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Dynamic mechanical analysis of segmental relaxation in unsaturated polyester resin networks: Effect of styrene content

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Abstract

The effect of styrene content on non-exponential and non-Arrhenius behavior of the α-relaxation of cured unsaturated polyester resins (UPR) was investigated by dynamic mechanical analysis (DMA). To compare the temperature dependence of the relaxation times, the Angell fragility concept was applied to samples with different crosslink densities. Furthermore, the number of structural units per cooperatively rearranging region (CRR) was estimated using random walk model and the modified Adam–Gibbs theory. The results showed that rising styrene content enhanced the crosslink density of the networks, which altered the intensity and broadness of the α-relaxation. The fragility index, a measure of temperature dependence of relaxation time, and the average size of CRR at glass transition region was also increased by styrene content. Therefore, the segmental relaxation in networks with higher crosslink density could be associated with stronger intermolecular coupling. In addition, it was observed that the mean required energy for internal rearrangement of structural units within the CRR decreased as the fragility index increased, while the mean barrier height for repositioning of a CRR in cooperation to its local environment was nearly constant.

Keywords: Segmental dynamics; Fragility; Unsaturated polyester resin

1. Introduction

Polymeric thermosets are important class of materials from both academic and technological points of view. Unsaturated polyester cured with styrene monomer is a typical widely used resin in coating and composite technologies. It is now well established that the resulting three dimensional network in UPR forms via complex reactions including styrene homo-polymerization and graft copolymerization through double bond functionalities of the unsaturated polyester and styrene monomer [1]. This quasi-conterminous crosslinked network generates a stiff product suitable as thin film and bulk structural material when reinforced with particulate or fibrous fillers.

Nowadays, the macroscopic properties of polymers and other complex materials are mainly interpreted based on understanding the underlying microscopic phenomena. Particularly, appreciating the temperature dependence of the average relaxation time τ, may end up designing molecular mobility and lead to fine tuning the final properties. Toward this end, Angell [2] has developed an energy landscape model based on the nature of structural evolution in a supercooled liquid approaching the glassy state. He proposed the configurational states density comprising the potential energy hyper-surface of the material as the governing parameter [2,3]. Therefore, the topology of energy landscape (i.e. the number of minima and the barrier height between them) provides a measure of the steepness of the excitation profile for glass-forming polymers. Kinetic and thermodynamic aspects are introduced by the height of energy barrier and the number of minima, respectively. According to this scheme, relaxation behavior could be considered as strong or fragile, depending on the rate with which the associated properties are modified as the temperature passes through the glass transition region [4–6]. Fragile liquids show a steeper increment in relaxation times approaching glass transition temperature, T_g, than do strong liquids as usually indicated by T_g-normalized

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Arrhenius plots. Specifically, fragile glass formers have broader relaxation functions than do strong, or less fragile liquids [3–5,7].

In this work, the effect of styrene content or network crosslink density on non-exponential and non-Arrhenius behavior of the α-relaxation of definite unsaturated polyester resins was investigated by dynamic mechanical analysis. The temperature dependence of the relaxation times of samples with different crosslink densities was compared through the Angell fragility concept. Then, the results were discussed based on application of random walk model (RWM) and the modified Adam–Gibbs theory.

2. Experimental section

The unsaturated polyester resin was provided by Bushehr resin Co. (Iran). This polyester resin consists of maleic anhydride (MA), phtalic anhydride (PA) and propylene glycol (PG) (0.5:0.5:1.1) as determined by ^{1}H NMR. The styrene monomer was supplied from industry and used as received.

The amount of styrene in the supplied resin was determined by monomer evaporation in an air-circulating oven at 110 °C for 2 h. Then, samples with various styrene contents were prepared by changing composition in the range of 35–60 w/w%. Each UPR solution was prepared by diluting the resin with styrene for 1 h at ambient temperature with a magnetic stirrer. Later, 0.5 w/w% cobalt octate (Activator) was dissolved in each mixture.

Plates 2 mm in thickness were molded from the resin mixtures. The curing was initiated at room temperature by adding 1 w/w% methyl–ethyl–ketone peroxide as catalyst. The thermal cycle of curing was consisted of isothermal heating at 25 °C for 24 h, followed by post-curing at 80 °C for 8 h and 120 °C for 2 h. This curing procedure led to the maximum degree of chemical transformation [8].

