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Thermochimica Acta 429 (2005) 1–5

thermochimica acta

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Characteristic length of dynamic glass transition based on polymer/clay intercalated nanocomposites

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Received 15 July 2004; received in revised form 24 September 2004; accepted 27 September 2004
Available online 11 November 2004

Abstract

The glass transition is an old physical problem. It has been accepted that there is a cooperatively rearranging region related to dynamic heterogeneity when temperature approaches the glass transition. However, there is no consensus with the characteristic length and the size of cooperatively rearranging region. This paper first employs the clay gallery in polymer/clay intercalated nanocomposites as a confined two-dimensional (2D) space to assess the characteristic length of dynamic glass transition. The five kinds of clays with different *d*-spacings were used to investigate the confinement effect. Theoretical calculation based on Donth's formula suggests that the characteristic lengths of polyol and polyol-based polyurethane are ∼3.20 and ∼1.45 nm, respectively. The experimental results agree with theoretical prediction using Donth's formula. The characteristic length varies with polymer types.

Keywords: Dynamic glass transition; Characteristic length; Polymer/clay intercalated nanocomposite

1. Introduction

The glass transition related to dynamic heterogeneity has attracted more and more attention recently [1–8]. When a liquid is supercooled towards the state of a solid glass, the temperature dependence of transport coefficients and relaxation time increases, and the time dependence of the relaxation functions changes from exponential to stretched exponential dependence [9]. In order to explain this fact, Adams and Gibbs first introduced the concept of cooperatively rearranging region (CRR) [10]. The characteristic length ξ_a was identified with the average size of CRR, $V_a = {\xi_a}^3$. However, they did not give any formula on the CRR size and the characteristic length. Donth assumed that CRR is a subsystem, which, upon a sufficient thermodynamic fluctuation, can rearrange into another configuration, independent of its environment [11]. Based on the von laue approach, they derived an explicit formula for measuring the CRR size by calorimetry from the fluctuation dissipation theorem FDT [12]. Calorimetric experiment on a wide assortment of molecular glass formers confirmed that characteristic length of glass transition near T_g is typically 1.0–3.5 nm and it is affected by individual properties of the molecules [13].

Nano-sized spaces including nanopore and nanolayer provide the opportunity to identify the characteristic length. A lot of investigations based on nanopore and nanoscaled polymer have been made [11,14–19]. Some characterization methods including solid NMR, atomic force microscopy, calorimetry, dielectric relaxation, dynamic and static light scattering, and non-resonant spectral home burning have been employed to verify the characteristic length [20–24]. However, more evidences are still needed and the length range should be further shortened and confirmed.

Recently, large amounts of polymer/layered silicate nanocomposites were prepared and its related physical and

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doi:10.1016/j.tca.2004.09.028

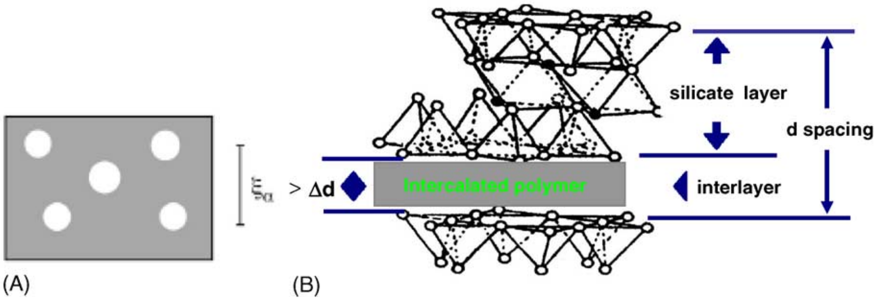

Fig. 1. Schematic drawing of (A) cooperatively rearranging regions (CRRs) for the Glarum defect diffusion realization of dynamic heterogeneity [28]. White: islands of mobility; gray: cooperativity shells; ξ_a, characteristic length = average size of a CRR. (B) Polymer intercalated clay structure.

