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An Approach for Prediction of Dynamic Fragility of Polymeric Glasses

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The nature of the glass transition is an outstanding unsolved problem in condensed matter theory[1−5] and also affects many other fields.[6,7] The lack of a reliable theory of glass physics has led to the pursuit of correlations between viscous liquid parameters.[8] The concept of liquid fragility is such a liquid parameter that has been extensively used to classify the behavior of glass-forming liquids. It can assist the study of relaxation processes and glass transition in the supercooled liquid state.[9,10] Recently, it has been shown that the concept of fragility is far more general than previously believed; i.e., it can be directly extended to suspensions of deformable colloidal particles.[11] This concept was broadly popularized by Angell to account for the differences in the tendency of a liquid to vitrify[12] and has both dynamic and thermodynamic manifestations. The dynamic fragility refers to deviations from Arrhenius temperature dependence of mass transport or relaxation properties. Strong liquids display approximately Arrhenius behavior, whereas fragile liquids exhibit Williams−Landel−Ferry or Vogel−Fulcher−Tamman behavior.[13,14] The origins of the fragility and the relationships between the fragility and other important properties of the glass-forming liquids, such as configurational entropy, nonexponentiality, and features of the energy landscape of a glass-former, have been analyzed.[15,16] However, an understanding of the physical origin of fragility is lacking.[11] In addition, despite many efforts,[17−20] the factors that determine the fragility of a given liquid or polymer remain poorly understood,[8,21−25] such that the fragility index m cannot be accurately predicted on the basis of molecular structure and intermolecular interactions,[26,27] which is a problem because the important aspects of the viscous liquid such as aging behavior and nonexponentiality of relaxation seem to be closely correlated with fragility.[22] On the other hand, it was suggested that, in going from the liquid state to the glassy state, the changes in the structures (local to intermediate range order) and in the properties of liquids would be small for strong liquids but much evident for fragile liquids.[10,13,14,28,29] This fact together with the lack of a reliable theory of glass physics[8] has led to the pursuit of correlations between fragility and chemical structure of the material.[10]

Scopigno et al.[3] found that the vibrational properties of the glass well below T_g are correlated with the value of fragility index m, and therefore, they extended the fragility concept to the glassy state. Novikov and Sokolov[23] showed that the value of m for a liquid changes linearly with the ratio of the instantaneous bulk and shear moduli of its glass. However, this correlation does not work for the m of polymers.[23] The empirical correlations between dynamic fragility and thermodynamic fragility also cannot well describe the variation of the m of polymers with the ratio of the liquid to glassy heat capacities at T_g, $C_{P,T_g}^{\;\;SL}/C_{P,T_g}^{\;\;g}$.[29] The typical example is that, while the thermodynamic fragility of poly(*R*-methacrylates) with R = ethyl to hexyl is nearly constant, their dynamic fragility varies by over a factor of 2.

Xia and Wolynes developed a microscopically motivated theory of glassy dynamics to explain the magnitude of free energy barriers for glassy relaxation.[30] Wang and Angell[31] established a predictive equation for the m values:

$$m = 56\frac{T_g}{\Delta H_m}\Delta C_P \tag{1}$$

where T_g, ΔC_P, and ΔH_m are the glass transition temperature, the heat capacity change at T_g, and the latent heat of fusion per mole. Stevenson and Wolynes[32] also derived a predictive equation:

$$m = 34.7\frac{T_m}{\Delta H_m}\Delta C_P \tag{2}$$

Both eq 1 and eq 2 have been checked by comparisons with the measured m values of 44 substances.[31,32] The prediction results are impressive for the systems credibly modeled as interacting spheres. However, considerable deviations are observed for the systems where the assumption of complete freezing of degrees of freedom in the crystal or release of degrees of freedom on melting was violated. The typical organic materials showing significant deviations are triphenylethene (m_{exp} vs $m_{pred}^{eq\,2}$: 91 vs 70), decahydronaphthalene (147 vs 54), and α-phenyl-*o*-cresol (83 vs 59). Significant deviations were also observed for polymers: the values of m_{exp} and $m_{pred}^{eq\,2}$ are 116 vs 55 for poly(styrene), 137 vs 40 for poly(propylene), 132 vs 24 for poly(carbonate), and 35.5 vs 59.7 for poly(ethylene sebacate). Furthermore, it is inconvenient to extend these equations to polymers, as the necessary information about the crystallization of polymers is hard to monitor.[32] In addition, unlike other classes of glass-formers, (1) polymer dynamic fragilities extend over the entire range from strong to fragile (from about 40 to more than 200) and (2) as already mentioned the dynamic and thermodynamic fragilities seem uncorrelated for polymeric glass-formers (the so-called fragility dilemma).[29] Therefore, it is difficult but very important to develop the new approaches that could yield accurate, or at least reasonable, predictions for the m values of the polymers due to the wide application of the polymer glasses.[33,34]

Ngai[35,36] interpreted the relationship of temperature dependence of segmental relaxation of polymers to their structures by means of his coupling model. He found that polymers having smooth and compact chain backbones tend to show a nearly Arrhenius temperature dependence of segmental relaxation, whereas the temperature dependence of segmental relaxation of the polymers with less flexible backbones exhibits fragile behavior.

The Adam−Gibbs equation[16,37] for the viscosity η can be expressed as

$$\eta = \eta_0 \exp\left(\frac{C}{TS_c}\right) \tag{3}$$

where η_0 and C are constants[12] and S_c is the configurational entropy. According to the definition of the fragility index m[21,38]

$$m = \left.\frac{\partial \log x}{\partial (T_g/T)}\right|_{T=T_g} \tag{4}$$

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where x can be viscosity, relaxation time, or other dynamic variable, the fragility index m can be expressed as

$$m = \frac{C}{2.303 T_g S_{c,T_g}{}^2}\left(S_{c,T_g} + \frac{T \partial S_c}{\partial T}\bigg|_{T=T_g}\right) \tag{5}$$

where S_{c,T_g} is the configurational entropy at T_g. Substitution of the relationship[12]

$$\log \frac{\eta}{\eta_0}\bigg|_{T=T_g} = \frac{C}{2.303 T_g S_{c,T_g}} = 17$$

into eq 5 yields

$$m = 17 + 665.55 \frac{T_g T \partial S_c}{C \ \partial T}\bigg|_{T=T_g} \tag{6}$$

If $\Delta T = (T - T_g)$ is sufficiently small, then it is assumed that $S_c = c_2 S$ at $T_g \leq T \leq (T_g + \Delta T)$, where c_2 is a constant and S is the total entropy. Under this condition, eq 6 can be rewritten as

$$m = 17 + 665.55 \frac{T_g}{E} C_{P,T_g}^{\mathrm{SL}} \tag{7}$$

with $E = C/c_2$. The parameter E was calculated by the summation of the atomic and group contributions:

$$E = \sum_i n_i E_i + \left(\sum_j n_j - 2\right) E_j \tag{8}$$

where n_i is the number of contributing component of the type i appeared in the chemical structure of the material ($i = -CH_3$, $-C_6H_5$, $-C_6H_4-$, $-(C{=}O)O-$, $-O-$, $-CN$, $-C(CH_3)_2-$, $-Si(CH_3)_2O-$, etc.). E_i is the numerical contribution of the component i. n_j is the number of contributing components of the type j appeared in the chemical structure of the material ($j = -CH_2-$, $\rangle CH-$, and $\rangle C\langle$). E_j is the numerical contribution of the component j. For example, the E for poly(ethyl methacrylate) is expressed as $E_{\mathrm{poly(ethyl\ methacrylate)}} = (3-2)E_j + 2E_{\mathrm{CH_3}} + E_{\mathrm{COO}} = E_j + 2E_{\mathrm{CH_3}} + E_{\mathrm{COO}}$. The reported m values of the 30 polymers and the 13 small molecule materials with several aromatic/paraffinic rings were used to test eq 7. The test procedure is as follows.

