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Anomalous Component Dynamics of a Binary Mixture of Associating Glass-Forming Liquids

Li-Min Wang,^{*,†} Yongjun Tian,[†] Riping Liu,[†] and K. L. Ngai^{*,†,‡}

State Key Lab of Metastable Materials Science and Technology and College of Materials Science and Engineering, Yanshan University, Qinhuangdao, Hebei, 066004 China, and CNR-IPCF Associate, Dipartimento di Fisica, Università di Pisa, Largo Bruno Pontecorvo 3, I-56127, Pisa, Italy

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The binary mixtures of propylene glycol (PG) with 2-ethylhexylamine (EHA) show changes of the dynamics of the higher- T_g component PG on increasing the concentration of the lower T_g component EHA very different or even opposite in trend from those found in other associating and nonassociating binary mixtures. For example, the fragility index m increases and the coupling parameter n of the PG component increases on adding EHA, while T_g of the PG component does not change up to 0.5 molar fraction of EHA. From the features present in the broadband dielectric spectra of the PG component at different compositions, the anomalies are identified to originate from the enhancement of intermolecular coupling in the primary relaxation of the higher- T_g PG component by the presence of the EHA component. The enhancement can be traced to the fact that neat EHA has larger intermolecular coupling than neat PG, despite the former having a lower T_g than the latter. The enhancement of intermolecular coupling of the PG component increases on increasing the concentration of EHA in the mixture, as evidenced by the appearance of the JG β -relaxation of the PG component well separated from the α -relaxation when the molar fraction of EHA has been increased to 0.75. In contrast, the JG β -relaxation of neat PG is too close to the α -relaxation and cannot be resolved. The anomalous dynamics of PG in the mixtures is challenging to all theories and models of glass transition to explain. The insight gained on the physical origin of the anomalous dynamics leads to a rationalization in the framework of the coupling model.

I. Introduction

The dynamics of a glass-former can be changed by mixing it with another glass-former having different molecular mobility or glass transition temperature T_g . As shown by various mixtures in previous studies,^{1–5} the structural α -relaxation of the faster (lower T_g) component is slowed down thereby raising its T_g , and fragility or steepness index m . The latter quantifies the change of structural relaxation time τ_α with T_g -scaled temperature at $T = T_g$, and is calculated by the expression, $[d \log(\tau_\alpha)]/d(T_g/T)|_{T=T_g}$.^{6,7} Increase of intermolecular coupling and cooperativity of the α -relaxation of the faster component can be deduced from the increase in the width of the frequency dispersion after having taken account of the contribution from concentration fluctuations. This increase is consistent with the increase of separation in time/frequency between the α -relaxation and the β -relaxation^{1–5} of the Johari–Goldstein (JG) kind,^{8,9} in accord with the coupling model relation.^{10,11} Examples of these changes of the faster component include 5 or 10 wt % of picoline ($T_g = 132.7$ K) in tristyrene ($T_g = 233$ K),^{1–4} quinaldine ($T_g = 181$ K) and *tert*-butylpyridine ($T_g = 164$ K) in tristyrene,^{2–4} and benzyl acetate, (BzAc) ($T_g = 165.1$ K) in ortho-terphenyl ($T_g = 244$ K).⁵ On the other hand, the α -relaxation of the slower (higher T_g) component is accelerated, resulting in decrease of its α -relaxation time, τ_α , and T_g . The decrease of T_g is accompanied by decrease of the fragility index m and decrease in the separation between the α -relaxation and the JG β -relaxation of the slower component. The decreases of both quantities are indicators of the decrease in intermolecular

coupling and cooperativity of the slower component due to the presence of the faster component. Examples of this normal behavior include tristyrene ($T_g = 232$ K) mixed with picoline of lower T_g ,¹ bromoethylbenzene with $T_g = 135.6$ K in ethylbenzene with $T_g = 115$ K,¹² concentrated solutions of poly(methyl methacrylate) (PMMA) in bis(2-ethylhexyl) phthalate (DOP) with concentration of PMMA equal to 0.9 and 0.8 g/mL,¹³ PMMA in the polymer blends $x\%$ PEO–(100– $x\%$)PMMA with $x = 0$ to $x = 30$,¹⁴ and sorbitol in mixtures with glycerol, $x\%$ sorbitol/(100– $x\%$) glycerol for $x = 100, 82, 67$, and 54 .^{15,16} One may notice that the examples of binary miscible mixtures come from diverse types of glass-formers, and yet the changes of component dynamics upon mixing are similar. The changes in T_g and m of both components can be readily rationalized by conventional theories and models, and the accompanying change in the separation between the α -relaxation and the JG β -relaxation has been explained by the coupling model.^{10,11}

