

A MTDSC analysis of phase transition in polyurethane–organoclay nanocomposites

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Abstract

Modulated differential scanning calorimetry (MTDSC) was applied to investigate the phase transition behaviour of polyurethane/organoclay nanocomposites. The endotherm transitions located at 50–80 and 140 °C were re-analysed through revealed thermal features in the MTDSC reversing, non-reversing and dC_p/dT curves. It was proposed that the diffused interfacial phase exists between hard and soft phases in the polyurethane system. The assignment of endotherm at 140 °C is attributed to the hard microphase domain transition, which is similar to an order–disorder transition. The transition in the region of 50–80 °C reveals the relaxation of segments in the interface resulted by annealing. The addition of organoclay resulted in a reduction of hard domain ordering level. A simple method for quantitatively estimating the amount of polymer chains intercalated into layers of clay was introduced, and the relationship between the weight fraction (ω_p), of the polymer intercalated into layers and the weight fraction (ω_c), of clay was established.

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1. Introduction

Polyurethanes (PUs) are multiple block copolymers composed of alternating hard and soft segments, which, due to the incompatibility of two dissimilar segments, form a two-phase microstructure. The soft segments are generally polyethers or polyesters with the glass transition temperature (T_g) in the range of –70 to –30 °C and the hard segments are formed from the extension of a diisocyanate with a low molecular weight diol having a high T_g . The segments aggregate into microdomains resulting in a structure consisting of glassy hard domain and rubbery soft domain at room temperature. Depending on the hard segment content, the morphology of hard domains changes from isolated domains to interconnected domains [1]. The material containing less than 50% hard segment by weight exhibits a discrete hard-segment morphology, and with higher amounts of hard segment, over 50%, hard-segment domains show a lamellar crystalline structure [1]. In polyurethanes, the hard domain serves as physical crosslinks or filler particles and also as reinforcement to the soft segment matrix. The

presence of hard domains in the materials is directly related to the physical properties.

However, domain morphology of the materials is also sensitive to sample thermal history. Morphological change in segmented polyurethane induced by thermal treatment has been widely studied in the past 30 years by a number of researchers by means of differential scanning calorimetry (DSC) [2–5]. Briefly, for polyurethane with a non-crystalline order structure (hard segment content less than 50%), three typical thermal transitions can be detected by a DSC curve at temperature regions of –70 to 190 °C. The transition located at between –70 and –30 °C behaves as step-change in the signal, which is well known to correspond to the glass-to-rubber transition of the soft segments. Other transitions located at 50–80 and 120–190 °C (denoted as I and II) present two endotherms. These endothermic behaviours have been considerably researched. The various points of view in understanding these thermal transitions have been reported. Seymour and Cooper [2,3] have demonstrated that these two endotherm transitions correspond to the disordering of hard segments. The endotherms in regions I and II are ascribed to disruptions of short range and long range segment ordering, respectively. The appearance of two peaks is partially the result of the wide distribution of hard segment lengths. However, Finnigan et al. [4] has suggested the endotherm II

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is attributed predominantly to the disruption of various degree of short-range hard segment ordering.

Hesketh et al. [5] have studied the microstructure changes accompanying annealing and quenching in segmented elastomer by DSC analysis. They have reported that the applied thermal history promoted increased mixing of hard and soft segments. The short-range ordered hard segment domain associated endotherm I resulted from storage and annealing. Endotherm in region II is attributed to the break-up of long-range hard segment ordering in hard domains resulting from the annealing process. Koberstein et al. [1] have investigated microdomain morphology of a series polyurethane block polymers as a function of hard segment content. They have identified the endotherm transition in region I as reflecting the appearance of glass transition-like process of hard microdomain. Eisenbach et al. [6] have pointed that in polyurethanes this endotherm could be attributed to the disordering of hard segments in the boundary region between the soft and hard phases. More recently, Wang [7] has studied thermal behaviours of fluorinated polyurethanes and believes that the endotherm in region I resulted from domain formed during ageing.

It is clear from above briefly review that, at present, there are different understanding physical meanings concerning the thermal events and that it is still not thoroughly understand what transition process results in these thermal events. The microphase transition induced by a thermal treatment could include more complex thermal events. However, when more than one phase transitions occur involving in a multiple thermal process the limitation of DSC measurements cannot separate the overlap thermal events [8,9].

