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Modulated differential scanning calorimetry: 6. Thermal characterization of multicomponent polymers and interfaces

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A quantitative thermal method of determining the weight fraction of interface and the extent of phase separation in polymer materials is described. It is based on the differential of heat capacity signal from modulated-temperature differential scanning calorimetry. By measurement of the increment of heat capacity at the glass transition temperature, the total interface content can be determined. The method assumes that the interface and the rest of the system can be modelled as a series of discrete fractions each with its own glass transition temperature. Several examples, including block copolymers, block copolymers blended with homopolymer, and two-phase and four-phase systems are given to illustrate the range of the method. The calculated results were close to the experimental data for two-phase and four-phase systems. Copyright © 1996 Elsevier Science Ltd.

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INTRODUCTION

Many types of multicomponent polymeric materials are commercially important. Of these, many exhibit phase separation. A common feature across the spectrum of such multiphase polymer materials is the presence of large regions of interface. These interfaces are invariably important in controlling the properties of the composite and the ability to understand and optimize the interface is recognized as a key feature in developing improved materials. The majority of polymer–polymer blends are two-phase and their morphologies depend on the type of molecular interaction present, the rheology of the components and the processing history.

Models used to describe multiphase materials show that properties of these materials can be correlated with the interface volume fraction[1,2]. Many techniques have been used to determine the fraction of materials contained in the mixed regions between micro-phases. Porod analysis[3] of small-angle X-ray and neutron scattering data can be used to estimate the thickness of the interface. However, the experimental difficulties of the methods and competing effects have been discussed fully by a number of authors[4,5]. Dynamic mechanical[6] data can be modelled by assuming interfacial profiles, but this method requires large interface volume fractions. A technique that yields both interfacial thickness

and composition gradient across the interface is transmission electron microscopy. Results from highly ordered systems have been obtained that are in good agreement with small-angle X-ray[7], dynamic mechanical[7] and ellipsometric measurements[8], but preparation of appropriately ordered samples for which this last technique may be used can be difficult.

However, it is also possible to estimate the volume fraction of interfacial material by means of thermal techniques[9,10]. One method, applied to phase separated block copolymers, uses the change in heat capacity due to the glass transition of each block relative to the corresponding values for the present homopolymers to estimate the quantity of material in the microphases[9]. It is difficult, however, to determine the heat capacities accurately and directly using conventional differential scanning calorimetry (d.s.c.).

Recently, a new thermal analysis instrument[11], modulated-temperature differential scanning calorimetry (M-t.d.s.c.), has become available. In this instrument, the calorimeter block is subjected to a temperature ramp that is linear, when averaged over time, but which has a sinusoidal modulation. A good review[12] of the technique has already been written. Heat capacity values can be determined readily and accurately by using this M-t.d.s.c. technique. In this paper, the differential of heat capacity signal was used to calculate the increment of heat capacity over the glass transition region and the use of this technique for
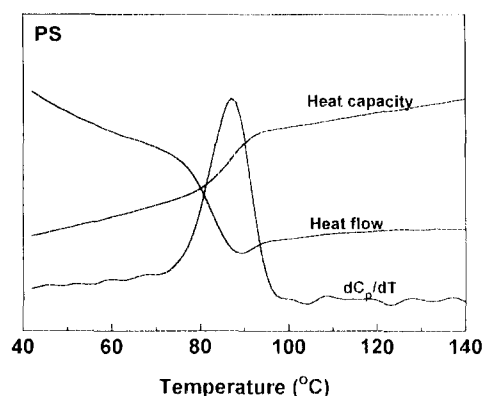
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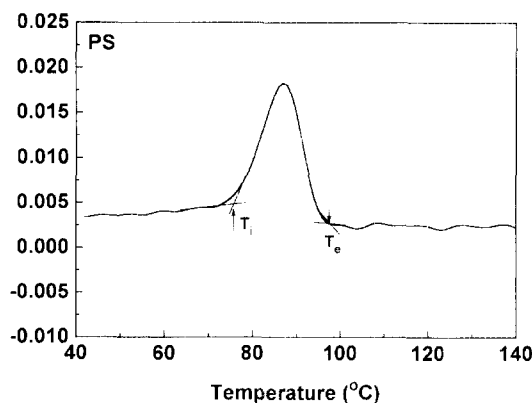**Figure 1** Changes of heat flow, heat capacity and dC_p/dT with temperature

Figure 2 Definition of temperatures T_i and T_e

probing the internal interfaces in multicomponent polymers is discussed in detail.