Notwithstanding, a recent study of the component dynamics of a binary miscible mixture of 1,2-propanediol or propylene glycol (PG) with 2-ethylhexylamine (EHA) showed very different changes of the dynamics of the higher- T_g component PG in the presence of the lower- T_g component EHA.¹⁷ The T_g of PG hardly changed at all with decreasing mole fraction x of PG down to 0.5 in the mixture $x\text{PG}-(1-x)\text{EHA}$, deviating strongly from monotonic decrease with decrease in x . Significant decrease of T_g of the PG component can only be observed when $x = 0.25$. The fragility index m of the PG component increases with decreasing x , opposite to the decrease of m of the higher T_g component normally observed in other mixtures. It is well-known that the JG β -relaxation of neat PG is too close to the

[†] Yanshan University.

[‡] Università di Pisa.

α -relaxation and is unresolved in dielectric spectroscopy except in the glassy state, and only after being subjected to physical aging for a long period of time.¹⁸ The same situation is found in the mixture $x\text{PG}-(1-x)\text{EHA}$ for $x \geq 0.5$ from the isothermal broadband dielectric loss data to be presented in this paper. However for $x = 0.25$, the JG β -relaxation of component PG becomes resolved and it is well separated from the α -relaxation. Again this change is opposite to the normally observed behavior of the higher T_g component of other mixtures where its JG β -relaxation instead moves closer to the α -relaxation. In this paper, new experimental data not published before will be presented to make the aforementioned deviations from the normal behavior quantitatively clear. These deviations observed in the mixtures of PG with EHA from the norm present a new challenge for explanation. We suggest the key to explanation of the anomalies is the enhancement of intermolecular coupling of higher- T_g PG component in the presence of the lower- T_g EHA component, which is unusual, but is justified by the more intermolecularly coupled structural relaxation dynamics of neat EHA than neat PG. This physical insight is the basis of an explanation of the observed anomalies given in this paper.

II. Experimental Section

The dynamics of the binary mixtures of 1,2-propanediol (PG 99.5%, Aldrich) with 2-ethylhexylamine (EHA 98%, Aldrich) was studied by dielectric relaxation measurements over a broad frequency range 0.01 Hz to 10 MHz. The two liquids are miscible at room temperature by visual inspection. Homogeneous mixtures are inferred from dielectric measurements, where single primary relaxation is observed. The two liquids are excellent glass-formers, and consequently crystallization can be avoided at low measurement temperatures. Frequency dependent impedance measurements were performed using a Solartron 1260 gain-phase analyzer equipped with a Mestec DM-1360 transimpedance amplifier and liquid nitrogen cooling system.¹⁹ The dielectric relaxation of the samples was isothermally measured at each temperature by holding the liquid between two brass electrodes, which are separated by Teflon strips of thickness 25 μm . The measurements start from a temperature of ~ 5 K below T_g for each measurement, and temperature is controlled by a Novocontrol Quatro controller with temperature accuracy within 0.1 K.