The dynamic mechanical analysis was performed in a TA instrument, DMA-2980, at both isothermal (frequency sweep) and non-isothermal (temperature scan) conditions for all samples in bending mode. Dual cantilever clamp was used on samples with rectangular geometry of $50\times13\times2\ \text{mm}^3$. The non-isothermal runs were carried out at 4 °C/min, from room temperature up to 200 °C at constant frequency of 3 Hz. The frequency sweep experiments were carried out in the glass transition region (determined by non-isothermal runs) for each sample at 2–4 °C intervals after temperature equilibration for 20 min. At each temperature the frequency was changed from 200 to 0.01 Hz.

3. Results and discussion

The tan δ-temperature curves for the UPR networks in the α-relaxation region as a function of styrene concentration are presented in Fig. 1. By increasing the styrene content, the curves maximum, the apparent glass transition temperatures, systematically shift to higher temperatures. Furthermore, the shape of the loss spectra (intensity and broadness) changes accordingly. Apparently, styrene content enhancement changes the structure of the resulted networks. Hietalahti et al. [9,10], reported a styrene content dependence for the length of styrene bridges in a resemble network. Their solid-state ^{13}C NMR results [10] showed an increment of the length of styrene sequences with increasing styrene content and molar ratio of the styrene to polyester double bonds decrement. This would mean that increasing styrene content enhanced the crosslink density of the network. Similar results were also obtained by Saiter group [11] who reported the modification of the average number of styrene units in the polystyrene chains of the final network from 1.3 to 2.6 by changing styrene content from 25 to 40 w/w%.

The average crosslink density (n) and the number of structural units between crosslinks, ν, of the UPR networks were calculated from elastomeric plateau modulus of E'-temperature curves (not shown here), using the theory of rubber elasticity [12].

The phantom model yields:

$$E' = 3nRT, \quad \nu = \frac{\rho}{M_{\text{m}}n} \tag{1}$$

where R is the universal gas constant, T is the absolute temperature, M_{m} is the molecular weight of the structural unit, while ρ and E' are density and modulus of the elastomeric region, respectively. Phantom model assumes that the network is ideal and all chains are effective in elastic deformation [12]. However, due to the complexity of the reactions involved, a number of network imperfections like intrachain loop formation may be occurred. The UPR density variation with temperature was calculated from: $\rho(T) = [0.9287\exp(5.131\times10^{-4}t)]^{-1}$, assuming the same temperature dependence as polystyrene [13]. The calculated results showed denser networks, higher crosslink density, for the UPRs with higher styrene content (Table 1).

The intensity, $(\tan\delta)_{\max}$, and the broadness of the α-transition are sensitive to the amplitude and homogeneity of the macromolecular chain motions, respectively [14]. In other words, restrictive chain motion causes the reduction of damping capability, intensity decrement, whereas raising the heterogeneity of the chain local environment leads to

Table 1
Average crosslink densities (n) and number of structural units between crosslinks (ν) obtained from rubbery modulus of the UPRs with different styrene contents

Styrene content (w/w%)	E' (MPa) at 150 °C	n (mol/m^3)	ν
35	9.4	891	10.8
40	22.43	2126	4.5
50	31.88	3021.7	3.2
60	35.7	3570	2.7