Modulated differential scanning calorimetry (MTDSC), which is a relatively new technique, has been successfully used to study miscibility of polymer blends, interface, physical ageing, and latex structure [10–15]. It can produce not only the total heat flow obtained from conventional DSC, its advantage is that it is able to separate complex transitions into more easily interpreted components and directly measure heat capacity changes from a single experiment [16,17]. And MTDSC measurement can also present more important information by a series of thermographs in characteristic of reversing and non-reversing heat flow signals, which reveal thermal behaviour such as the glass and melting transitions, and physical ageing and crystallisation, etc [18,19].

In this report, MTDSC was applied to investigate the phase transition in PU/organoclay nanocomposites. The two main purposes in this research are re-analysing the physical meaning of the endotherm signals, and establishing a simple method for estimating the amount of PU intercalated into the gallery of the layered clay.

2. Experiments

2.1. Materials

Poly(propylene glycol) (Luprane 2090, molecular weight = 6000, function = 3), was kindly provided by Elastogran UK Ltd. 4,4'-Methylene bis(cyclohexyl isocyanate) and 1,4-butanediol

were purchased from Aldrich Chemical Company. Dabco-33LV was obtained from Air Products and Chemicals. Stannous 2-ethyl hexanoate was purchased by Sigma Chemical Company. Layered silicate (clay) used in our experiments was Cloisite[®] C20 purchased from Southern Clay Products (TX, USA). Na⁺-montmorillonite (Na⁺-clay) – PGW was obtained from Nanocor in USA.

2.2. Sample preparation

A series of PU/organoclay nanocomposites were prepared. The process was as follows: firstly, the polyether polyol and the organoclay were blended and stirred for 4 h at 60 °C. Then the mixture was blended with 1,4-butanediol, Dabco-33Lv, stannous 2-ethyl hexanoate and 4,4'-methylene bis(cyclohexyl isocyanate) at room temperature for 1 min and was vacuum degassed for 5 min. Then the viscous prepolymer was poured into an O-ring metal mould and cured at 50 °C for 24 h, and then 80 °C for 1 week.

2.3. Differential scanning calorimetry and modulated differential scanning calorimetry

Differential scanning calorimetry (DSC) and modulated differential scanning calorimetry (MTDSC) were used in this research for the characterisation of the phase transition behaviour. A TA Instrument DSC 2920 calorimeter was employed. Oscillation amplitude of 1 °C and oscillation period of 60 s with heating rate of 3 °C/min was used for the MTDSC experiments. Heating rate for DSC was 10 °C/min.

3. Results and discussion

3.1. Analysis of phase transition behaviour in PU/organoclay nanocomposites

A series of PU/organoclay (C20 clay) intercalated nanocomposites [20–22] were prepared with 36% hard segment content, which means the samples used in this study are the non-crystallized and ordered structures. Fig. 1 shows a typical thermal curve of total specific heat flow versus temperature for the PU/organoclay nanocomposites (downward is endothermic). Three transitions are clearly observed: one is the glass transition of soft segments at about –60 °C, the other two transitions are located at about 50–80, and 140 °C, respectively, which show an endothermic peak as a melting-like transition. Addition of organoclay resulted in a significant shift of the endothermic peak at about 50–80 °C to a greater temperature and a decrease in the area of the peak. The peak at about 140 °C has a slight movement to lower temperature.

The non-reversing specific heat flow signals versus temperature for these PU nanocomposites are shown in Fig. 2, giving a clearer picture of the three transitions compared with Fig. 1.

For further understanding of the nature of the transition of the hard domains, the reversing signals of heat capacity versus temperature for these PU nanocomposites are presented in Fig. 3. It can be seen that there are only two clear step-

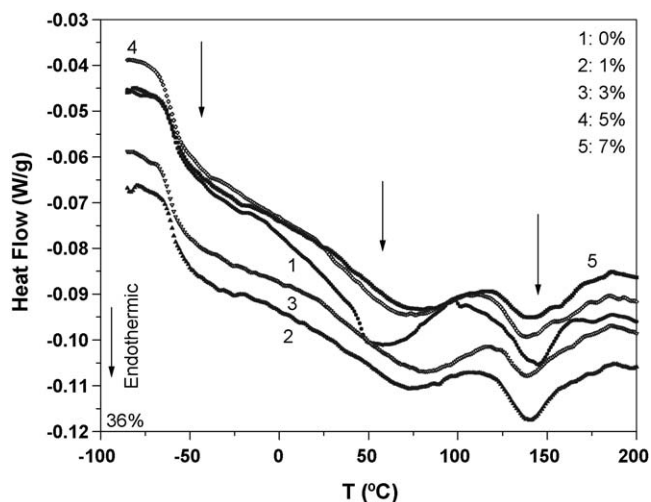


Fig. 1. MTDSC thermograms of PU/organoclay nanocomposites.