III. Results and Discussion

Isothermal dielectric loss spectra of the mixtures, $x\text{PG}-(1-x)\text{EHA}$, with $x = 1.0, 0.71, 0.49, 0.25$, and 0.0 were obtained over a range of temperature above and below T_g . For each mixture, measurements were made starting at a temperature of ~ 5 K below T_g and continuing to temperatures well above it. Comparing the results of neat PG with neat EHA, it is clear that the dielectric strength of PG is about an order of magnitude larger than that of EHA. Thus the observed loss spectra reflect the dynamics of the PG component for all samples except neat EHA with $x = 0$. There is no need to present the loss spectra of neat PG ($x = 1$) because they are exactly the same as those published before by others¹⁸ in the same temperature and frequency ranges. The loss spectra $\varepsilon''(\nu)$ for $x = 0.49$ shown in Figure 1 and for $x = 0.71$ (not shown) are similar to neat those of PG in practically all respects. Like neat PG, $\varepsilon''(\nu)$ exhibits only one loss peak contributed by the α -relaxation, and no resolved secondary relaxation of any kind. The relaxation time τ_α of $x = 0.71$ and $x = 0.49$ is about a factor of 2 and 10 respectively faster than that of neat PG for all temperatures investigated, indicating little difference in temperature depen-

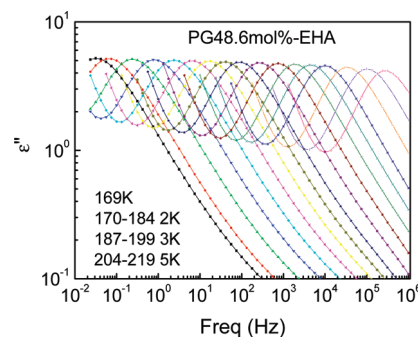


Figure 1. Dielectric loss spectra of a mixture of 48.6 mol % propylene glycol (PG)–2-ethyl-1-hexylamine (EHA). The measurements are from 169 to 219 K. The spectra resemble neat PG in all respects including no resolved Johari–Goldstein β -relaxation at all measurement temperatures.

dence. This remarkable insensitivity of τ_α of PG to mixture composition for x in the range $1 \geq x \geq 0.49$ has been shown before in ref 17, and from which follows the observed small decrease in T_g , small increase in m , and small decrease in the fractional exponent β_{KWW} of the Kohlrausch–Williams–Watts function, the one-sided Fourier transform of which is used to fit the α -loss peak. This behavior of PG in the mixtures with $1 \geq x \geq 0.49$ is different from that of the higher- T_g component in other mixtures where larger decrease of its T_g and decrease (instead of increase) of m are found when its molar fraction in the mixtures is greater than or equal to $x = 0.49$. This suggests that some physical factor present in $x\text{PG}-(1-x)\text{EHA}$, but not in other mixtures, is the cause of the observed difference. One likely factor is the large negative heat found when mixing the alcohol PG with the amine EHA.²⁰ From this fact, intermolecular interaction between PG and EHA coming from their associations is expected to be strong compared with that in other mixtures. The introduction of more mobile EHA molecules into the mixture in principle should make the host PG molecules more mobile. This has the effect of lowering the degree of cooperativity of the α -relaxation originating from the PG component, and hence decreasing its T_g and m value, and narrowing the width of its dispersion. For evidence of the last effect, see ref 12. These effects normally seen in the higher- T_g component of mixtures without strong association, as those examples mentioned in the Introduction, should also be present in the case of PG. Apparently the enhanced intermolecular interaction of the PG molecules with the EHA molecules, caused by the strong association between PG and EHA molecules, has the opposing effect of slowing down the PG relaxation. This factor unique to the strong associated mixture accounts for the small decrease of T_g of the PG component for mixtures in the range $1 \geq x \geq 0.49$. The observed increase of m and width of the α -dispersion of the PG component with decreasing x instead of the normal decrease can be rationalized by the presence of the opposing effect. The increase of the width of the α -dispersion at $T = T_g$ where $\tau_\alpha(T_g) = 100$ s was shown before¹⁷ by the decrease of the stretched exponent $\beta_{\text{KWW}}(T_g)$ of the fit by the Kohlrausch–Williams–Watts correlation function,

$$\phi(t) = \exp(-(t/\tau_\alpha)^{\beta_{\text{KWW}}}) \quad (1)$$

where $\phi(t)$ is the relaxation function, τ the relaxation time, and β_{KWW} the stretching exponent.