BACKGROUND OF THE ANALYSIS

The glass transition temperature, T_g, is a parameter whose value is sensitive to many microstructural aspects of the material. For a miscible two-polymer blend, T_g depends on the composition ratio. The increment of heat capacity, ΔC_p, at T_g, which has been shown[13] to be larger than in an immiscible polymer blend, will vary with the proportion of the two polymers. For immiscible polymer blends, the total ΔC_p is just the algebraic sum of the ΔC_p values of the two pure polymers[9,13].

$$\Delta C_p = \omega_{10}\Delta C_{p1} + \omega_{20}\Delta C_{p2} \qquad (1)$$

ω_{10} and ω_{20} are the weight fractions of polymer 1 and polymer 2, respectively. ΔC_{p1} and ΔC_{p2} are the values of the increment of heat capacity at the corresponding T_{gs}. During d.s.c. studies of a partially miscible polymer blend, Kang[14] found that the values of ΔC_{p1} and ΔC_{p2} decreased when the proportion of two components was changed. Fried[15] observed similar behaviour. He attributed the behaviour in his system to the presence of a large amount of material in the interfacial regions, and postulated that the amount of this material could be related to the ratio F as defined below.

$$F = (\omega_{10}\Delta C_{p1} + \omega_{20}\Delta C_{p2})/(\omega_{10}\Delta C_{p10} + \omega_{20}\Delta C_{p20}) \qquad (2)$$

Table 1 Polymers used in these experiments

Polymer	Source	$M_w \times 10^{-5}$	M_w/M_n
PS	BP Chemicals	2.1	2.3
PPO	Aldrich	2.4	3.2
PVAc	Aldrich	5.2	3.8
PMMA	Aldrich	2.0	2.0
PVC	Aldrich	3.3	2.8
SIS(PS 27.4%)	Polysciences	1.8	1.4

ΔC_{pi0} values are the increments of heat capacity at the T_gs before mixing. When no interface exists, the value of F is equal to 1.0. The Fried[15] ratio provides only a qualitative measure of the amount of interface in polymer blends. In fact, the use of the actual weight fractions contributing to the ΔC_{p1} and ΔC_{p2} values can provide an analytical expression which yields the amount of material in the interface regions. According to equation (1), when a system exhibits an interface, the following equations hold.

$$\Delta C_p = \Delta C_{p1} + \Delta C_{p2} + \Delta C_{pi} \qquad (3)$$

$$\Delta C_{p1} = \omega_1\Delta C_{p10} \qquad (4)$$

$$\Delta C_{p2} = \omega_2\Delta C_{p20} \qquad (5)$$

ω_1 and ω_2 are the weight fractions of components 1 and 2, respectively, in the mixed phases. ΔC_{pi} is the increment of heat capacity of the interface in its glass transition region, and δ_1 and δ_2 in the following equations are the weight fractions in the interface of polymers 1 and 2, respectively, which can be obtained from the following equations.

$$\delta_1 = \omega_{10} - \Delta C_{p1}/\Delta C_{p10} \qquad (6)$$

$$\delta_2 = \omega_{20} - \Delta C_{p2}/\Delta C_{p20} \qquad (7)$$

ω_{i0} is the weight fraction of the polymers before mixing.

It is very important to get the ΔC_p value accurately. The glass transition is a thermokinetic phenomenon with no true order parameter[16]. It results from motions of segments which exhibit a glass transition spectrum. Thus, the heat capacity does not change suddenly in the glass transition region. Its differential, Δ, is not a delta function of temperature, but is sensitive to the glass transition process[17].

Figure 1 shows the changes of heat flow, heat capacity and dC_p/dT with temperature for polystyrene from M-t.d.s.c. data. The quantity ΔC_p is defined as follows.

$$\Delta C_p = \int_{T_i}^{T_e} [dC_p/dT]dT \qquad (8)$$

T_i and T_e are the initial and final values of the temperature in the glass transition region (see *Figure 2*). Thus, according to equation (8), it is possible to obtain accurate ΔC_p values experimentally[18].