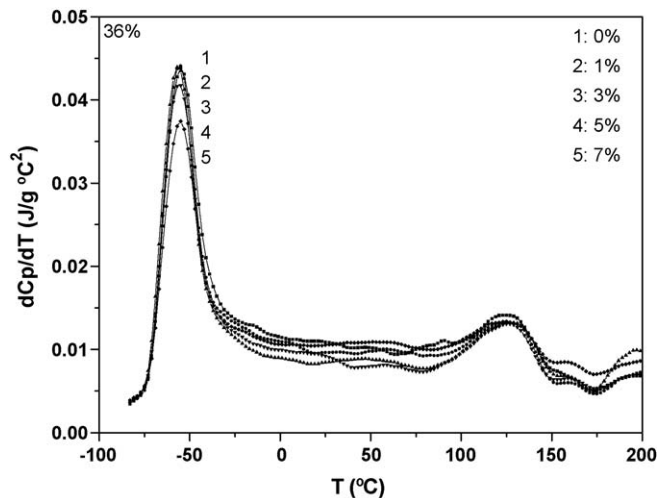


Fig. 4. Differential of specific heat capacity signals vs. temperature, dC_p/dT , for PU/organoclay nanocomposites.

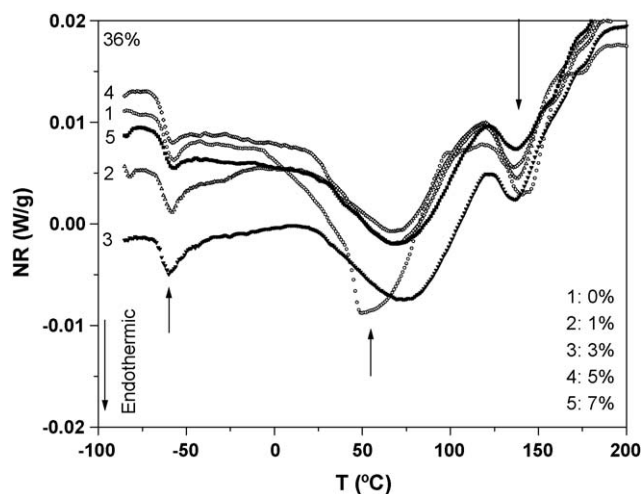


Fig. 2. Non-reversing heat flow signals vs. temperature for PU/organoclay nanocomposites.

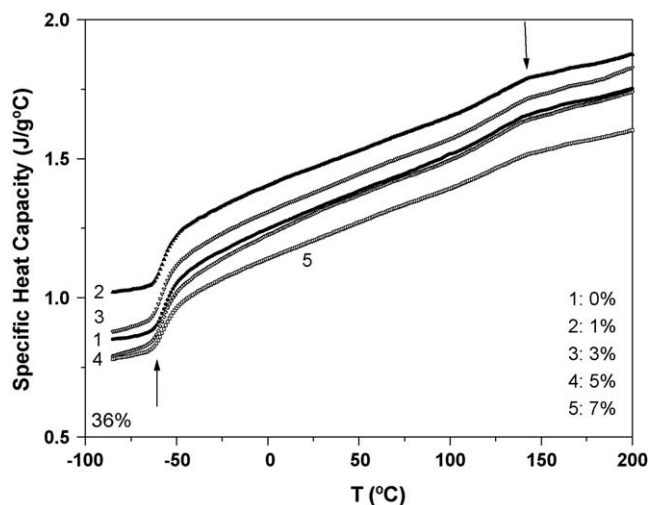
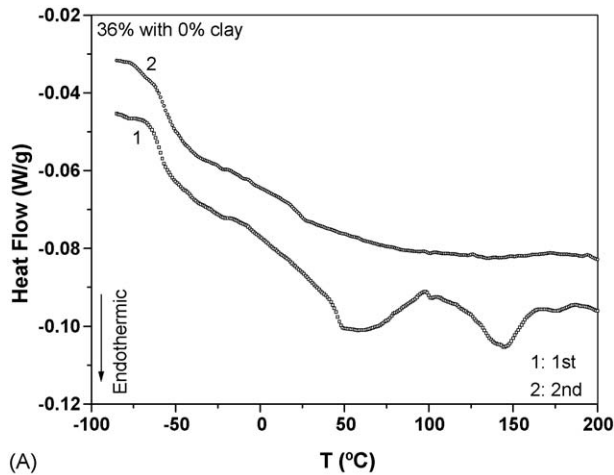


Fig. 3. Specific heat capacity vs. temperature signals for PU/organoclay nanocomposites.