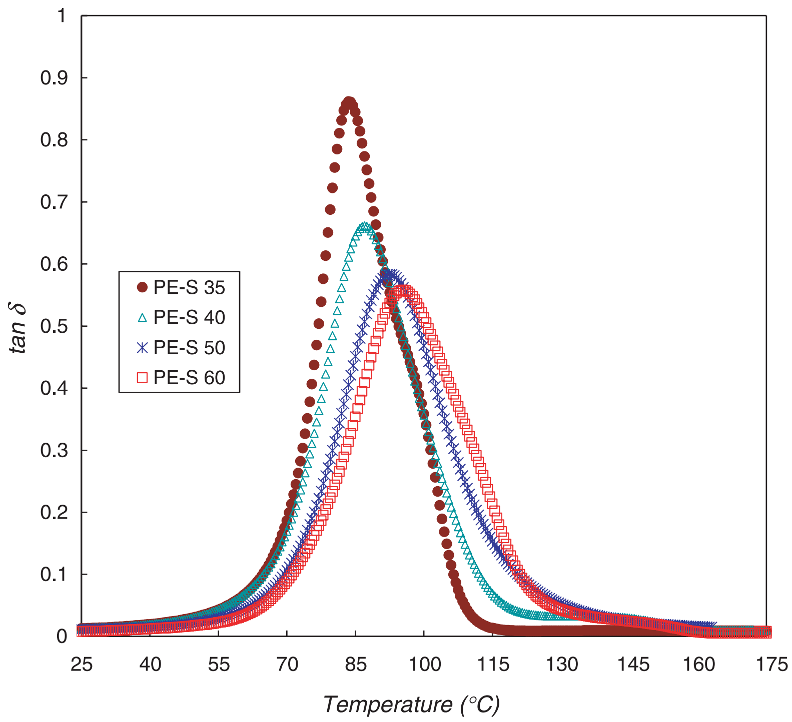

Fig. 1. Loss function (tan δ) vs. temperature for the UPR networks with different styrene content.

wider relaxation spectra, which imply relaxation broadening [14–18] (Fig. 1).

The relaxation width is often characterized by the inverse β parameter of the Kohlrausch–Williams–Watts (KWW) function [19]. A smaller β implies a broader distribution while a β close to unity means a perfect narrow relaxation spectrum.

The observed heterogeneity increment through adding more styrene monomer to the system is mainly attributed to the formation of tighter microgel structures. This microstructure is composed of distinct regions of densely crosslinked network distributed among a loosely crosslinked matrix [20]. Great dynamic heterogeneities of a thermoset resin system via formation of a complex structure were also reported by Wang and Ediger [21]. They actually found a bimodal distribution of local relaxation times due to slow and fast relaxing regions of their thermoset system.

A typical frequency dependence of the measured tan δ at several temperatures in the glass transition region is shown for the UPR with 35 w/w% styrene (PE-S 35) in Fig. 2. Apparently, with increasing the temperature, the intensity of the glass transition peak enhances and shifts to the higher frequencies. The characteristic time for local segmental relaxation was calculated by the frequency corresponding to the loss function peak, $\tau = 1/\omega_{\max}$. Later, the temperature dependence of the relaxation times for the UPR samples with various compositions were calculated and plotted in Fig. 3. The curves through the data represent the best fits to the Vogel–Fulcher–Tamman (VFT) equation [22].

$$\tau = \tau_0 \exp\frac{B}{T - T_\infty} \tag{2}$$

where B is a material parameter defining its relaxation activation energy while T_∞ is Vogel temperature representing the point, where relaxation time diverges to infinity. The pre-exponential τ_0, corresponds to the relaxation time at infinite temperature. A constant value of $\tau_0 = 1.0 \times 10^{-14}$ s was used for all fitting procedures [23]. The VFT parameters for the various UPR samples are listed in Table 2.

The log(τ) vs. T_g/T curves for the UPRs with various styrene contents were plotted in Fig. 4. The fragility (m) or the curve slope at T_g was calculated based on the VFT parameters (Tables 2) using the following equation [24]:

$$m = \frac{\mathrm{d}\log\tau}{\mathrm{d}(T_g/T)}\Big|_{T=T_g} = \frac{B/T_g}{\ln(10)}\left(1 - \frac{T_\infty}{T_g}\right)^{-2} \tag{3}$$

The calculated fragilities vs. the styrene content of the cured resins are also presented in Table 2 and shown in Fig. 5. A typical error of ±5 in calculations based on the DMA results is unavoidable [25]. The fragility index of the UPR resins increases by raising the styrene content. Similar results have been reported recently by Saiter et al. [26] and Bureau et al. [11] on UPRs with slightly different structures using dielectric analysis (DEA) and calorimetry, respectively. Whereas, the reported m values by Bureau et al. [11] were higher considerably, good similarities were observed between our results and those of Saiter et al. [26]. Recently, Alves et al. [25] used various techniques to study the fragility of their samples and figured out the disparity