EXPERIMENTAL

Materials

Characteristics and source details of the polymers used are given in *Table 1*. The molecular weight averages and polydispersities were determined by g.p.c. relative to polystyrene (PS) standards. The poly(n-butyl acrylate)
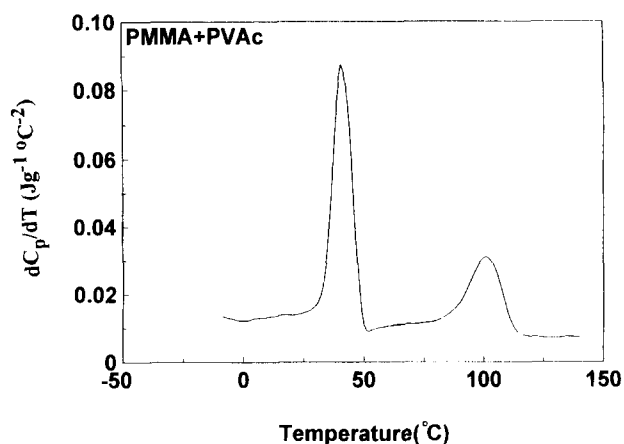
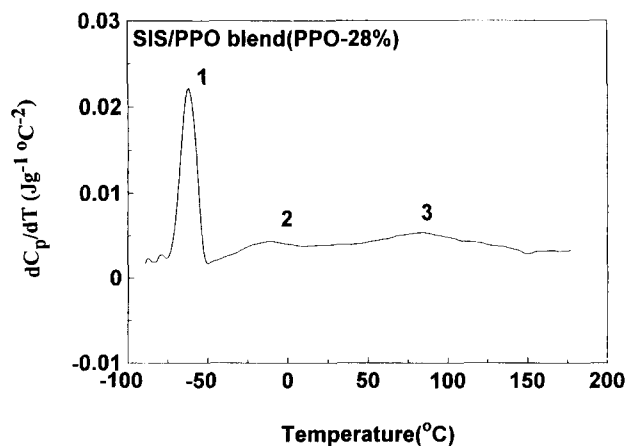**Figure 3** Variation of dC_p/dT with temperature for the PMMA + PVAc system. (PMMA/PVAc = 46/54, wt/wt)
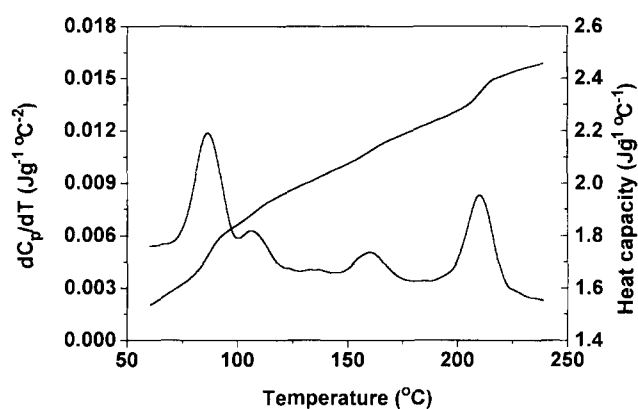

Figure 4 Variation of dC_p/dT and heat capacity with temperature for the PS + PPO + PPO30 + PPO70 system
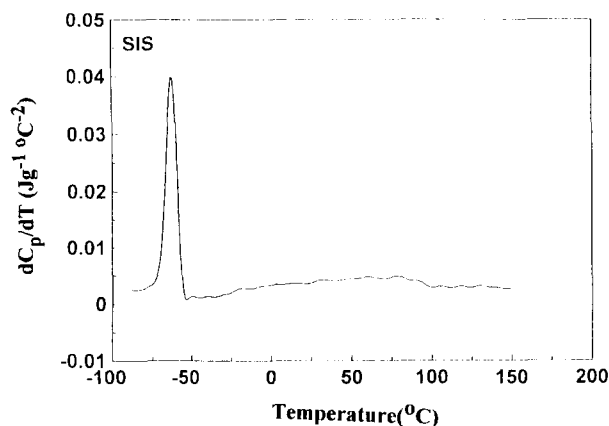

Figure 5 Variation of dC_p/dT with temperature for the SIS (PS 28 wt%) triblock copolymer

(PnBA) was synthesized in our laboratory. Its number-average molecular weight of 9.3×10^4 was determined by membrane osmometry.