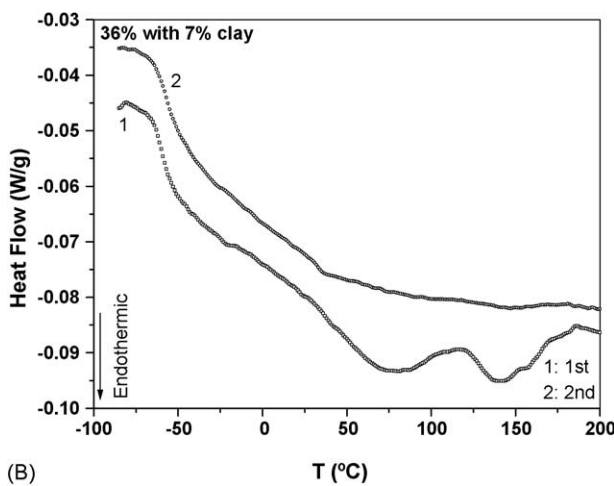
change transitions at -60 and 140 °C, respectively, and there is no obvious change at about 50 – 80 °C. These results illustrate that the step-change at -60 °C is evidence of the glass transition of soft segment and the other at 140 °C is the transition of hard domains. So here it is concluded that the transition of such structured hard domains is like an order–disorder transition [23]. Fig. 4, showing the differential of specific heat capacity signal, dC_p/dT versus temperature for the PU/organoclay nanocomposites, illustrates that the transition of hard domains is similar to the glass transition of soft segments. However, the non-reversing specific heat flow and dC_p/dT signals reveal that thermal event located at 50 – 80 °C is quite different from that located at 140 °C.

The thermal event located at 50 – 80 °C may likely be a result of annealing treatment. In order to confirm this assumption, some experiments were carried out with controlled thermal histories. The results are shown in Fig. 5a and b for pure PU containing 36% hard segments and its nanocomposite with 7% organoclay content, respectively. The experimental procedure is as follows: the sample were prepared and stored at 25 °C for 20 days, and tested (first), in which there are three transitions observed as discussed in Fig. 1. Then, the sample was rapidly quenched from 200 to -100 °C, retested immediately (second). In contrast, the endothermic events, except for the glass transition, in the second MDSC trace were absent for both the PU and its nanocomposites.

In order to know what happen to these thermal events, the differential of specific heat capacity signals, dC_p/dT versus temperature for the PU and the PU nanocomposite are also given in Fig. 6a and b, respectively. It can be found that that a broad transition peak from -20 to 140 °C appears instead of the peak located at 140 °C in the dC_p/dT signal, which suggests that the content of the interface between soft and hard segment domains increased [24]. It is believed that there are three phases in segmented polyurethane; soft and hard segment domain phases, and diffused interface between the soft and hard domain phases. The phase transition in polyurethanes is directly related to the



(A)

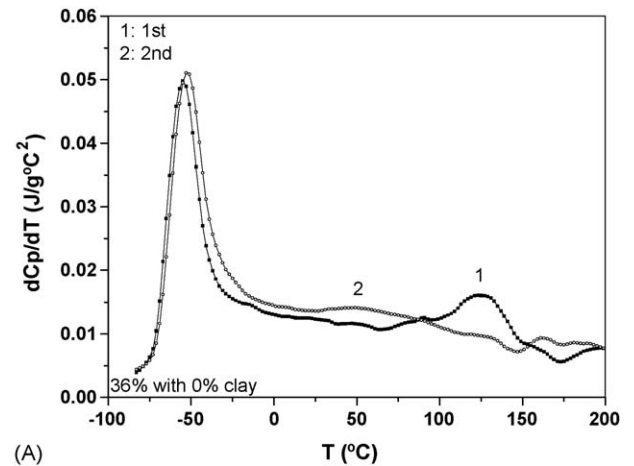


(B)

