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Correlations between dynamic fragility and dynamic mechanical properties of several amorphous polymers

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ABSTRACT

In the present paper, dynamic mechanical properties were measured for several amorphous polymers ranging from strong to fragile. The results indicate that the storage modulus changes steadily, and the loss modulus peak and the tanδ peak are broader for strong glass-forming polymers. Three variables, the steepness index (*S*), the transition wideness (*W*) of storage modulus and the integration area (*A*) of tanδ, were defined to illustrate the potential correlation between the dynamic fragility index (*m*) and the dynamic mechanical properties. It is found that *W* and *A* can be correlated with *m* by power law equations, while an exponential relationship between *S* and *m* is observed. Moreover, as *m* decreases, the tanδ peak is more and more apart from the loss modulus peak and the point where the storage modulus begins to drop. These phenomena are interpreted in terms of chain packing efficiency.

1. Introduction

Since Angell [1] brought forward the liquid fragility in 1985, it has become an important concept for classifying the glass-forming liquids along a strong to fragile scale. The dynamic fragility is generally represented by a reduced Arrhenius profile (Angell plot), in which the logarithm values of viscosity η, relaxation time τ or shift factor $\log a_T$ are plotted against T_g/T. In the plot, strong liquids generally nearly behave in Arrhenius fashion, while fragile liquids typically exhibit non-Arrhenius behavior. The non-Arrhenius behavior is usually described by Vogel–Fulcher–Tamman–Hesse (VFTH) equation [2–4] or Williams–Landel–Ferry (WLF) equation [5]. For quantitative illustration, the dynamic fragility index *m* is defined as [1]:

$$m = \left[\frac{d\log\eta}{d(T_g/T)}\right]_{T=T_g} \quad \text{or} \quad m = \left[\frac{d\log\tau}{d(T_g/T)}\right]_{T=T_g}. \tag{1}$$

According to the equation, a higher *m* value refers to higher fragility.

It has been found that the dynamic fragility is correlated with various properties of glass-forming liquids, such as fast dynamics in the deep glasses [6–10], Poisson ratio [11,12], glass transition temperature [13], thermodynamic fragility [10,14–16] and chain packing efficiency [28,29]. In the current work, we are interested in the relationships between dynamic fragility and dynamic mechanical properties of amorphous polymers. The motivation for this work comes from our long-term work on the damping materials, which require polymers possess a wide mechanical loss peak around their glass transition region, i.e., their dynamic mechanical properties should change slowly with the variation of temperature near T_g [17–19]. On the other hand, it is pointed out that strong liquids tends to have stable structures and local to intermediate range of order, so their properties do not change dramatically with the temperature; whereas the structures of the fragile liquids are unstable and their molecules show largely nondirectional packing and dispersive forces on each other, so their properties change quickly with temperature [1,20]. Therefore, the potential correlation between the fragility and the dynamic mechanical properties of polymers may afford us an alternative way to choose damping materials according to the strong–fragility scale. In the present study, seven kinds of amorphous polymers ranging from strong to fragile were studied, and we also compiled some data of other amorphous polymers from the literature.

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2. Experimental

The number average molecular weight of polyisobutylene (PIB) is about 12 0000 g/mol. The degree of polymerization of polyvinyl chloride (PVC) is about 700–800. The melting indices of polycarbonate (PC), poly(methyl methacrylate) (PMMA) and polystyrene (PSt) are 18 g/10 min, 16 g/10 min and 4 g/10 min, respectively. Chlorinated butyl rubber (CIIR) and lightly cured chlorinated butyl rubber (CCIIR) are the same as those used in a previous work [18]. Polyvinyl acetate (PVAc) was synthesized by emulsion polymerization with $FeSO_4–K_2S_2O_8$ as redox initiator at a temperature of 25 ± 2 °C.

Dynamic mechanical analysis (DMA) was carried out by using a dual or single cantilever clamp and a testing method of temperature step-frequency sweep with each temperature step of 2–6 °C and a frequency range between 0.1 Hz and 30 Hz (just the isochronal data at 1 Hz was discussed in this paper). The sample dimensions were 20 mm long, 12 mm wide and 3 mm thick for the dual cantilever clamp and 17.5 mm long, 12 mm wide and 3 mm thick for the single cantilever clamp. The oscillation strain amplitude was set to be 15 μm. Because each sample was tested for once, just the systematic errors can be determined. The systematic error for temperature is ±0.1 K.

3. Results

If one takes a minute to compare the dynamic mechanical spectra of a strong amorphous polymer with those of a fragile one, it is evident that the loss tangent peak is further from the loss modulus peak for the strong amorphous polymer than the fragile one. For quantitative discussion, three glass transition temperatures, denoted as $T_{g,1}$, $T_{g,2}$ and $T_{g,3}$, are determined from the storage modulus (E'), loss modulus (E'') and loss tangent (tanδ), respectively. Fig. 1 is a schematic representation of determining $T_{g,1}$, $T_{g,2}$ and $T_{g,3}$. The results are tabulated in Table 1 for the seven amorphous polymers as well as their fragility index and T_g compiled from references. The data of four other polymers, including poly(*n*-butyl methacrylate) (PBMA), poly(ethyl methacrylate) (PEMA), poly (ethyl acrylate) (PEA) and amorphous unoriented poly(ethylene terephthalate) (PET), are compiled from previous works and also shown in Table 1. If we define $\Delta T_2 = T_{g,3} - T_{g,2}$ and $\Delta T_3 = T_{g,3} - T_{g,1}$, it is evident that ΔT_2 and ΔT_3 decrease when the glass-forming polymers go from the strong side to the fragile side. Approximately, $\Delta T_2 \propto m^{-1.05}$, $\Delta T_3 \propto m^{-0.99}$. That is to say the tanδ peak is more and more apart from the loss modulus peak and the point where the storage modulus begins to drop as the fragility of the glass-forming polymers decreases. From Fig. 2, it can also be observed that ΔT_1 seems to be independent of the fragility index. Therefore, the variation of ΔT_3 with the fragility index mainly comes from the contribution of ΔT_2.