chemical phenomena, such as molecular confinement have been investigated [25–27]. Clay gallery can provide a better two-dimensional space to study the dynamic glass transition behavior of intercalated polymer. In this study, five kinds of clays with different interlayer *d*-spacings as the confined space were employed to study the characteristic length (ξ_a) of polyol and polyol-based polyurethane (PU) at dynamic glass transition. A modulated differential scanning calorimetry (MDSC) technology was used in this study. The basic ideas are (1) if the interlayer spacing Δd of clay is less than the characteristic length of dynamic glass transition (ξ_a) the intercalated polymer will show different behavior with the bulk polymer at the crossover of glass transition of bulk polymer; as a result, the increment of heat capacity (ΔC_p) will decrease. This case is shown in Fig. 1. On the contrary, if Δd is bigger than ξ_a, the intercalated polymer will show similar glass transition behavior as the bulk polymer, and ΔC_p will remain invariable, and (2) according to Donth's formula, due to the different temperature fluctuations, there will be different ξ_a for polyol and polyol-based polyurethane, and thus, different dependence of the characteristic length with the Δd for polyol and PU should be observed.

2. Experimental

2.1. Materials

Poly(propylene glycol) (Luprane 2090, molecular weight = 6000, function = 3), was kindly provided by Elastogran U.K. Ltd. 4,4′-Methylene bis(cyclohexyl isocyanate) (MDI) and 1.4-butanediol (BD) were purchased from Aldrich Chemical (UK). Dabco-33LV was obtained from Air Products and Chemicals. The unmodified clay and organoclays were purchased from Southern Clay Products, Inc. (USA). The original Na^+ clay was marked as S0. The triethanolamine hydrochloride ($(HOCH_2CH_3)_3N\cdot HCl$) modified clay was made in this lab and marked as S3. The modifiers for organoclay 20A, 25A and B30 were dehydrogenated tallow quaternary ammonium (2M2HT), dimethyl hydrogenated tallow, 2-ethylhexyl quaternary ammonium (2MHTL8), and methyl tallow bis-2-hydroxyethyl quaternary ammonium (MT2EtOT), respectively.

2.2. Preparation of PU-organoclay nanocomposites

A series of PU-organoclay nanocomposites were prepared. The preparation process was as follows: 10 g of polyol and 0.7 g of clay were blended and stirred for 4 h at 60 °C. The polyol/clay mixture was blended for a particular PU/clay nanocomposite with 0.68 g of 1,4-butanediol, 5.0 g of MDI and 0.03 g of Dabco-33LV at room temperature for 1 min and was vacuum-degassed for 5 min. Then the viscous prepolymer was cured at 50 °C for 24 h and 80 °C for 1 week.

3. Characterization

The polyol/clay intercalated mixture was characterized by modulated different scanning calorimetry (MDSC), and the prepared PU/clay intercalated nanocomposites were characterized by wide angle X-ray diffraction (WAXD) and MDSC.

3.1. MDSC

MDSC test was conducted on a modulated differential scanning calorimeter (TA Instruments 2920 calorimeter). An oscillation amplitude of 1 °C and an oscillation period of 60 s with a heating rate of 3 °C/min were used.

3.2. WAXD

The intercalated nanocomposite films were mounted individually onto a Philip-X' Pert X-ray diffractometer fitted with a goniometer detection device (anode 40 kV, filament current 35 mA). Nickel-filtered Cu Kα radiation of wavelength 0.1542 nm was directed at the samples in their through direction. The goniometer scanned diffracted X-rays in the 2θ range 1–10° at a scan speed of 1°/min and with a step size of 0.02°.