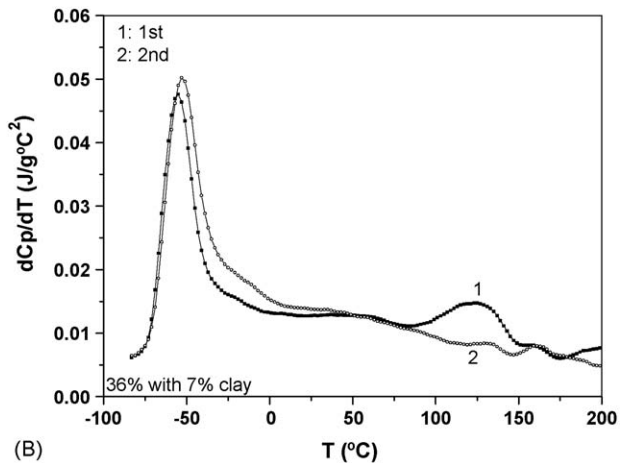
Fig. 5. Specific heat flow signals vs. temperature for first and second heating scan: (A) for pure PU and (B) for PU nanocomposite with 7% organoclay content.

state of the interface. By rapid cooling from 200 to -100°C , the degree of the phase mixing could remain in the origin state of the interface at 200°C . The part of hard segments dissolved into the soft segment domains could be frozen. Hence, a wider and less ordered phase formed. So the transition located at 140°C became very weak as revealed by the dC_p/dT signal, which implies the disappeared peaks in the second heating scan (in Fig. 5a and b) resulted from phase dissolution being composed of hard segment rich-phase [25]. Thus, the formed hard domain rich-phase shows a broad transition.

The effects of the concentration of hard segments and organoclay on thermal transition were also studied as shown in Fig. 7a and b, respectively, presented by the non-reversing signals of specific heat flow versus temperature for the two systems of pure PUs and PU nanocomposites (5% C20) with different hard segment contents. As seen from Fig. 7a, the transition located at 140°C significantly correlates to hard segment content. The endothermic peak area increased with increasing hard segment content, which reflects an increase in the ordering degree of hard domain. The peak area (at $50\text{--}80^{\circ}\text{C}$) also increased and the peak position shifted to a lower temperature as the concentration of hard segments was increased.



(A)



(B)

Fig. 6. dC_p/dT signals vs. temperature for first and second heating scan: (A) for pure PU and (B) for PU nanocomposite with 7% organoclay.

As indicated in Fig. 7b, the incorporation of clay resulted in a reduction of the peak area (at 140°C), indicating that the ordering degree of hard domains decreased. This effect is the same as the effect on a block copolymer [23]. From Fig. 7a and b, the endothermic peaks as shown in the non-reversing signals reveal that the transition located at $50\text{--}80^{\circ}\text{C}$ is a relaxation of chain segments in the interface.

From the above discussion it is proposed that the endothermic behaviour located at $50\text{--}80^{\circ}\text{C}$ is not a microphase-domain transition but is the relaxation of chain segments in the diffused interface between soft and hard segment phases. In order to confirm this conclusion, a further investigation was performed by means of DSC. The steps of the experiment are as follows. First of all, the specimens initially were heated to 180°C and annealed at this temperature for 5 min, then cooled down to 65 (or 85°C) and annealed at this temperature for different times. DSC scan was taken at heating rate of $10^{\circ}\text{C}/\text{min}$ from 30 to 150°C after annealing immediately.

Fig. 8 shows DSC specific heat flow signals versus temperature for three samples treated at different annealing temperatures and times. As indicated in Fig. 8, the transition temperature is related to the annealing temperature, and approximates 25°C higher than annealing temperature. With increasing anneal-

