

Modulated differential scanning calorimetry: XVI. Degree of mixing in interpenetrating polymer networks¹

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Abstract

Quantitative analysis using the differential of heat capacity with temperature, dC_p/dT , signal from modulated-temperature differential scanning calorimetry (M-TDSC) allows the extent of phase mixing to be calculated for interpenetrating polymer networks (IPNs). As an example, the extents of phase mixing of polyurethane–polystyrene (PUR/PS) (60/40, wt/wt) IPNs with different levels of grafting agent, benzene-1-(1-isocyanato-1-methyl ethyl)-3-(1-methylethenyl) (TMI) have been analysed. At lower TMI contents, the dC_p/dT with temperature signal shows two significant glass-transition temperatures. With increasing TMI contents, a broad transition peak appears in the dC_p/dT with temperature signal. This indicates that with increasing TMI contents, the degree of phase mixing increases. It is believed that the dC_p/dT vs. temperature signal will become a useful tool and a powerful complement to solid-state NMR, scattering and direct non-radiative energy-transfer methods in analysing the morphology of IPNs. © 1998 Elsevier Science B.V.

Keywords: Heat capacity; Interpenetrating polymer networks; Modulated-temperature DSC

1. Introduction

Over the past twenty years, a substantial effort has gone into analysing the detailed morphology of interpenetrating polymer networks (IPNs). The fundamental phenomenon associated with all IPNs is the phase separation occurring during IPN formation. However, the extent of phase separation is limited by the spatial scale over which interpenetration occurs at the onset of phase separation, and this, in turn, is related to the rates of polymerisation. IPN properties are sensitive to preparation conditions. One can, in principle, achieve materials with different properties by varying only the processing conditions. The IPN properties will be determined by phase continuity, domain size, interfaces and degree of component mixing.

Transmission electron microscopy (TEM) can be used to analyse domain size, domain distribution and phase continuity [1]. Small angle X-ray and neutron scattering techniques can be used to obtain information about interfaces [2–4]. However, to address this problem of the degree of phase mixing, one needs new techniques. Two approaches reported recently by Meyer et al. [5] and Winnik et al. [6] involve solid-state NMR spin-diffusion [5] and direct non-radiative energy-transfer [6] experiments to study the degree of mixing in the various phases. Meyer et al. [5] estimated the degree of phase mixing in IPNs based on the measurements of the solid-state NMR spin-lattice relaxation times. The results gave information about the intimacy of mixing of the two polymer networks. Winnik et al. [6] also calculated the extent of phase mixing in IPNs quantitatively based on the analysis of direct non-radiative energy-transfer measurements. They compared the results obtained from direct

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¹Presented at TAC 97, Oxford, UK, 14–15 April 1997.

non-radiative energy-transfer measurements with those of dynamic mechanical analysis which were calculated by the Fox equation [6] based on the glass-transition temperature values. They were in good agreement with the dynamic mechanical analysis. These analyses were based on a two-phase model. These studies are very important from an academic point of view. However, in some cases, it is difficult to describe the morphology of IPNs, using just a two-phase model, because the morphology of most of IPNs is a multi-phase structure.

Recently, Hourston et al. [7] have developed a new signal, the differential of heat capacity with temperature, dC_p/dT , from modulated-temperature differential scanning calorimetry (M-TDSC) [8]. For the study of polymer–polymer miscibility, the basic limitation of the utility of glass-transition determination exists with blends composed of components which have similar ($<15^\circ\text{C}$ difference) glass-transition temperatures, where resolution of the T_g by conventional DSC and dynamic mechanical thermal analysis is difficult [9,10]. Also, for small concentrations ($<10\%$) the weak transition signal is difficult to resolve [9,10]. Now, this limitation is reduced. We have shown that when the difference in T_g is ca. 10°C [11], the dC_p/dT with temperature signal given by M-TDSC may be used to characterise polymer–polymer miscibility with high resolution. Weight fractions of $<7\%$ in multi-phase polymeric materials can also be determined [7]. This provides a new quantitative method for the composition analysis of multi-component polymeric materials.

In this paper, the degree of phase mixing of polyurethane–polystyrene (PUR/PS) (60/40, wt/wt) IPNs with different grafting agent contents, such as benzene-1-(1-isocyanato-1-methyl ethyl)-3-(1-methylethenyl), has been analysed, as have the glass-transition temperature and composition distribution.

2. Theoretical background to M-TDSC analysis in the glass-transition region

A differential equation to describe the kinetics of enthalpy (H) relaxation for conventional differential scanning calorimetry (DSC) [12] was suggested.

$$d\delta/dt = \Delta C_p q - \delta/\tau(T, \delta) \quad (1)$$

where $\delta(=H-H_\infty)$ is the excess enthalpy relative to the equilibrium value (H_∞), C_p the difference between the liquid (C_{pl}) and glassy (C_{pg}) specific heat capacities, q the heating rate and t the time.