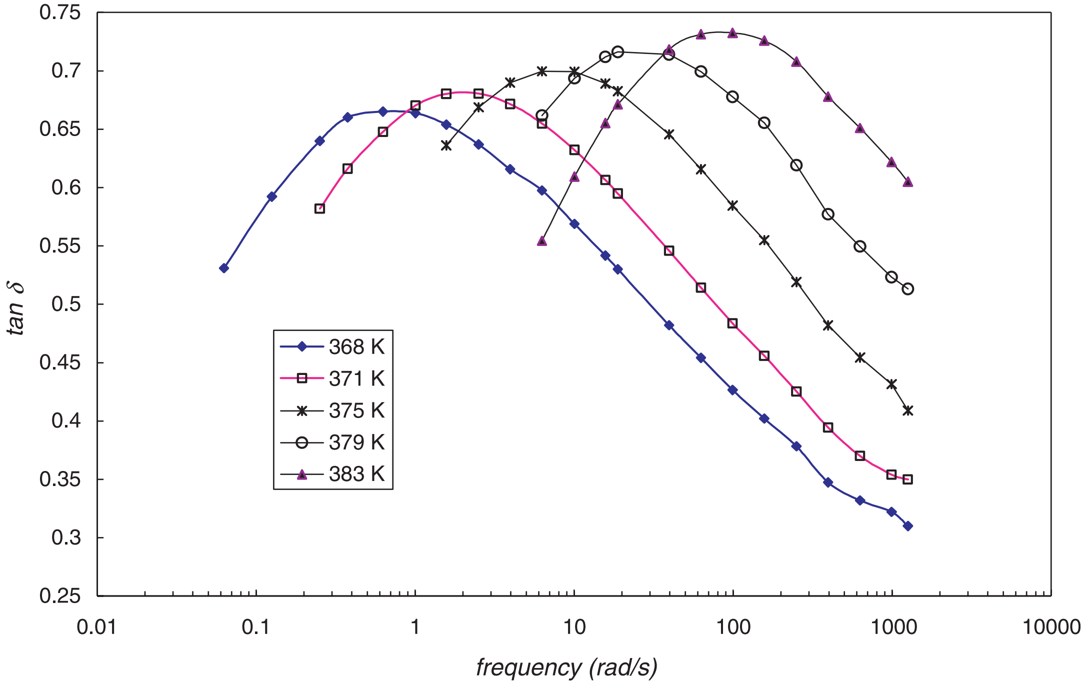

Fig. 2. Frequency dependence of tan δ at several temperatures in the glass transition region for PE-S 35.

among the resulted data. Furthermore, Roland and Ngai [3] pointed out that dynamic fragility obtained by DMA did not need to be the same as the thermodynamic fragility extracted from $\Delta c_p(T_g)$ in differential scanning calorimetry (DSC).

Recently, a great deal of attention has also been devoted to the rationalization of the glass transition phenomenon in term of the cooperatively rearranging regions (CRR). The CRR concept which was introduced by Adam and Gibbs [27] defined a subsystem size with independent configurational rearrangement capability. Modifying the Adam and Gibbs model, Donth and his collaborators [28,29] pointed

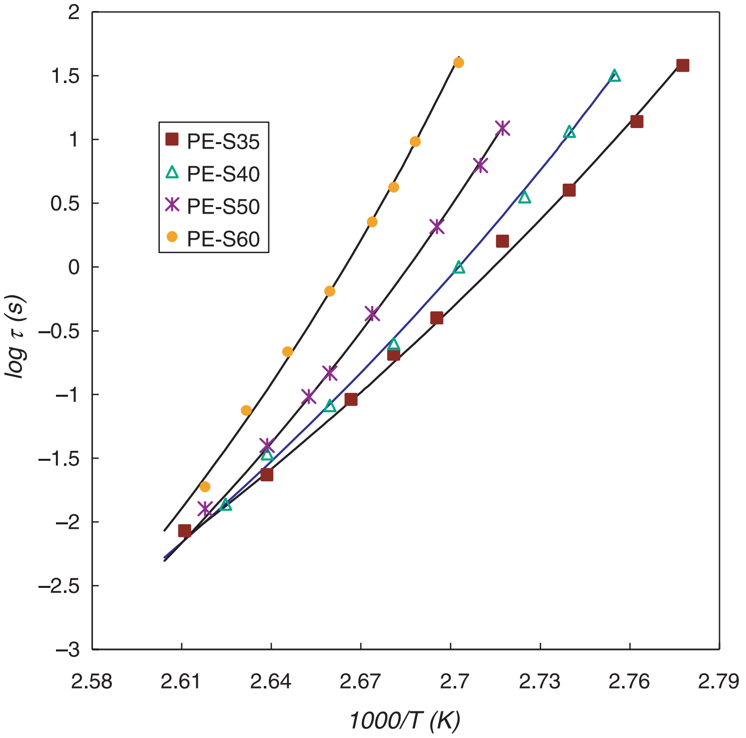

Fig. 3. Temperature dependence of the networks segmental relaxation times with various styrene contents. The solid lines are the VFT fits to the data.