Sample preparation

(1) Samples of PS blended with poly(phenylene oxide) (PPO), pure PS and PPO, a styrene-isoprene-styrene (SIS) triblock copolymer and SIS blended with PPO were prepared by solvent casting 5 wt% chloroform solutions

Figure 6 Variation of dC_p/dT with temperature for the SIS/PPO (PPO 28%) blend

into glass trays. After evaporation of the solvent at room temperature, the films were further dried under vacuum at 50°C for 28 days.

Two-component and four-component physical blends were also prepared by cutting the films of the pure polymers and blends into small pieces and mixing them manually at room temperature. Samples for M-TDSC measurements were flattened by applying heat (120°C) and pressure for *ca* 30 s in a Moore hot press.

(2) Samples showing phase separation were prepared by solvent casting 3 wt% chloroform solutions of poly-(methyl methacrylate) (PMMA) blended with poly(vinyl acetate) (PVAc) (50/50 wt/wt) into glass trays. After very slow evaporation of the solvent at room temperature, the sample was dried under vacuum at 40°C for 40 days.

(3) For the sample used to study thermal diffusion, sheets about 1.0 mm thick of poly (vinyl chloride) (PVC) and PnBA were sandwiched together into a M-t.d.s.c. pan with the PnBA on top. The sample was annealed at 135°C under N_2 for different times.

Instrumentation

A modulated-temperature differential scanning calorimeter from TA Instruments was used. An oscillation amplitude of 1.5°C and period of 60 s were used throughout the investigations which were conducted at a heating rate of $3°C min^{-1}$. The TA Instruments Graphware software was used to measure the heat flow, the heat capacity and the differential of heat capacity. The calorimeter was calibrated with indium and sapphire standards.

RESULTS AND DISCUSSION

Responses of dC_p/dT to morphology of multiphase materials

As is known from the literature[19], information about immiscibility in polymer blends can be obtained from T_g studies. There exist two T_gs for immiscible blends. The dC_p/dT signal for multi-phase materials also shows the same behaviour. *Figure 3* shows the variation of dC_p/dT with temperature for a PMMA/PVAc (46/54, wt/wt) two-phase system prepared as described in section 1 of the sample preparation given in the Experimental section.

Table 2 Determination of composition in multi-phase systems

		Weight fraction (%)	
Sample	Component	Experimental	Calculated
PVAc + PMMA	PVAc	54.0	51.1
	PMMA	46.0	44.3
PS + PPO + PPO30 + PPO70	PS	45.0	43.8
	PPO	34.5	37.3
	PPO30	7.1	6.6
	PPO70	13.4	12.2
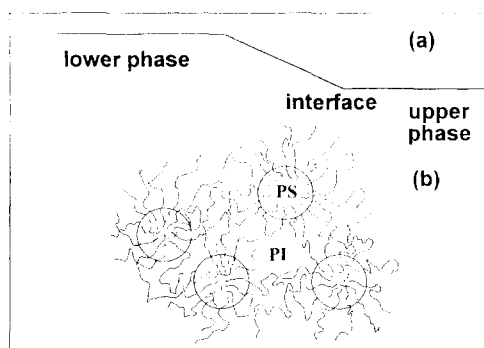
Figure 7 (a) Concentration profile of SIS triblock copolymer. (b) Morphological model for the SIS triblock copolymer

Table 3 Weight fraction of each component in the SIS and SIS/PPO blend samples

Sample	Component	Weight fraction (%)
SIS	PI	63
	PI–PS interface	37
SIS blended with PPO	PI	59
	PI/PS/PPO	29
	PS–PI interface	12

The sample was cooled from 150 to $-20°C$ at a cooling rate of $10°C\,min^{-1}$. The two transition regions, with no indication of an interface zone, are very clear.

Figure 4 shows the dC_p/dT and heat capacity change in a four-component [(PS +PPO + PPO70 (PPO/PS = 70/30, wt/wt) + PPO30 (PPO/PS = 30/70, wt/wt), 47/34/12/7, wt/wt)] physical blend. This four-component blend was prepared as described in section 1 of the sample preparation given in the Experimental section. From the heat capacity signal, two transitions between the transitions of pure PS and PPO are not particularly clear. Four transitions are clearly evident despite the fact that the PPO30 is present at 7% by weight only. The individual transition maxima in the four-component blend were observed to be occurring at the same temperature as for the individual components.

