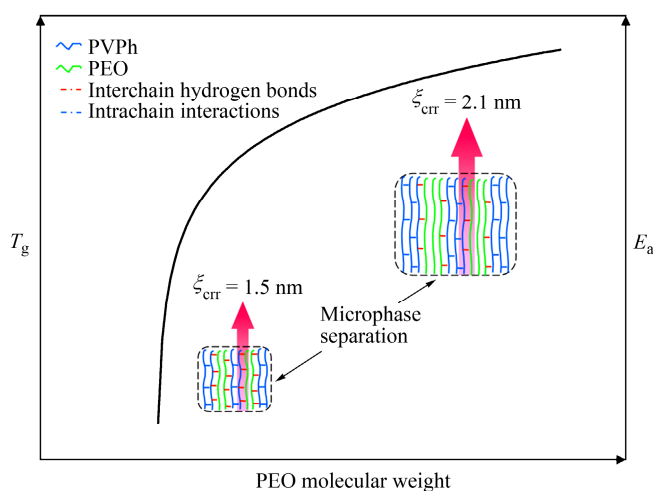


Fig. 11 A schematic diagram of the relationship between the PEO molecular weight dependent glass transition behavior and the corresponding evolution of microscopic spatial and dynamic heterogeneity, as well as their mutual interactions in PVPh/PEO blends

In subsequent article, a variety of multiple-scale solid-state NMR techniques will be used to systematically investigate the spatial and dynamic heterogeneities in PVPh/PEO blends, including the local dynamics of different components, the interchain cooperative motion, microdomain structure and interphase thickness. On the basis of the DSC and NMR results on different length and time scale, a comprehensive understanding and a clear physical picture of the glass transition behavior in these complex hydrogen bonded polymer blends are expected to be established.

CONCLUSIONS

In this work, we have systematically studied the relationship between the PEO molecular weight dependent glass transition behavior and the microscopic spatial and dynamic heterogeneities in PVPh/PEO blends with different PEO molecular weight by using DSC, FTIR and NMR techniques. DSC experiments show that the glass transition temperature (T_g) strongly depends on the PEO molecular weight, and a turning point of molecular weight at around 10×10^3 is determined. With increasing PEO molecular weight, the interchain hydrogen bonding interactions, determined using the FTIR measurements and deduced from the related parameter q obtained from Kwei equation, decrease, indicating a decrease of the componential miscibility and an increase of microphase separation strength. NMR relaxation results reveal the existence of obvious phase separation large than 5 nm. We also conclude that PEO end groups have no effect on such dependence. TOPEM experiments further show that a series of parameters related to the spatial and dynamic heterogeneities, such as the activity energy E_a , fragility m , nonexponential factor β_{KWW} and the size of cooperatively rearranging regions ξ_{cr} are monotonically dependent on PEO molecular weight during the glass transition process. Our results demonstrate that adjusting the componential molecular weight is an effective approach to precisely manipulate the spatial and dynamic heterogeneities, and we also suggest that the cooperatively rearranging regions should be closely related to the interphase region between the two components. The above obtained origin and evolution of spatial and dynamic heterogeneities provide a new insight into the glass transition behavior of polymer blends.

SUPPORTING INFORMATION

Calculations of theoretical critical miscible temperature of PVPh/PEO blends. ^1H $T_{1\rho}$ and T_1 stack spectra of PVPh/PEO1.5k and PVPh/PEO300k.

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