(1) Determine the n_i and n_j according to the chemical structure of the material (see Table 2 of the Supporting Information). Then, the E_i ($i = -CH_3$, phenyl, $-(C{=}O)O-$, $-O-$, $-C(CH_3)_2-$, $-CN$, cyclohexyl, and $-Si(CH_3)_2O-$) and the E_j were determined by fitting eq 8 to the m values of poly(methyl acrylate), poly(propylene), poly(*n*-propyl methacrylate), poly(styrene), poly(isobutylene), poly(propylene oxide), side chain LCP1, side chain LCP8, and decahydronaphthalene (see Table 2 for their chemical structures).

(2) Insert the (n_i, E_i) and the (n_j, E_j) into eq 8 to calculate the E values for the rest materials. Note that the E_i value of the contributing components having similar structures is approximately connected to their molar mass M by the relationship $E_1/E_2 = M_1/M_2$, e.g., $E_Y = E_{\mathrm{Cl}} M_Y / M_{\mathrm{Cl}}$ (Y = F and Br), $E_S = 2E_O$, $E_{\mathrm{decahydronaphthalene}} = 2E_{\mathrm{cyclohexyl}}$, $E_{\mathrm{cyanoadamantane}} = 4E_{\mathrm{cyclohexyl}}$, $E_{\mathrm{phenanthrene}} = 3E_{\mathrm{phenyl}}$, and $E_{-C_6H_5} \simeq E_{-C_6H_4-}$.

(3) Insert the E values into eq 7 to predict the m values for the rest materials. Preliminary results show that the use of $C_{P,T_g}{}^{\mathrm{g}}$ instead of $C_{P,T_g}{}^{\mathrm{SL}}$ could achieve slightly better results. The more detailed information for the calculations of the $C_{P,T_g}{}^{\mathrm{g}}$ and of the E_i for some materials has been given in the footnote of Table 1 (Supporting Information).

It emerges from Figure 1 and Table 1 that the parameters E_i and E_j determined from the m values of the 8 polymers and 1 small molecule material can provide nice predictions for the m values of the 22 polymers and the 12 typical small molecule organics with several aromatic/paraffinic rings.

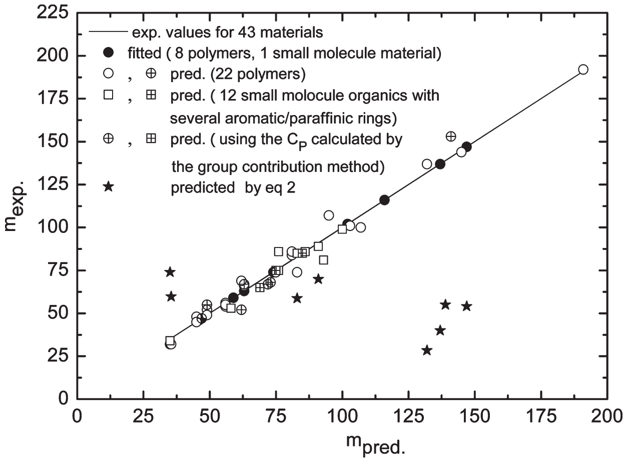

Figure 1. Comparison of measured (line) and fitted/predicted (symbols) m values for 43 materials. The detailed calculations and comparisons are given in Tables 1−3 of the Supporting Information.

The approach developed herein correlates/predicts the widely used fragility index m in terms of the chemical structures of the polymers and the highly fragile organic materials; no recourse to free volume considerations is necessary. This meshes nicely with the previous findings, which shows that chemical structure underlies viscoelastic behavior of polymers.[33,34] The robust predictability of this approach will be significant in the future for sorting out the dependence on chemical structure of the viscoelastic properties of polymers in the glass−rubber transition zone,[33,34] for understanding the nature of the glass transition of the polymers,[9,10] for applying the widely used concept fragility,[12] and for designing the structure of polymers and molecular materials to meet specific demands in various applications (structural and optical glassy materials, drug delivery, and biological tissue preservation and transportation, etc.).[7,38,39]

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Supporting Information Available: Comparison of fitted/predicted and measured fragility index m of examined polymers and small molecule organics (Table 1); number of the groups in calculations/predictions of the fragility index m of examined polymers and small molecule organics (Table 2); $C_{P,T_g}{}^{\mathrm{g}}$ of some polymers and small molecule organics calculated by the group contribution method (Table 3). This material is available free of charge via the Internet at http://pubs.acs.org.

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