Figure 5 shows a result for a styrene-isoprene-styrene (SIS) triblock copolymer. The sharp peak is the dC_p/dT change at the glass transition for polyisoprene (PI). However, the weaker transition is very wide, ranging from *ca* -30 to $95°C$. This is taken to indicate that the morphology of the block copolymer is complex.

Figure 6 shows the dC_p/dT change with temperature for the same SIS triblock copolymer blended with PPO (SIS/PPO, 72/28, wt/wt). The results show three transitions. According to equations (1) and (3)–(7), it is possible to calculate the weight fraction for each component polymer.

The comparisons of the known values with the calculated ones are shown in *Table 2* for the earlier PMMA + PVAc and PS + PPO + PPO70 + PPO30 systems. The results show that the values calculated using these equations are close to the experimental values. It was, however, rather difficult to analyse the SIS and SIS/PPO systems. The data shown in *Figure 5*, compared to that in *Figures 3* and *4*, show that the morphology is obviously not a simple two-phase structure with sharp boundaries. It can be regarded as consisting of an essentially pure-PI phase, a PS-PI interfacial phase, and possibly an essentially pure-PS phase.

A schematic diagram representing a composition profile for the SIS triblock copolymer is shown in *Figure 7a*. The bulk PI and PS regions are considered to be of constant composition, while the PI concentration in PI–PS interface region may be considered to be varying continuously. The morphology can be assumed to be as shown in *Figure 7b* with the PI blocks entering the PS phase. The T_g of the interface is a function of its composition. In the interfacial zone, the composition changes relatively slowly from the PI phase to the PS phase such that dC_p/dT varies smoothly from $T_{g(PI)}$ to $T_{g(PS)}$. This morphology results in the signal from the PS phase transition becoming very broad and weak. The dC_p/dT peak of the PS phase ranges from 85 to $105°C$ in the pure PS sample. Clearly, the dC_p/dT peak of the PS phase between 85 and $105°C$ disappears in the SIS sample. This implies that the pure PS phase is considerably reduced in scale, leading to the conclusion that the morphology is a two-phase structure: a pure-PI phase and a PI-PS mixed phase.

When PPO is added, the morphology changes. It is probable that some PPO blends miscibly with PS. It can be further speculated that some PS and PI blocks maintain the same morphology as in the SIS triblock copolymer itself, and that the interfacial content decreases. Because peak 3 in *Figure 6* is quite wide, it is believed that there exists some PI in the PS–PPO phase. Although it is difficult to estimate the amount of each component in each phase, the amount of PI in the interfacial phase and in the PS–PPO phase can be estimated approximately using equations (1) and (3)–(7) as is shown in *Table 3* for the SIS triblock copolymer and for the SIS/PPO blend.