The isothermal loss spectra of the mixture with $x = 0.25$ are shown in Figure 2. This mixture is related to the mixtures with

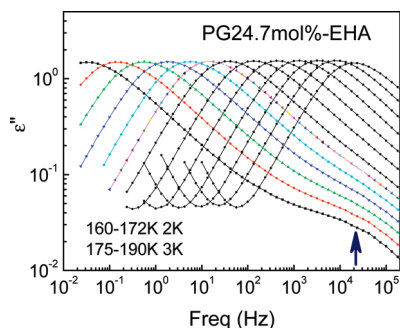


Figure 2. Dielectric loss spectra of a mixture of 24.7 mol % propylene glycol (PG)–2-ethyl-1-hexylamine (EHA). The measurements are from 160 to 190 K. The arrow indicates the location of the primitive relaxation frequency at 160 K calculated by the CM relation, which is in order of magnitude agreement with the Johari–Goldstein β -relaxation frequency of the PG component.

$1 > x \geq 0.49$ discussed in the above by a higher concentration of EHA. The preponderance of EHA in this mixture further enhances the intermolecular interaction of the PG component. This makes the opposing effects from enhanced intermolecular coupling more important, which can be clearly seen from the significantly broader α -loss peak in Figure 2 than in Figure 1 when compared at the same relaxation time τ_α . Fit of the frequency dispersion of the α -loss peak at $T = 160$ K yields the value of $\beta_{\text{KWW}}(T_g) = 0.52$ for the mixture with $x = 0.25$, as compared with the larger value of $\beta_{\text{KWW}}(T_g) = 0.7$ of neat PG.¹⁵ A supplementary evidence of enhanced intermolecular coupling in the mixture with $x = 0.25$ is the appearance of a resolved secondary relaxation of the PG component. It is likely the JG β -relaxation of the PG component since neat PG has no intramolecular (non-JG) secondary relaxation. Well established for many glass-formers²¹ is the approximate (order of magnitude) agreement between the relaxation time τ_{JG} of JG β -relaxation and the primitive relaxation time τ_0 calculated by the coupling model relation,^{8,9,21}

$$\tau_0 = t_c^n \tau_\alpha^{1-n} \quad (2)$$

with $t_c = 2$ ps for molecular glass-formers, and n is the coupling parameter related to β_{KWW} by $n \equiv (1 - \beta_{\text{KWW}})$. At 160 K, τ_0 of the PG component in the mixture with $x = 0.25$ has been calculated by the equation, $\tau_0(160 \text{ K}) = t_c^n (\tau_\alpha(160 \text{ K}))^{1-n}$, with $t_c = 2$ ps, and $n(160 \text{ K}) \equiv 1 - \beta_{\text{KWW}}(160 \text{ K}) = 0.48$. The location of the corresponding primitive frequency, $\nu_0 \equiv 1/\tau_0$, indicated by the vertical arrow in Figure 2, is in approximate agreement with the most probable relaxation time of the resolved secondary relaxation. Concentration fluctuations may contribute to some small extent to the broadening of the α -loss peak, although it is expected to be small because concentration fluctuations are suppressed in the presence of intermolecular hydrogen bonding shown before in the dynamics of hydrogen bonded polymer blends of poly(4-vinylphenol)-poly(ethyl methacrylate) [PVPh/PEMA],²² blends of PVPh with two other polymeric proton acceptors, poly(vinyl acetate) [PVAc] and an ethylenevinyl acetate random copolymer [EVA70, with 70 wt % vinyl acetate content],²³ and blends of PVPh with another proton acceptor, poly(vinyl ethyl ether) [PVEE].²⁴ Notwithstanding, if residual concentration fluctuations are present, the actual value of n could be slightly smaller than 0.48, the calculated ν_0 slightly lower than indicated in Figure 2, and the agreement between ν_0 and ν_{JG} could be even better. From this

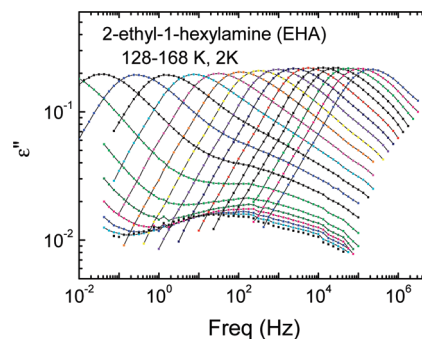


Figure 3. Dielectric loss spectra of neat 2-ethyl-1-hexylamine, showing the α - and the JG β -relaxations. The low frequency flank of the α -loss peak shows a ν^κ dependence with $\kappa \sim 0.65\text{--}0.7$, different from the $\nu^{1.0}$ dependence.