Table 2
The best fit parameters of the VFT equation on various UPR samples

	PE-S 35	PE-S 40	PE-S 50	PE-S 60
Styrene content (w/w%)	35	40	50	60
τ_0 (s)	1.0×10^{-14}	1.0×10^{-14}	1.0×10^{-14}	1.0×10^{-14}
B (K)	2624	2321	1912	1621
T_∞ (K)	287	298	313	325
$D=B/T_\infty$	9.14	7.78	6.1	4.98
T_g (K)	357	360	365	369
T_g-T_∞ (K)	70	62	52	44
Fragility	83	94.3	112	134.2

out that at temperatures much higher than T_g the system contains elementary CRRs, which their number increase by temperature decrement. Finally, at a given temperature namely crossover temperature, T_c, the system would be entirely filled by such elementary CRRs. A number of evidences extracted from several experimental methods on many glass-formers showed different relaxation mechanisms at above and below this temperature [30–34]. In other words, molecules at lower temperatures ($T<T_c$) move by crossing substantial potential energy barriers. However, at higher temperatures ($T>T_c$), thermal energies are comparable to the barrier heights and translational motion have a fundamentally different character [31]. The change in relaxation mechanism coincided with the following different experimentally detectable events: (a) Departure from Vogel behavior [32,33], (b) the enhancement of translational diffusion rate compared to rotational motion [34], and (c) splitting of a single relaxation process into α and slow β processes [29]. It should be, however, mentioned that the crossover temperature is not identical with the T_g. The T_c value scatters from $\approx 1.1\ T_g$ in fragile liquids up to $\approx 1.6\ T_g$ in the case of strong systems [35].

The crossover temperatures for the UPR samples were estimated using the so called random walk model (RWM) proposed by Arkhipov and Bässler [36]. In their model, the structural relaxation or transition from one configuration to another was considered as a structural unit jump within a complex energy landscape. In this framework, two temperature regimes of structural unit jumps are possible for fragile systems. In the low temperature regime ($T<T_c$), the relaxation time could be calculated as follow [36]:

$$\tau = \tau_0\left(\frac{\pi}{2(\alpha-1)}\right)^{0.5}\alpha^{(2\alpha-3)/(2(\alpha-1))}\left(\Gamma\left(\frac{1}{\alpha}\right)\right)^{-1} \times\left(\frac{T_0}{T}\right)^{(2-\alpha)/(2(\alpha-1))}\exp\left[(\alpha-1)\left(\frac{T_0}{\alpha T}\right)^{\alpha/(\alpha-1)}\right] \qquad (4)$$

where τ_0 characterizes the relaxation time of a single-free

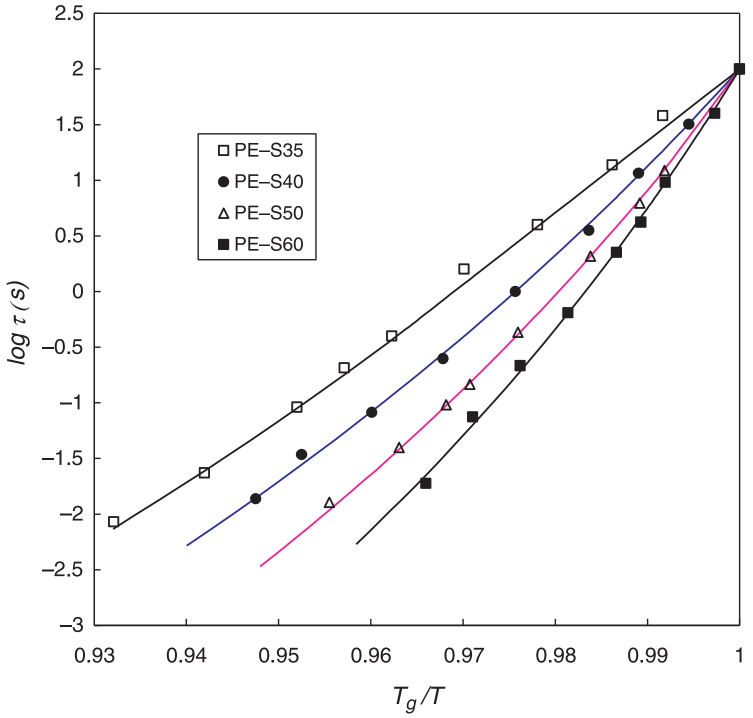

Fig. 4. Fragility plots for the UPR networks with different styrene content.