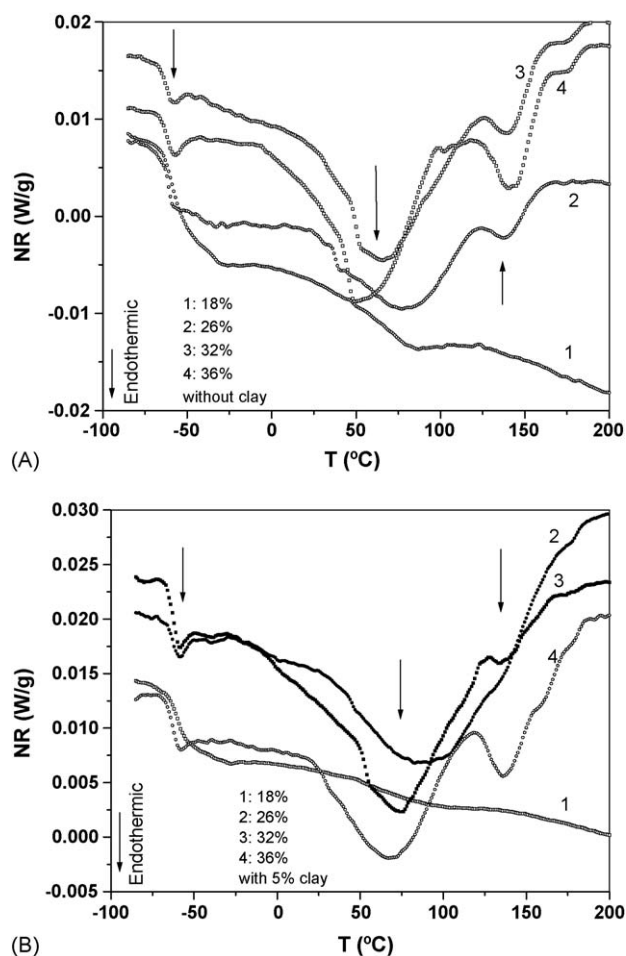


Fig. 7. The non-reversing specific heat flow signals vs. temperature: (A) pure PU with different hard segment contents and (B) PU nanocomposites (5% C20) with different hard segment contents.

ing time the peak area increased, suggesting that the relaxation enthalpy increased. Why does a long annealing treatment lead to an increase in the relaxation enthalpy, where does it come from?

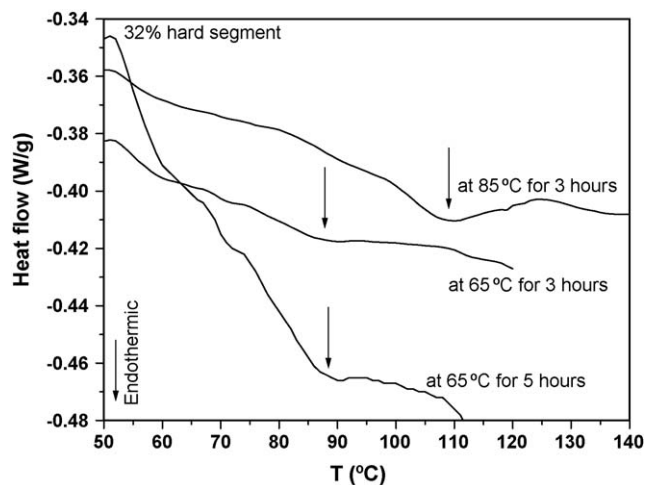


Fig. 8. DSC specific heat flow vs. temperature signals for the samples with different annealing temperatures and annealing times.

In a segmented PU system, the diffused interfacial phase could be considered as multi-systems and the glass transition temperature is a function of distance from a discrete phase boundary between the soft and hard segment phases. The interfacial phase can be divided into N subsystems. For the N subsystems, there is a glass transition temperature spectrum, $T_g^1, T_g^2, T_g^3, \dots, T_g^N$. The values for our samples range from -60°C (soft segment's T_g) to 140°C (hard segment's T_g), i.e. $T_g^1 \approx -60^\circ\text{C} < T_g^2 < T_g^3 < \dots < T_g^N \approx 140^\circ\text{C}$. When the annealing temperature is 65°C (or 85°C), the physical ageing in the subsystems, in which the glass transition temperatures are higher than 65°C (or 85°C), is able to take place. With increasing annealing time, the relaxation enthalpy will increase.

Here it can be concluded that the endothermic behaviour at $50\text{--}80^\circ\text{C}$ is not the glass transition of hard microdomain, it is a result of the relaxation of chain segments in the diffused interface between soft and hard domains. The endotherm observed at 140°C in our samples, which is a non-crystallized order structure, is attributed to order–disorder transition of hard domains.

3.2. Estimation of polymer intercalated into the gallery of the layered clay

Recently, various intercalated polymer/layered silicate nanocomposites have been prepared. The performance improvements of polymer nanocomposites depend to a large extent on the distribution and arrangement of the clay layers as a result of intercalation and/or exfoliation, and on the interfacial bonding between the clay layers and the polymer [26,27]. So in practice, in order to prepare polymer nanocomposites with expected physical properties for a certain application it is important to identify what percentage of polymer is intercalated into the layers of clay. In this section we will introduce a simple method to estimate the weight fraction of polymer intercalated into the layers of clay.