result and the established approximate agreement between the relaxation time τ_{JG} of JG β -relaxation and the calculated τ_0 , we conclude that the resolved secondary relaxation is the JG β -relaxation of PG in the mixture with $x = 0.25$. Moreover, from this we infer that the intermolecular coupling of PG is enhanced by EHA. This deduction is counterintuitive if consideration is based solely on T_g or τ_α of neat PG compared with that of neat EHA because, from these quantities alone, it is difficult to understand why EHA with lower T_g or shorter τ_α can enhance intermolecular coupling of PG when the two are mixed together. Understanding is regained by recognizing that intermolecular coupling in neat EHA is actually larger than that of neat PG. The isothermal spectra of neat EHA shown in Figure 3 supports this assertion by showing the presence of a broader α -loss peak than that of neat PG, and a resolved JG β -relaxation not found in neat PG. The dielectric relaxation of EHA has been reported before.²⁵ By contrast, for all the mixtures exhibiting normal behavior of the higher T_g component cited above, the lower T_g component has lower intermolecular coupling than the higher T_g component. It is worthwhile to point out that the limiting low frequency flank of the α -loss peak has the ν^κ -dependence with $\kappa \sim 0.65\text{--}0.7$ instead of the $\nu^{1.0}$ dependence as frequently observed from dielectric measurements in small molecule liquids.^{26–28} The dielectric behavior resembles the case of a long-chain alkane of squalane.²⁹ The unusual sublinear frequency dependence might suggest the presence of loss from an unknown process slower than the α -relaxation, and makes good fit by the Fourier transform of the KWW function of the α -relaxation difficult if not impossible. Despite this complication, the broader α -loss peak and the resolved JG β -relaxation located at much higher frequencies are sufficient evidence to support that intermolecular coupling in neat EHA is larger than in neat PG.

Enhanced intermolecular coupling of the PG component leads to larger coupling parameter n in eq 2 rewritten here as

$$\tau_\alpha = [t_c^{-n} \tau_0]^{1/(1-n)} = \tau_0 (\tau_0/t_c)^{n/(1-n)} \quad (3)$$

Considering this form and the fact that $(\tau_0/t_c) \gg 1$, it can be easily verified that increase of n of the PG component due to the presence of EHA will lead to increase of τ_α . This increase of τ_α by the enhanced intermolecular coupling of PG counters the decrease of τ_0 of PG by the “plasticization effect” due to the presence of the more mobile component EHA with lower T_g . The increase of n in the mixtures with $1 \geq x \geq 0.49$ is not large, which can be deduced from the observed very slight

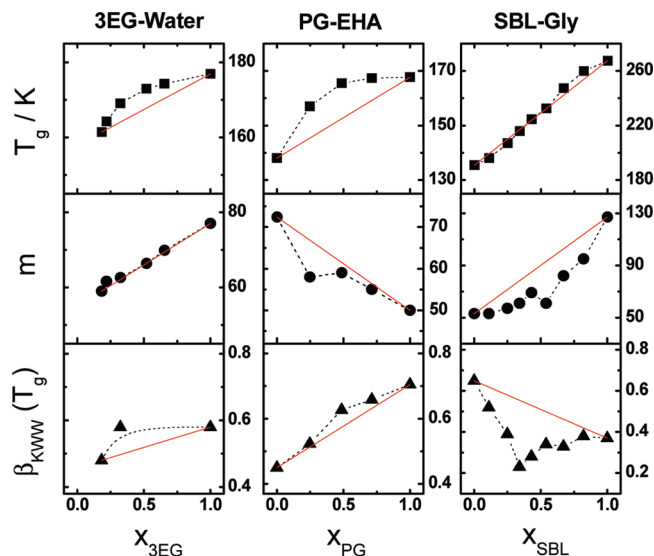


Figure 4. Composition dependence of glass transition temperature (T_g), liquid fragility (m) and nonexponential parameter ($\beta_{\text{KWW}}(T_g)$) for the higher- T_g component of three associating binary liquid mixtures, (left) triethylene glycol (3EG) in mixtures with water, (middle) propylene glycol (PG) in mixtures with 2-ethyl-1-hexylamine (EHA), and (right) sorbitol (SBL) in mixtures with glycerol (GLY).