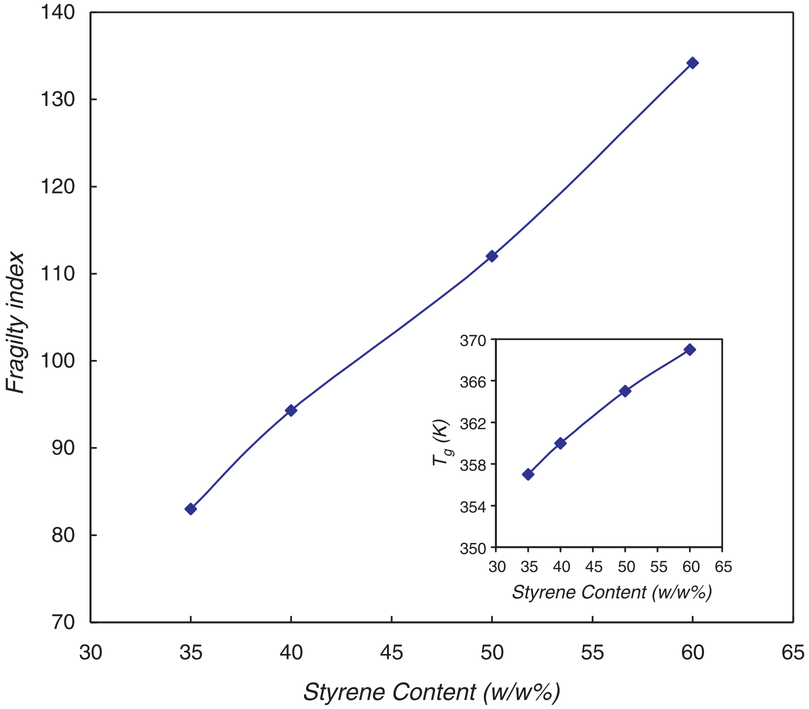

Fig. 5. Fragility index dependence on styrene content of the UPR. The inset plot shows the variation of the corresponding glass transition with styrene content.

structural unit. The value of $\tau_0 = 1\times10^{-14}$ s was considered for all systems. Γ is gamma function and α is a measure of the fragility which is close to 1 for fragile liquids and increases to 2 for strong systems. Eq. (4) reduces to a simple Arrhenius type correlation for a strong system when $\alpha = 2$.

On the other hand, high temperature regime ($T > T_c$), leads to the following equation:

$$\tau = \tau_0 2^{(2\alpha-1)/(2(\alpha-1))}\left(\frac{1}{\alpha}\right)\Gamma\left(\frac{1}{\alpha}\right)\left(\frac{T_0}{T}\right) \times \exp\left[(\alpha-1)\left(1-2^{-1/(\alpha-1)}\right)\left(\frac{T_0}{\alpha T}\right)^{\alpha/(\alpha-1)}\right] \tag{5}$$

Fig. 6 presents the typical calculated log(τ) vs. T_g/T based on the Arkhipov and Bässler model [36] for PE-S 40 in two temperature regimes. The intersection of the two curves locates an estimate of the characteristic T_c temperature. The calculated values of α, T_0 and T_c for all the UPR samples were reported in Table 3. The RWM was recently applied to the analysis of the glass transition of unsaturated polyester resin by Saiter et al. [26].

Table 3
Random walk model and crossover parameters for unsaturated polyester networks with various styrene contents

Parameter	PE-S 35	PE-S 40	PE-S 50	PE-S 60
α	1.2337	1.2108	1.17	1.153
T_0 (K)	1141	1063	925	871
T_c (K)	379	384.5	391	398
T_c–T_∞	92	86.5	78	73
$\langle U\rangle$ (KJ mol^{-1})	30.3	26.1	19.5	17.1
x_g[a]	0.76	0.717	0.667	0.603
$N_\alpha(T_g)$	4.86	6.00	6.76	8.41
Fragility	83	94.3	112	134.2

[a] $x_g = (T_g - T_\infty)/(T_c - T_\infty)$.