The increment of specific heat capacity, ΔC_p , at the glass transition temperature is characteristic of a polymer. The value of ΔC_p can be used as an indication of the relative purity of the polymer. [28].

Fig. 9 shows the dC_p/dT versus temperature for PU with 18% hard segment and its nanocomposites with 5%, or 10% C20-clay by weight. It is notable that the addition of the organoclay had no significant effect on the glass transition of soft segments and the peak area of dC_p/dT .

The glass transition behaviour of intercalated polymer chains in the PU/clay intercalated nanocomposites with different kinds of clay has been studied in our previous work [29]. The glass transition behaviour for the intercalated polymer nanocomposite is dominated by the relative size between interlayer d -spacing of the clays and the characteristic length of dynamic glass transition (ξ_a). The clay gallery in polymer/clay intercalated nanocomposites as a confined two-dimensional (2D) space to assess ξ_a . In the PU/clay intercalated nanocomposites, if the interlayer d -spacing of clays is bigger than the ξ_a of the PU chains, the intercalated polymer will show the same glass transition behaviour as the pure polymer and there is no change in ΔC_p . If the interlayer

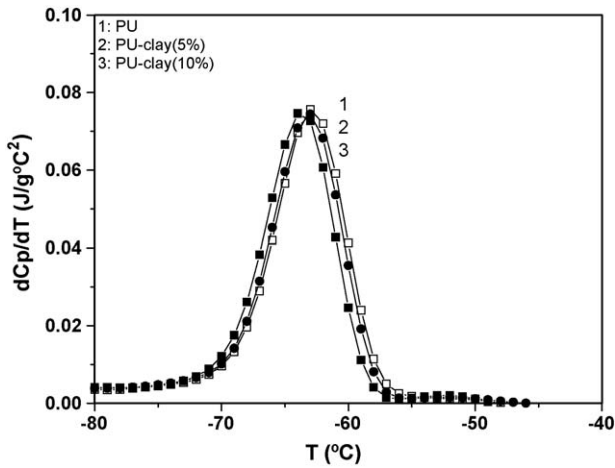


Fig. 9. dC_p/dT signals vs. temperature for PU/C20-clay nanocomposites.

d -spacing is smaller than the ξ_a , the intercalated polymer will not involve transition at the crossover of the glass transition of pure polymer. So it was suggested that the transition of polymer chains intercalated into the gallery of the layered C20-clay cannot be restricted due to the bigger interlayer d -spacing than the ξ_a of the PU chains. For C20-clay the interlayer d -spacing is big enough for cooperatively rearranging of PU chains during dynamic glass transition, ΔC_p value remains as the same as that of pure PU.

Figs. 10 and 11 show dC_p/dT signals versus temperature for the pure polyol of poly(propylene glycol) and the polyol C20-clay (5% by weight) blend, and PU/Na⁺-clay intercalated nanocomposites (0%, 5% and 21% by weight), respectively. Obviously, effects on ΔC_p and T_g exist in these systems. The addition of clay leads to the increase in T_g and the decrease in ΔC_p , which indicates that part of the PU chains intercalated into the layers of the clays did not participate in the glass transition process. It is believed that the PU chain segments intercalated into the layers of the clays could be confined.

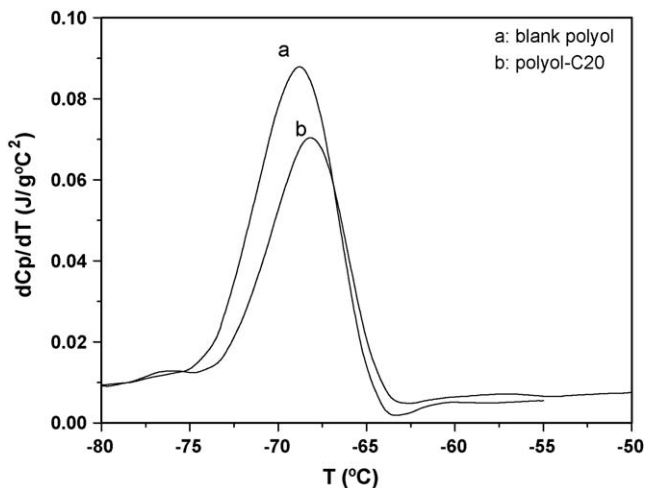


Fig. 10. dC_p/dT signals vs. temperature for polyol/clay nanocomposite (5% by weight).