decrease of β_{KWW} , and no resolved JG β -relaxation of the PG component (see Figure 1). At $x = 0.25$ the decrease of β_{KWW} and hence the increase in n is noticeably more significant, and this accounts for the appearance of the JG β -relaxation of the PG component.

The mixtures of sorbitol (S) with glycerol (G), $x\text{S}-(1-x)\text{G}$,^{15,16} offer a case to contrast with the properties of $x\text{PG}-(1-x)\text{EHA}$. Both systems are hydrogen bonded mixtures. Sorbitol has higher T_g than glycerol, and thus sorbitol corresponds to PG, and EHA to glycerol as far as T_g and τ_α are concerned. If prediction of component dynamics of mixtures from the Fox–Flory equation, Gordon–Taylor equation or analogue is valid, then the behavior of the high- T_g component PG will be similar to that of sorbitol. This prediction fails, as can be seen in Figure 4. The changes of T_g , m , and $\beta_{\text{KWW}}(T_g)$ of the high- T_g PG component on increasing concentration of the low- T_g component EHA found in $x\text{PG}-(1-x)\text{EHA}$ are entirely different from those of the high- T_g component sorbitol on increasing the concentration of the low- T_g component glycerol. Coming to the rescue for understanding the contrasting behavior of the two mixtures is the difference in relation between the degrees of intermolecular coupling of the two components in the two mixtures. Intermolecular coupling of the lower T_g component is smaller than the higher T_g component in the case of the $x\text{S}-(1-x)\text{G}$, opposite to the relation in the case of $x\text{PG}-(1-x)\text{EHA}$. Consequently intermolecular coupling of sorbitol will be reduced instead of enhanced by mixing it with glycerol. We have proposed that the increase of intermolecular coupling of the high- T_g PG component on increasing the concentration of the low- T_g component EHA is responsible for the anomalous behavior of T_g , m , and $\beta_{\text{KWW}}(T_g)$ of the high- T_g PG component found in $x\text{PG}-(1-x)\text{EHA}$. The corollary of this for $x\text{S}-(1-x)\text{G}$ is that the behavior of T_g , m , and β_{KWW} of the high- T_g sorbitol component is entirely different from that for the high- T_g PG component in $x\text{PG}-(1-x)\text{EHA}$. The differences in the dynamics of the components PG and sorbitol in the two mixtures are made clear by their contrasting changes on varying x , shown in the middle and right panels of Figure 4 respectively. The contrasting

behavior is consistent with the opposite directions of change in the intermolecular coupling of the higher- T_g component on varying x in the two mixtures.

Mixtures of hydrophilic substances with water are also associated by hydrogen bonding and offer another case to compare with the anomalous dynamics shown by the higher- T_g component PG in the $x\text{PG}-(1-x)\text{EHA}$ mixtures. Here we choose the aqueous mixture $x\text{3EG}-(1-x)\text{H}_2\text{O}$, where 3EG stands for triethylene glycol, and x for its molar fraction like in all the other mixtures discussed in this paper. The data of T_g , m , and β_{KWW} for the mixtures $x\text{3EG}-(1-x)\text{H}_2\text{O}$ were obtained from broadband dielectric relaxation measurements supplied by N. Shinyashiki and co-workers, most of which have not been published before. The high- T_g component in the mixtures $x\text{3EG}-(1-x)\text{H}_2\text{O}$ is 3EG, and its dynamic parameters T_g , m , and β_{KWW} are presented in the left panel of Figure 4. Although the dynamics of supercooled water is controversial, all estimates of its T_g are less than that of neat 3EG. The water component in various aqueous mixtures invariably shows up like a secondary relaxation, indicating that intermolecular coupling of water is weak compared with 3EG.^{30,31} Thus water, the lower- T_g component in the mixtures $x\text{3EG}-(1-x)\text{H}_2\text{O}$, cannot enhance intermolecular coupling of 3EG, unlike the lower- T_g component EHA in the mixtures of $x\text{PG}-(1-x)\text{EHA}$. From this, changes of T_g , m , and $\beta_{\text{KWW}}(T_g)$ of the 3EG component with x are expected to be different from those of PG. The expectation is fulfilled as can be verified by comparing the data in the left panel for 3EG with the middle panel for PG.