4. Results and discussion

4.1. *Calculation of characteristic length (ξ_a) of dynamic glass transition of bulk polyol and PU*

The characteristic length (ξ_a) of dynamic glass transition of blank polyol and PU was calculated by Donth's formula as shown in Eqs. (1) and (2) [11,13].

$$N_a = \frac{R\,T^2\,\Delta(1/C_v)}{M_0\,(\delta T)^2} = \frac{R\,T^2\,\Delta C_p}{\overline{C_p}^2\,M_0\,(\delta T)^2} \tag{1}$$

$$V_a = {\xi_a}^3 = \frac{N_a\,M_0}{\rho} \tag{2}$$

where N_a is cooperativity, i.e., the number of such particles in one average CRR with volume V_a; ξ_a the characteristic length of dynamic glass transition; M_0 the weight for a whole molecule, or for polymer, a monomer unit; R the molar gas constant; ρ the mass density; $\Delta(1/C_v)$ the step of reciprocal specific heat capacity at constant volume at the glass transition (C_p is at constant pressure); $(\delta T)^2$ the mean square temperature fluctuation of one average CRR at temperature T_g; $\overline{C_p}$ the average C_p value between the glass zone and the flow zone, and ΔC_p the increment of heat capacity at glass transition, i.e., the step at the glass transition between these zones. δT is temperature fluctuation, the peak of $\mathrm{d}C_p/\mathrm{d}T$ signal is approximated by a Gauss curve as expressed in the formula (3), that determines δT as the dispersion of this approximation.

$$\frac{\mathrm{d}C_p}{\mathrm{d}T} = \text{const}\,\exp\frac{(-T - T_\omega)^2}{2\delta T^2} \tag{3}$$

The C_p, ΔC_p and δT values can be obtained from the curves of the reverse heat capacity C'_p and $\mathrm{d}C_p/\mathrm{d}T$ signal versus temperature. Figs. 2 and 3 show C'_p and $\mathrm{d}C_p/\mathrm{d}T$ signal versus temperature curves of blank polyol 6000 and blank polyurethane. For blank polyol, $T_g = 204.24$ K; $C_p^{\text{glass}} = 0.841$ J/g °C; $C_p^{\text{liquid}} = 1.282$ J/g °C; $\Delta C_p = 0.441$ J/g °C; $2\delta T \sim 5.30$ K; $\rho = 1.02$ g cm^{-3}; $M_0 = 58$, $\overline{C_p} = 1.062$ J/g °C; $\Delta(1/C_v) = 0.406$, then ξ_a was found to be 3.20 nm and $N_a \approx 346$. For blank PU, $T_g = 216.44$ K; $C_p^{\text{glass}} = 0.953$ J/g °C; $C_p^{\text{liquid}} = 1.205$ J/g °C; $\Delta C_p = 0.252$ J/g °C; $2\delta T \sim 13.01$ K; $\rho = 1.1$ g cm^{-3}; $M_0 = 58$; $\overline{C_p} = 1.079$ J/g °C, and $\Delta(1/C_v) = 0.219$, then ξ_a was found to be 1.45 nm and $N_a \approx 35$. For polyol and polyol-based polyurethane, the main contributions to the glass transition both come from the polyol part. However, there is marked difference in characteristic length and cooperativity for polyol and polyol-based polyurethane. We also calculated ξ_a value of polyol in polyol/clay and the ξ_a value of PU in PU/clay intercalated nanocomposite according to the Eqs. (1) and (2), and found that there is no marked change with different clays. Thus, ξ_a values of polyol and PU are still applicable for polyol/clay and PU/clay intercalated nanocomposite. In ref. [13], it is noted that, among the 28 kinds of investigated substances, there is a similar trend, i.e., for the substance that has a large value of temperature fluctuation δT, mainly for macromolecules, there is a small value of ξ_a about ~1.0 nm, and for the substance that has a small value of δT, mainly for small molecules, there is a large value of ξ_a about ~3 nm. From our calculation, we noted that the cooperativity (N_a) also has a marked difference, the N_a value of polyol (~356) is about 10 times that of polyol-based polyurethane (~34). This should be mainly attributed to the temperature fluctuation δT. However, the intrinsic reason is still not clear. The glass transition temperature of PU is about 12 °C higher than that of polyol. This phenomenon indicates that hard segments have a significant influence on the movement of polyol segment at the glass transition. The value of T_g depends on the mobility of the polymer chain, the more immobile the chain, the higher the value of T_g. In particular, anything that restricts rotational motion within the chain should raise T_g.