The characteristic T_c, or the temperature for onset of significant intermolecular cooperativity increases with raising the styrene content. In other words, T_c could also be considered as the temperature below, which the system packs completely by multiple CRRs. From Ngai's coupling model point of view [37], the degree of intermolecular cooperativity ($n_\alpha = 1 - \beta_{\mathrm{KWW}}$) increases enormously below T_c. Consequently, the onset of cooperativity in unsaturated polyester resin networks may move to the higher temperatures (lower T_g/T) with raising the styrene content. On the other hand, the CRR size increment would be expected with decreasing temperature near glass transition [27]. Korus et al. [38] proposed an equation for temperature dependence of CRR size or N_α, number of particles per CRR:

$$N_\alpha^{1/2} = A\frac{1-x}{x} \quad \text{for } 0 < x < 1 \tag{6}$$

where $x = (T - T_\infty)/(T_c - T_\infty)$ is a reduced temperature and A is an individual constant.

Assuming $(A/(T_g - T_\infty)) = 0.1$, for all investigated systems, $N_\alpha(T_g)$ increases with T_c. Systematic decrement of $N_\alpha(T_g)$ when crossover temperature approaches T_g has also been reported by Hempel et al. [39] in poly(n-alkyl methacrylate) series. Based on Eq. (6), $N_\alpha(T_g)$ of PE-S 60 is 1.7 times of the number of particles per CRR at glass

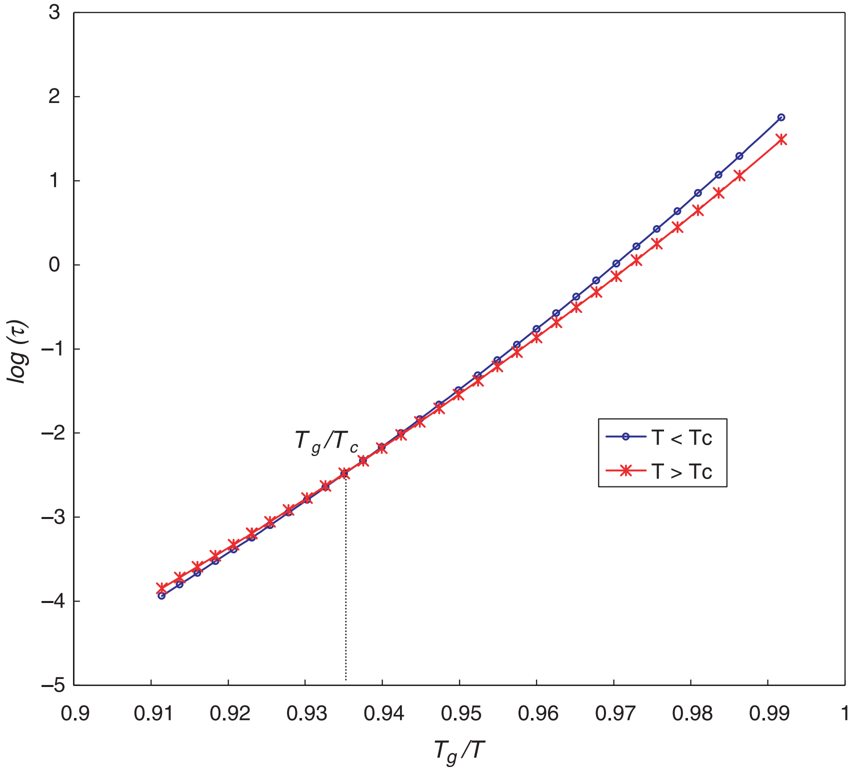

Fig. 6. Temperature dependence of segmental relaxation times calculated based on RWM for PE-S 40. The intersection of two curves is T_g/T_c.

transition of PE-S 35 (Table 3). Therefore, the segmental relaxation in the tighter networks (with higher styrene content) is associated with stronger intermolecular coupling. This effect could be correlated with either the increment of fragility index (m) or the magnitude of strength parameter ($D = B/T_\infty$). While, fragility increases with enhancing the styrene content, strength parameter shows the reverse trend (Table 2). Strength parameter, $D = B/T_\infty = \langle U\rangle/(RT_\infty)$, reflects the effectiveness of thermal energy at T_∞ to change the configurational state of a structural unit inside the CRR. The essential average barrier height for a mole of structural units to relax, $\langle U\rangle$, can be calculated using equation proposed by Richert and Bässler [40]:

$$\langle U\rangle = \frac{(RT_0)^2}{RT} \tag{7}$$

where T_0 and R are the characteristic temperature of RWM and universal gas constant, respectively. The calculated values at $T = T_g$ showed the decrement of the average barrier height with increasing the fragility of the system (Table 3). In other words, systems with higher $\langle U\rangle$ showed signs of stronger behavior. Apparently, this characteristic average energy controls the internal rearrangement capability of the structural units within the cooperative regions. In other words, by increasing the styrene concentration, decreasing the strength parameter, the degree of freedom for the molecular relaxation of polyester chains inside each CRR increases (Fig. 7). However, the average energy required for rearrangement of a CRR, $N_\alpha(T_g)\langle U\rangle$, seems nearly constant for the UPR networks with different styrene content (Fig. 7). As mentioned before, raising the styrene content is equivalent to decreasing the strength parameter (Table 2).

Kahle et al. [41] reported a correlation between fragility index and the length scales of cooperativity (cube root of the mean volume of the CRR). Also a linear correlation between fragility and the size of cooperative units has been found by Solunov [42] for some polymers and inorganic supercooled liquids.

Recently, Schroeder and Roland [43] suggested the existence of a critical cooperative length scale for segmental dynamics if the effect of crosslink density on fragility supposes to be detected. Therefore, the enhanced temperature dependence of the relaxation times or fragility index of the unsaturated polyester resins via enhancing the styrene content (crosslink density) led the authors to postulate larger cooperative domain size or the length scale of cooperativity at the glass transition region than the average distance between two consecutive junctions for all prepared samples except PE-S 35. So, the average number of structural units between crosslinks, ν, could now be compared with the average number of particles per CRR, $N_\alpha(T_g)$. As a result, the fragility enhancement in the networks with higher styrene content could be attributed to larger cooperative domain size of these networks in comparison with the average mesh size, i.e. $N_\alpha(T_g) > \nu$.

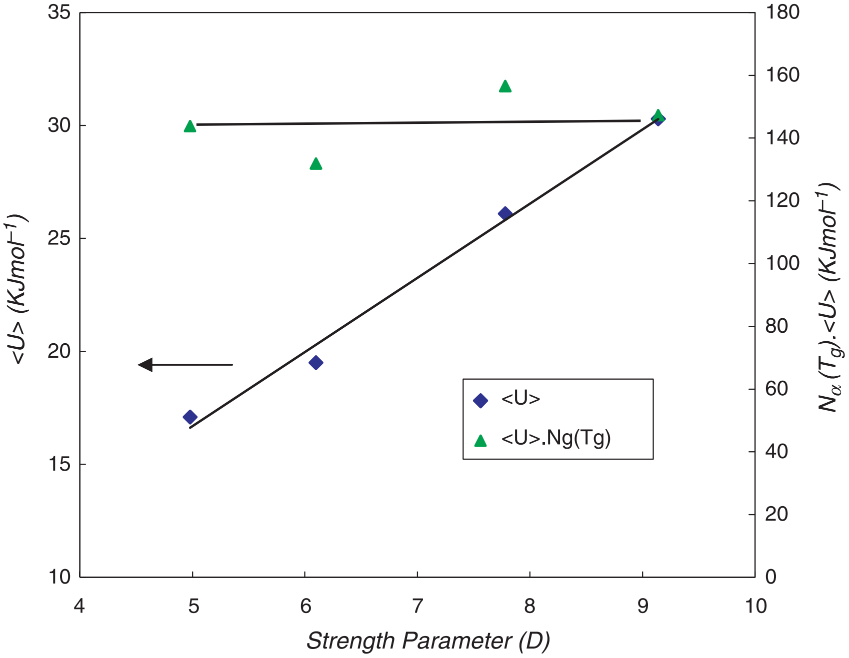

Fig. 7. The energy barrier height of a structural unit, $\langle U \rangle$, and a cooperative rearranging region as a function of strength parameter.

4. Conclusions

Dynamic mechanical analysis of the segmental relaxation in the cured unsaturated polyester resin with various styrene contents along with applying the existing models led to the following conclusions. The fragility index of the samples increased with raising the styrene content, which accompanied with higher network heterogeneity and relaxation broadness. The characteristic T_c, calculated based on applying the RWM for the UPR samples shifted to higher temperatures with making tighter networks. Finally, the observed stronger temperature dependence of relaxation time via raising the styrene content could be rationalized based on comparing the cooperativity length scale with the average distance between crosslinks.

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