Interfacial phase formed by thermal diffusion in a miscible polymer pair

Thermal diffusion between two miscible polymers results in an interfacial phase developing. With increasing diffusion time, the thickness of the interface will increase and the concentration will change. Thermal diffusion of two miscible polymers, PnBA and PVC, has been studied by M-t.d.s.c. for the first time. The results are shown in *Figure 8(a–d)*. *Figure 9* presents the results expanded for the interface region. The thermal diffusion temperature was $135°C$. The dC_p/dT signal from the interface formed by thermal diffusion is very clear. *Figure 10* shows the changes of heat capacity with temperature at different annealing times. The data presented in this way obviously do not indicate the presence of an interfacial region. According to equations (1) and (3)–(7), the weight fractions of PVC and PnBA in the interface region can be calculated. The average thickness
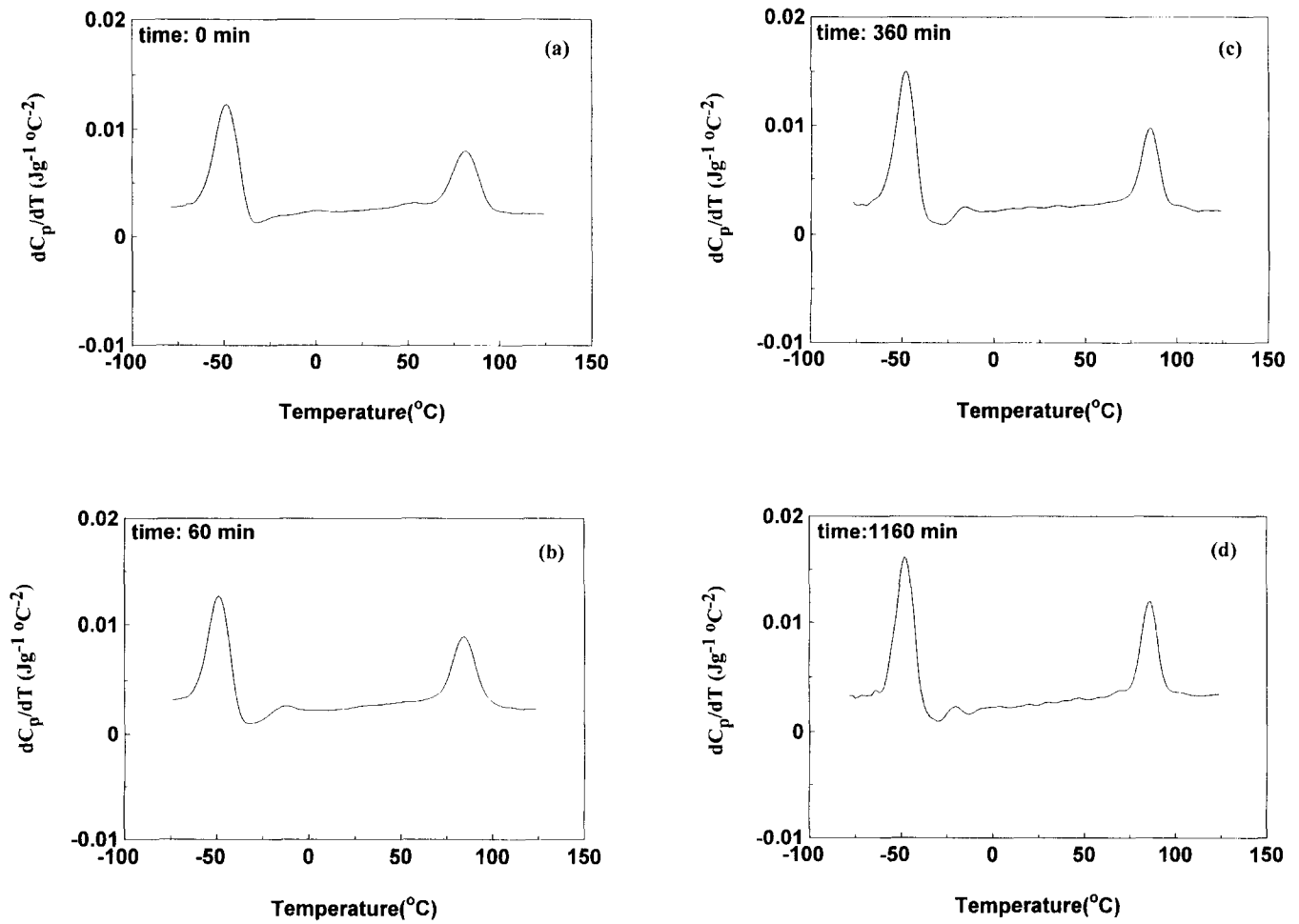
Figure 8   Variation of dC_p/dT with temperature at different diffusion times for the PnBA + PVC system

of the interface can also be estimated approximately from the following equations.

$$M_i = \delta_1 M_1 + \delta_2 M_2 \qquad (9)$$

$$V_i = M_i/\bar{\rho}_i \qquad (10)$$

$$L_i = V_i/S \qquad (11)$$

M_i, M_1 and M_2, respectively, are the mass of interface, polymer 1 and polymer 2. $\bar{\rho}_i$ is the average density of polymers in the interface. S is the cross-sectional area of the sample. L_i is the average thickness of the interface. The densities of PVC and PnBA at room temperature were used to calculate the average density.

The changes of weight fraction with diffusion time for PVC and PnBA in interface are shown in *Figure 11*. The thickness of the interface was about 3.8 μm at a diffusion time of 1160 min. Because PnBA is in a liquid-like state at 135°C, the diffusion of PnBA is quite rapid. From *Figure 8*, it can be seen that the peak arising from the interface region formed by thermal diffusion shifts to lower temperature with increasing diffusion time. The changes of the glass transition temperature of the interfacial phase with diffusion time are shown in *Figure 12*.