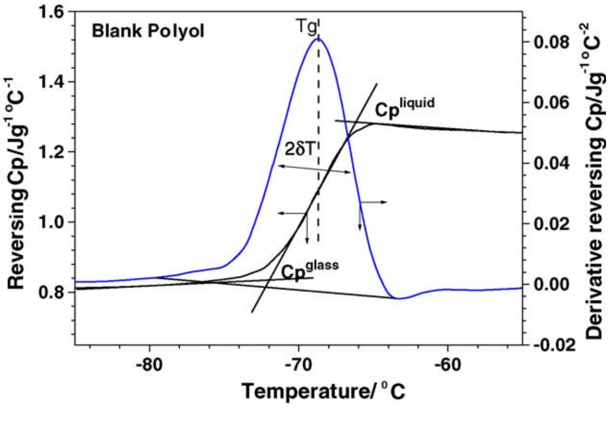

Fig. 2. Reversing heat capacity (C'_p) and $\mathrm{d}C_p/\mathrm{d}T$ signal of bulk polyol 6000 vs. temperature.

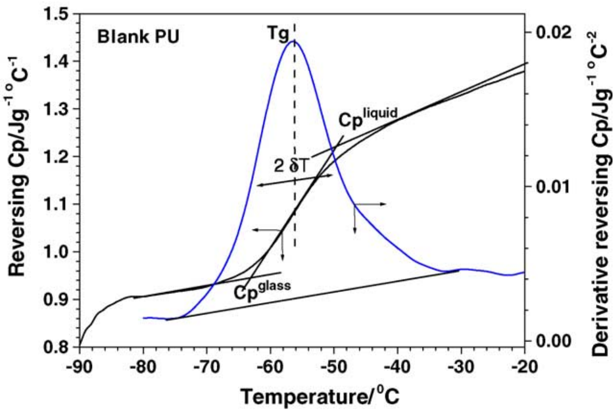

Fig. 3. Reversing heat capacity (C'_p) and $\mathrm{d}C_p/\mathrm{d}T$ signal of bulk PU vs. temperature.

4.2. *Experimental determination of characteristic length (ξ_a)*

In this study, polyol/clay intercalated nanocomposites were prepared through mixing with polyol and clay for 4 h

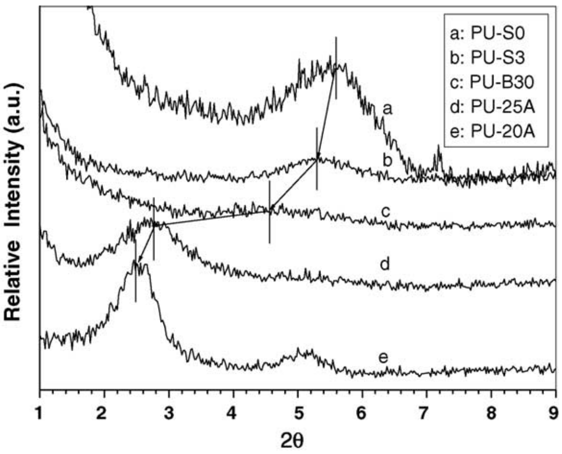

Fig. 4. X-ray diffraction pattern of PU nanocomposites with different clays.