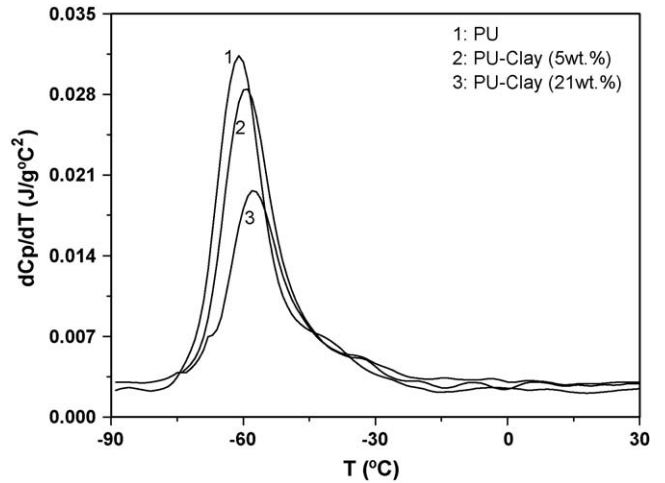


Fig. 11. dC_p/dT signals vs. temperature for PU/Na⁺-clay nanocomposites with different weight fractions of layered clay.

Fig. 12 shows the linear relationship between clay content and ΔC_p for the PU/Na⁺-clay intercalated nanocomposites. By using a simple method [30], the weight fraction, ω_p of polymer chain intercalated into the layers of the clay can be estimated.

$$\omega_p = \frac{1 - \Delta C_p(\text{PU intercalated nanocomposite})}{\Delta C_p(\text{pure PU})} \quad (1)$$

A relationship between the weight fraction (ω_p) of PU intercalated into the layers of the layered clay and the weight fraction (ω_c) of the layered clay can be obtained as follows.

$$\omega_p = 1.18 \omega_c. \quad (2)$$

This relationship was tested and satisfactory for several intercalated systems, in which the interlayer d -spacing is smaller than the ξ_a of polymer used. We believe that by applying Eq. (2) the weight fraction of the polymer chains intercalated into the layers of clay can be estimated.

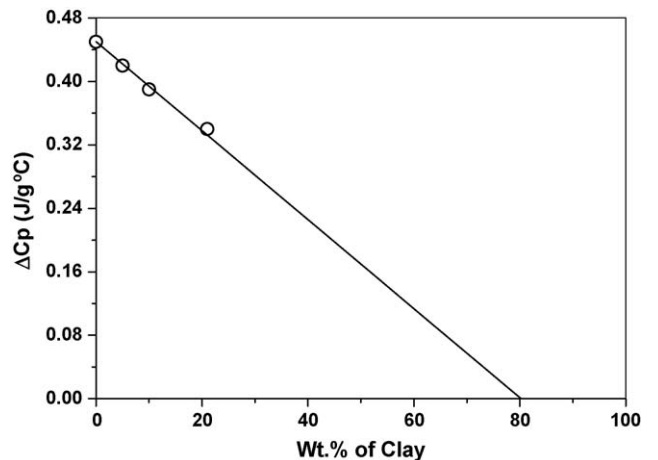


Fig. 12. Relationship between clay content and ΔC_p of PU/Na⁺-clay intercalated nanocomposites.

4. Conclusion

In the study of PU/organoclay nanocomposites, the transition behaviours at 50–80 and 140 °C were clearly observed by means of MTDSC. The reversing, non-reversing and dC_p/dT signals versus temperature provide direct information regarding the thermal transition process, which help us to better understand and re-analyse the endothermic behaviours. It was proposed that the diffused interfacial phase exists between soft and hard segment domains in a PU system. The transition at 50–80 °C resulted from by the relaxation of the PU chain segments in the interface in which the glass transition temperature is higher than annealing temperature, and the assignment of endotherm at 140 °C corresponded to the order–disorder transition of hard segment microdomains. The addition of organoclay resulted in a reduction of ordering level of hard segment domains. A simple method for estimation of the content of polymer chains intercalated into the layers of clay was established. This method may be helpful in practice for preparing intercalated polymer/clay nanocomposites.

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