Interface in a phase-separated system

Figure 13 shows the dC_p/dT change with temperature for PMMA blended with PVAc (50/50, wt/wt). The result shows

a single transition peak. However, the transition range is quite wide, running from 30 to 100°C, covering almost the transition ranges of pure PMMA and PVAc. This implies that the change of concentration in the domains is continuous. Each morphology is related to a particular transition temperature which together constitute a transition spectrum. Although one can prepare a PMMA/PVAc sample which has only one glass transition temperature under some experimental conditions[20], and the blend appears
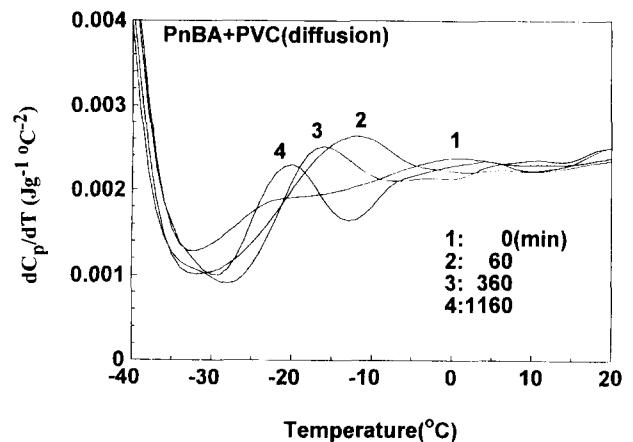

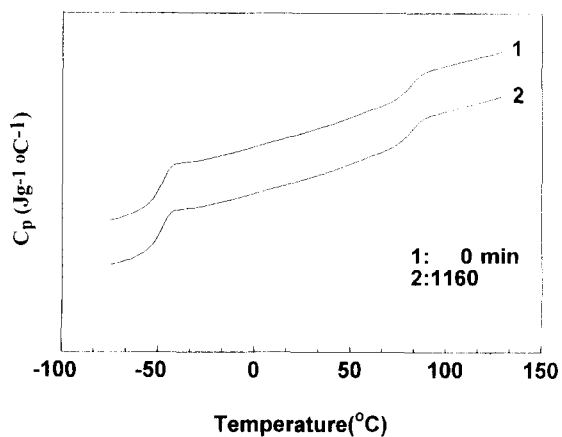**Figure 9**   Enlargements of the transition regions from the data shown in *Figure 8*

Figure 10 Variation of heat capacity with temperature at diffusion times of 0 and 1160 min for the PVC + PnBA system
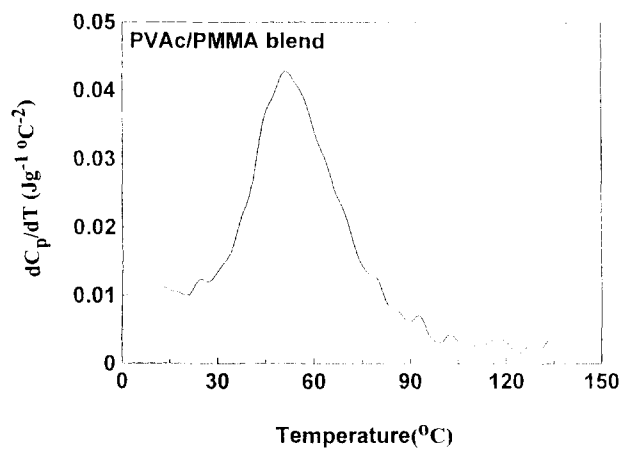

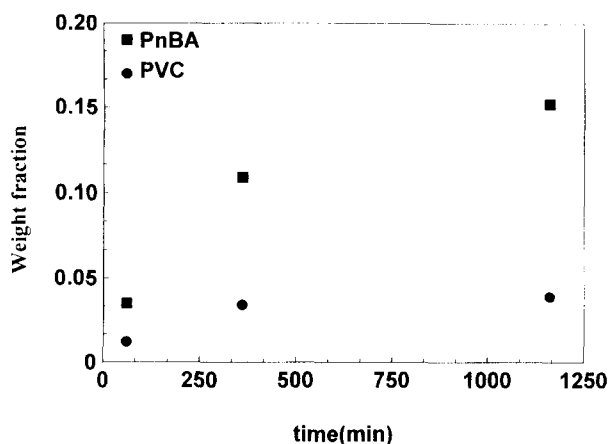**Figure 11** Variation with diffusion time of the weight fraction of PVC and PnBA in the interface region