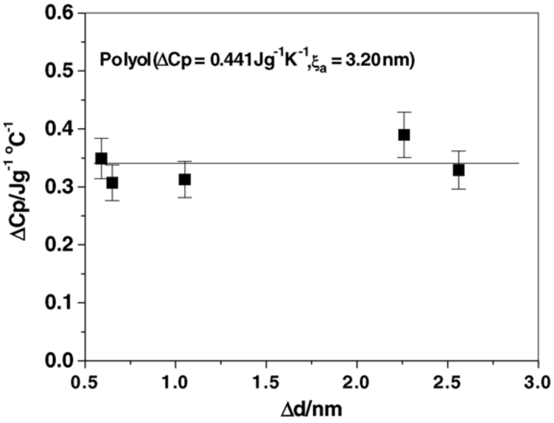

Fig. 6. Relationship between interlayer distance (Δd) and the increment of heat capacity (ΔC_p) for polyol/clay intercalated nanocomposites.

at 60 °C, and then chain extender BD and MDI was added into the mixture to form polyurethane. Fig. 4 shows the X-ray diffraction pattern of PU nanocomposites with the clays of different *d*-spacings. The original *d*-spacings of clays for S0, S3, B30, 25A and C20A are 1.17, 1.37, 1.81, 1.86 and 2.42 nm, respectively. After intercalation, *d*-spacings of clay for S0, S3, B30, 25A and C20A are expanded to 1.59, 1.65, 2.05, 3.26 and 3.56 nm, respectively. The thickness of the clay layer is about 1 nm [25], so the interlayer distances as illustrated in Fig. 1 for S0, S3, B30, 25A and C20A are 0.59, 0.65, 1.05, 2.26 and 2.56 nm, respectively.

Fig. 5 shows the dC_p/dT signals versus temperature curves for blank polyol 6000 and polyol/clay intercalated nanocomposite. The peak area of dC_p/dT versus temperature is equal to the increment of heat capacity ΔC_p, at the glass transition temperature [26]. Fig. 6 shows the relationship between the interlayer distance (Δd) and the increment of heat capacity (ΔC_p) for polyol/clay intercalated nanocomposite. As calculated above, all the interlayer distances for S0, S3, B30, 25A and C20A are smaller than the characteristic length ξ_a of polyol (3.23 nm); it is clear that the ΔC_p values for polyol/clay intercalated nanocomposite are smaller than that of blank polyol (0.441 J/g °C). The decrease of ΔC_p should be attributed to the confinement of polymer chains in the interlayer spacing. It is believed that a certain immobilization near an interface exists. However, measurement of ΔC_p cannot provide such information because the change of ΔC_p resulting from immobilization near an interface is very small, which is within experimental error. The interlayer spacing of the expanded clay is too little for polyol to the occurrence of cooperatively rearranging at the dynamic glass transition. However, there is another situation for polyol-based polyurethane system. Fig. 7 shows the dC_p/dT signals versus temperature curves for blank PU and PU/clay intercalated nanocomposite. Fig. 8 shows the relationship between interlayer distance (Δd) and the increment of heat capacity (ΔC_p) for PU/clay intercalated nanocomposite. For clays S0, S3 and B30, there are small interlayer distances, smaller than the characteristic length ξ_a of bulk polyurethane (1.45 nm), the ΔC_p values are reduced. However, for clays 25A and 20A, the interlayer *d*-spacing is big enough for cooperatively rearranging of polyurethane molecular chain at dynamic glass transition, ΔC_p values remain the same as that of bulk polyurethane. It is necessary to mention again that

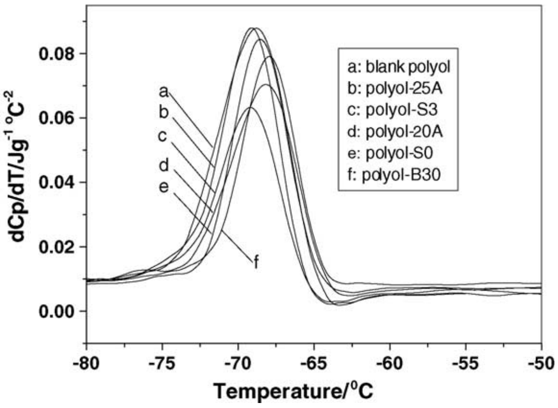

Fig. 5. dC_p/dT vs. temperature signals for blank polyol 6000 and polyol/clay intercalated nanocomposites.