Fig. 3 exhibits the scaled dynamic mechanical spectra for the seven polymers at 1 Hz. In the figure, the storage modulus, loss modulus and tanδ are normalized by the storage modulus at the glassy state, the maximum loss modulus and the maximum tanδ, respectively. While the corresponding abscissas are normalized by $T_{g,1}$, $T_{g,2}$ and $T_{g,3}$. It is evident that the shapes of the dynamic spectra change systematically with fragility.

As can be seen in Fig. 3(a), the plot of $\log(E'/E'_{max})$ vs. $T_{g,1}/T$ looks like an Angell plot. Strong glass-forming liquids like PIB and CIIR display a slow descending process in their storage modulus in going from the glassy state to the liquid state. With the increase of fragility, the storage modulus curve becomes steeper and steeper around the glass transition region. Finally, fragile liquids like PSt and PVC reveal a dramatic decrease of storage modulus above $T_{g,1}$. Taking the derivative $d\log(E'/E'_{max})/d(T_{g,1}/T)$ immediately reveals the great differences among these curves, as shown in Fig. 4. It can be observed from Fig. 4 that strong glass-forming

Table 1
Fragility index and T_g obtained from literature and three kinds of T_g determined from DMA data for amorphous polymers.

Polymers	m From ref.	T_g (K) From ref.	$T_{g,1}$ (±0.1 K)	$T_{g,2}$ (±0.1 K)	$T_{g,3}$ (±0.1 K)	References
PIB	46	201	206.4	208.6	236.1	[15,22]
CIIR	49	203	208.3	210.8	238.3	[18]
C-CIIR	63	203	211.9	214	241.6	[18]
PVAc	95	311	310.8	311.7	322.4	[15,21]
PMMA	103	367	384.8	386	402.1	[15,21]
PC	132	423.5	419.3	420.2	426.3	[15,21]
PSt	139	375	359.1	362.0	371.0	[15,21]
PVC	191	354	349.6	350.6	357.4	[15,21]
PBMA	56	–	317	–	338	[15,23]
PEMA	81	–	348.4	–	372	[15,24]
PEA	83	–	250.5	–	263	[15,25]
PET	156	–	354.4	–	363	[15,26]

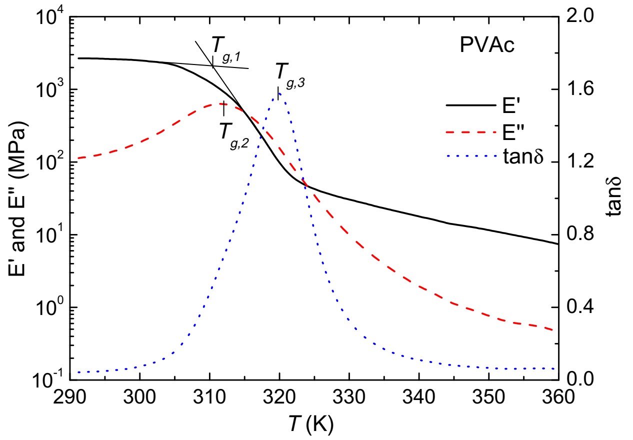

Fig. 1. A schematic representation of determining $T_{g,1}$, $T_{g,2}$ and $T_{g,3}$ at 1 Hz. $T_{g,1}$ is the corresponding temperature of the intersection of the two tangent lines. $T_{g,2}$ and $T_{g,3}$ are the corresponding temperatures of E'' peak and tanδ peak.

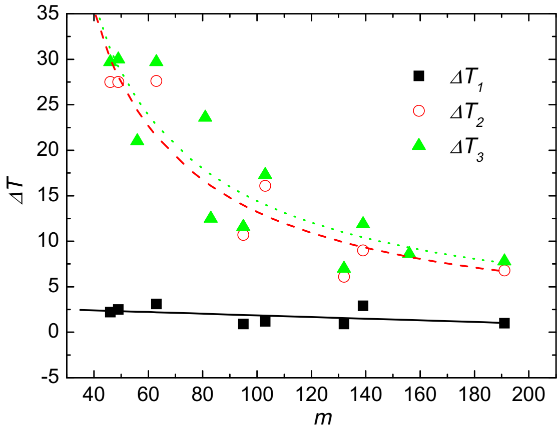

Fig. 2. The fragility index dependence of ΔT_1, ΔT_2 and ΔT_3. The data of ΔT_1 were fitted to $\Delta T_1 \approx 2.773(\pm 0.747) - 0.009(\pm 0.007)\, m$ with a correlation coefficient of 0.49. The data of ΔT_2 were fitted to $\Delta T_2 \approx 1696(\pm 1321) \times m^{-1.054(\pm 0.189)}$ with a correlation coefficient of 0.88. The data of ΔT_3 were fitted to $\Delta T_3 \approx 1362 (\pm 992) \times m^{-0.987(\pm 0.174)}$ with a correlation coefficient of 0.81. ΔT_3 data for PBMA, PEMA, PEA and amorphous unoriented PET were obtained from literatures. Polymers are listed in ascending fragility order: PIB, CIIR, PBMA, C-CIIR, PVAc, PEMA, PEA, PMMA, PC, PSt, PET, PVC.