It is instructive to contrast the component dynamics of our $x\text{PG}-(1-x)\text{EHA}$ mixtures with the component dynamics of several hydrogen bonded polymer blends where the higher- T_g component is always poly(4-vinylphenol) [PVPh].^{22–24} First, the much larger dielectric strength of PG than EHA enables the dynamics of PG, the higher- T_g component, to be isolated and monitored from $x = 1$ down to $x = 0.25$. On the other hand, the dielectric strengths of the two components are comparable in all the polymer blends of PVPh with PEMA, PVAc, EVA70, or PVEE. For all these polymer blends, we have converted wt % to molar fraction of PVPh for objective and quantitative comparison with our $x\text{PG}-(1-x)\text{EHA}$ mixtures.

The left panel of Figure 5 shows the data of T_g , m , and $\beta_{\text{KWW}}(T_g)$ for the $x\text{PVPh}-(1-x)\text{PVEE}$ blends from ref 24, where x is the mole fraction of PVPh. The data of $x\text{PG}-(1-x)\text{EHA}$ shown before in Figure 4 is duplicated and given in the middle panel of Figure 5 for ease of comparison with those of the $x\text{PVPh}-(1-x)\text{PVEE}$ blends. For these $x\text{PVPh}-(1-x)\text{PVEE}$ blends, the molar fraction of PVPh has values of x equal to 1, 0.397, 0.305, 0.220, 0.141, 0.068, and 0 corresponding to wt % of 100, 50, 40, 30, 20, 10, and 0 respectively. In the range of smaller values of x , the parameters displayed reflect the change in dynamics of the lower- T_g component PVEE. No information can be deduced on the change of dynamics of PVPh, the higher- T_g component, continuously from neat PVPh to mole fraction down to $x = 0.4$. The absence of data of the dynamics of the PVPh component in these polymer blends does not permit a comparison with the anomalous dynamics observed in PG, the higher- T_g component in $x\text{PG}-(1-x)\text{EHA}$, which is the focus of the present paper. Moreover, it can be seen that the changes with x of m and $\beta_{\text{KWW}}(T_g)$ of the lower- T_g component PVEE shown in the left panel of Figure 5 are opposite to those exhibited by the lower- T_g component EHA in our mixtures, $x\text{PG}-(1-x)\text{EHA}$. There is decrease (increase) of $\beta_{\text{KWW}}(T_g)$ (m) of PVEE on blending