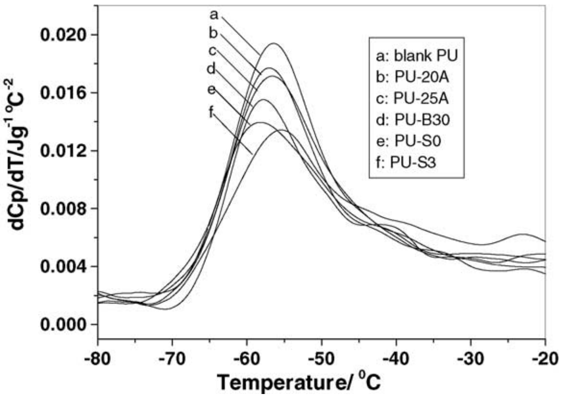

Fig. 7. dC_p/dT vs. temperature signals for blank PU and PU/clay intercalated nanocomposites.

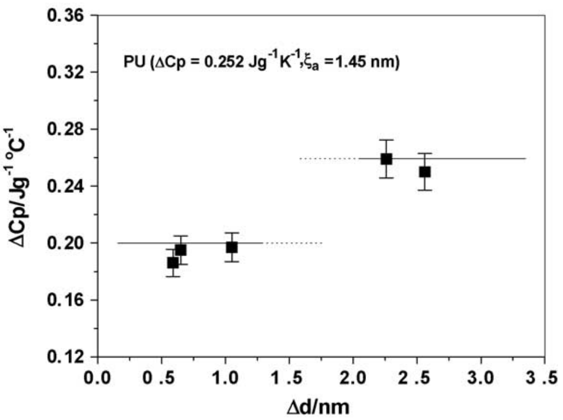

Fig. 8. Relationship between interlayer distance (Δd) and the increment of heat capacity (ΔC_p) for PU/clay intercalated nanocomposites.

the calculated ξ_a value for polyol and PU/clay intercalated nanocomposite does not nearly change with different clays.

So, our results suggest that if the interlayer spacing Δd of clay is less than the characteristic length of the dynamic glass transition (ξ_a), the intercalated polymer will show no transition at the crossover of the glass transition of bulk polymer, and the increment of heat capacity determined (ΔC_p) will decrease. This situation occurred for all kinds of clays we investigated in this study in polyol system and for S0, S3 and B30 clays in polyurethane system. On the contrary, if Δd is bigger than the ξ_a, the intercalated polymer will show the same glass transition behavior as the bulk polymer and the increment of heat capacity will remain invariable. This situation occurred for clays 25A and 20A in polyurethane system. The dependence of ΔC_p with clay interlayer distance shows that the calculated characteristic lengths, i.e., ξ_a (polyol) ~ 3.20 nm and ξ_a (PU) ~ 1.45 nm with Donth's formula are reliable.

5. Conclusion

Polymer/clay intercalated nanocomposites with different *d*-spacings provide a good two-dimensional (2D) space to determine the characteristic length of the dynamic glass transition. The characteristic length (ξ_a) varies with polymer types, i.e., ξ_a (polyol) ~ 3.20 nm and ξ_a (PU) ~ 1.45 nm. In the polyol/clay intercalated nanocomposites, the interlayer *d*-spacings Δd for all kinds of clay investigated in this study are smaller than the characteristic length ξ_a of polyol; the intercalated polyol were immobilized, consequently, ΔC_p decreased. In the PU/clay intercalated nanocomposites, the interlayer *d*-spacings of clays S0, S3 and B30 are smaller than the ξ_a of polyurethane, ΔC_p decreases; however, the interlayer *d*-spacings of clays 20A and 25A is bigger than ξ_a (PU), ΔC_p remains the same as that of PU. The experimental determination of the characteristic length based on the different dependence of ΔC_p with Δd between polyol/clay and PU/clay nanocomposites agrees with the theoretical calculation from Donth's formula.

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