Figure 12 Variation of interfacial glass transition temperature with diffusion time

Figure 13 Variation of dC_p/dT with temperature for PMMA blended with PVAc (50/50, wt/wt)
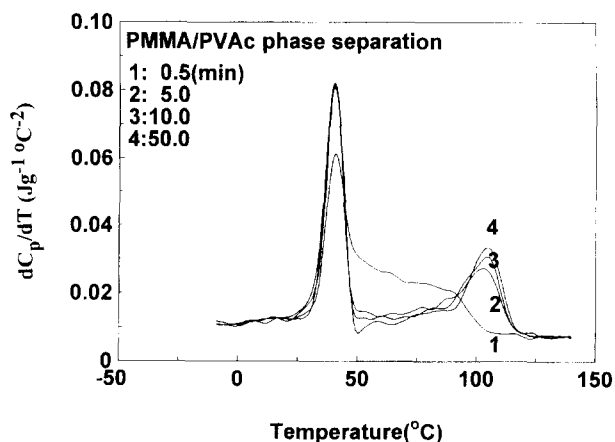

Figure 14 Variation of dC_p/dT with temperature at different phase separation times for the PMMA/PVAc (50/50, wt/wt) blend

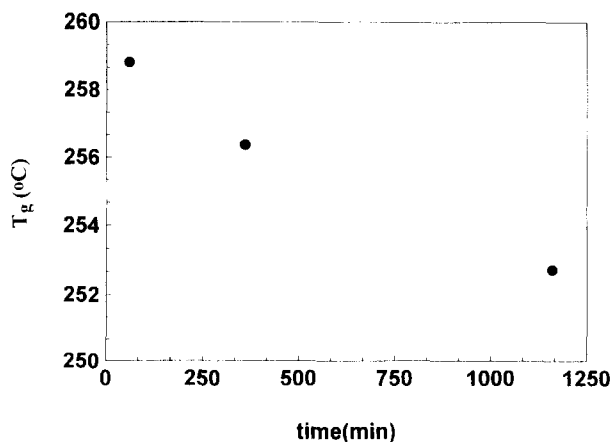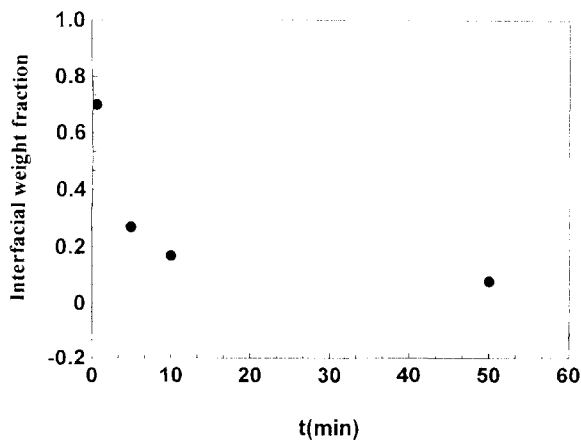**Figure 15** Variation of interfacial weight fraction with phase separation time in the phase-separated PMMA/PVAc blend

to be fully miscible, in fact the morphology is heterogeneous. Thus, the extent of miscibility of polymer blends can be checked on the basis of their M-t.d.s.c. dC_p/dT signal.

Figure 14 shows the dC_p/dT changes with temperature for this blend at different phase separation times. In the early stages, there exists a PVAc-rich phase and a PMMA–PVAc phase with a very wide composition

distribution. With increasing time, it can be seen clearly that a multi-phase structure—PVAc-rich, PMMA-rich and the interface—can be found. According to equations (1) and (3)–(7), the weight fraction of PMMA and PVAc in the interface can also be estimated. The results are shown in *Figure 15*. The amount of interface decreases with time and finally the two-phase structure is formed.

CONCLUSIONS

The composition of interface material in microphase-separated systems has been determined by a thermal method. From the measurement of the increment of heat capacity in the glass transition region, the total content of interface and the polymer composition in the individual phases in multi-component polymer materials can be obtained. The interface was modelled as discrete fractions each with its own characteristic increment of heat capacity.

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