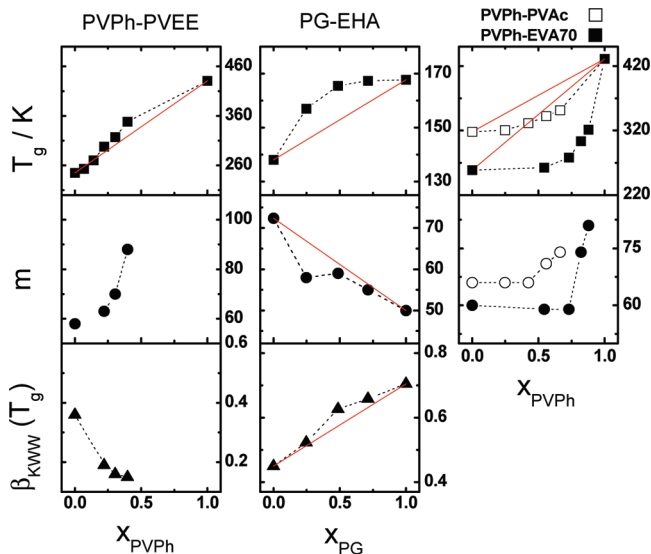


Figure 5. Composition dependence of glass transition temperature (T_g), liquid fragility (m) and nonexponential parameter ($\beta_{\text{KWW}}(T_g)$) for the polymer blends and the $x\text{PG}-(1-x)\text{EHA}$ mixtures. Left panel: The polymer blends $x\text{PVPh}-(1-x)\text{PVEE}$. Right panel: $x\text{PVPh}-(1-x)\text{PVAc}$ (open symbols) and $x\text{PVPh}-(1-x)\text{EVA70}$ (closed symbols), where x is the molar fraction of PVPh. T_g values of $x\text{PVPh}-(1-x)\text{PVEE}$ are from calorimetric measurements, and T_g or T_{ref} of $x\text{PVPh}-(1-x)\text{PVAc}$ and $x\text{PVPh}-(1-x)\text{EVA70}$ are defined at the temperature where the relaxation time is 1 s. m is determined by using the reference temperature T_{ref} to scale temperature. Middle panel: mixtures of propylene glycol (PG) with 2-ethyl-1-hexylamine (EHA). Data of the polymer blends are exactly those reported by Zhang et al. in refs 22–24 except wt % of PVPh in all blends has been converted to molar fraction x in here.

with PVPh instead of the increase (decrease) of $\beta_{\text{KWW}}(T_g)$ (m) for EHA on mixing with PG.

The right panel of Figure 5 shows the data of T_g and m of the $x\text{PVPh}-(1-x)\text{PVAc}$ and $x\text{PVPh}-(1-x)\text{EVA70}$ blends from ref 23, but not $\beta_{\text{KWW}}(T_g)$ because it is not given in the reference. The blends, $x\text{PVPh}-(1-x)\text{EVA70}$, have values of x equal to 1, 0.878, 0.822, 0.729, 0.544, and 0 corresponding to wt % of 100, 40, 30, 20, 10, and 0 respectively. The parameters T_g and m of blends with high x values are associated with the PVPh, higher- T_g component. The precipitous drop of T_g of the PVPh component on decrease of x from 1 to 0.544 is in stark contrast to the negligible decrease of T_g of PG, the higher- T_g component of our mixtures in the same range of x . The fragility index m of PVPh decreases rapidly with decreasing x down to $x = 0.729$, while m of PG increases in the same range. The changes of T_g and m of the PVPh component with decreasing x in the blends, $x\text{PVPh}-(1-x)\text{PVAc}$, are similar to those of $x\text{PVPh}-(1-x)\text{EVA70}$, although not as drastic. Therefore these two polymer blends show trends of T_g and m of the higher- T_g component that are very different from or opposite to PG in our mixtures. All the trends in change of T_g , m , and $\beta_{\text{KWW}}(T_g)$ of these hydrogen bonded polymer blends can be considered close to normal, contrasting the distinctly anomalous ones of the mixtures of PG with EHA.

From the comparison with other hydrogen bonded binary mixtures of molecular glass-formers and hydrogen bonded polymer blends given in the above, it is clear that the component dynamics of $x\text{PG}-(1-x)\text{EHA}$ are different and uniquely anomalous, particularly that of the higher- T_g component, PG.

IV. Conclusion

The main thrust of this paper is to point out the drastically different dynamics exhibited by the higher- T_g component PG in the mixtures of $x\text{PG}-(1-x)\text{EHA}$ than those commonly found in the higher- T_g component of most, if not all, binary mixtures of glass-formers studied before with or without association by hydrogen bonding. This anomalous behavior of PG in $x\text{PG}-(1-x)\text{EHA}$ is worth noticing by the glass transition research community because it poses a challenge for understanding and explanation. We propose and make an attempt to justify that enhancement of intermolecular coupling of PG by the presence of the lower- T_g component EHA is the key to understanding the physical origin of the anomaly. With the assist of the coupling model, the anomalous properties of the PG component have been rationalized. Notwithstanding, we welcome others to offer their own explanations of this worthwhile problem that surfaced from the experimental discovery of the anomaly.

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