The single relaxation time τ depends [12] upon both T and δ , according to Eq. (2).

$$\tau = \tau_g \exp[-\theta(T - T_g)] \exp[-(1-x)\theta\delta/\Delta C_p] \quad (2)$$

τ_g is the equilibrium relaxation time at the glass-transition temperature T_g , x the non-linearity parameter ($0 \leq x \leq 1$), and θ the constant defining the temperature dependence of t . It is given by the approximation:

$$\theta = \Delta h^*/(RT_g^2) \quad (3)$$

Δh^* is an apparent activation energy. Eqs. (1) and (2) define the response of the glass to any prescribed thermal history. For simplicity, the following approximate equation will be used in this paper for the relaxation time τ .

$$\tau = \tau_g \exp[-\theta(T - T_g)] \quad (4)$$

The basic principle is to superimpose upon the conventional DSC heating rate a periodically varying temperature modulation. In M-TDSC, this modulation is sinusoidal, giving a time-dependent temperature [8].

$$T = T_0 + qt + A_T \sin(\omega t) \quad (5)$$

T_0 is the initial temperature of the DSC scan, A_T the amplitude of the temperature modulation, and ω the frequency of modulation.

Using the variable $\eta = \delta + T\Delta C_p$, Lacey et al. [13] made approximations to Eq. (1) which led to the following equations:

$$d\eta/dt = \exp[\Delta h^*/(RT_g^2)(T - T_g)](T\Delta C_p - \eta)/$$

$$\tau_g = [\Delta C_p qt + A_T \Delta C_p \sin(\omega t) - \eta] \times \exp[Kqt + KA_T \sin(\omega t)]/\tau_0 \quad (6)$$

$$\tau_0 = \exp(\Delta h^*/(RT_g))\tau_g \quad (7)$$

For M-TDSC, Lacey et al. [13] proposed that $\eta = \langle \eta \rangle + A_T \text{Re}\{\phi \exp(i\omega t)\}$, where $\langle \eta \rangle$ is the underlying part of η which satisfies the following equation:

$$d\langle \eta \rangle/dt = [\Delta C_p qt - \langle \eta \rangle] \exp(Kqt)/\tau_0 \quad (8)$$

ϕ is the ‘complex amplitude’ [13].

$$i\omega\phi \exp(i\omega t) = \exp(i\omega t) [K(\Delta C_p q t - \langle \eta \rangle) + \Delta C_p] \times \exp(Kqt)/\tau_0 - \exp(Kqt)/\tau_0 \phi \exp(i\omega t) \quad (9)$$

Then

$$\langle \eta \rangle = A \exp[-e^{Kqt}/(Kq\tau_0)] + qt\Delta C_p - q\Delta C_p \exp[-e^{Kqt}/Kq\tau_0] \times \int_0^\infty \exp[e^{Kqt'}/(Kq\tau_0)] dt' \quad (10)$$

and

$$\phi = i\{K(\langle \eta \rangle - qt\Delta C_p) - \Delta C_p / [1 + i\omega\tau_0 \exp(-Kqt)]\} \quad (11)$$

For M-TDSC [14],

$$dQ/dt = C_{pr}dT/dt + f(t, T) = qC_{pr} + \langle f(t, T) \rangle + \omega A_T C_{pr} \cos(\omega t) + C \sin(\omega t) \quad (12)$$

dQ/dt is the heat flow into the sample, C_{pr} is the reversing heat capacity of the sample due to its molecular motions at a heating rate q , $f(t, T)$ the heat flow arising as a consequence of a kinetically retarded event, $\langle f(t, T) \rangle$ the average of $f(t, T)$ over the interval of at least one modulation and C the amplitude of the kinetically retarded response to the temperature modulation.

Consider the complex heat capacity, C_p^*

$$C_p^* = A_{HF}/A_q \quad (13)$$

A_{HF} and A_q are the amplitudes of heat flow and heating rate, respectively.

The complex heat capacity is out of phase with the heating rate, and a real part, C_p' , and an imaginary part, C_p'' may be assigned [14]

$$C_p' = C_p^* \cos \alpha \quad (14)$$

$$C_p'' = C_p^* \sin \alpha \quad (14)$$

$$C_p^* = C_p' - iC_p'' \quad (15)$$

where α is the phase angle between heat flow and heating rate.

Also, we have [14]

$$dQ/dt = C_{pr}dT/dt + f(t, T) = qkC_{pr} + \langle f(t, T) \rangle + \omega A_T C_p \omega \cos(\omega t) + C \sin(\omega t) \quad (16)$$

$C_{p\omega}$ is the reversing heat capacity at the frequency ω .

Since $dQ/dt = C_{pg}dT/dt + d\eta/dt$, we have [13]

$$qC_{pr} + \langle f(t, T) \rangle = qC_{pg} + d\langle \eta \rangle/dt \quad (17)$$

and

$$\omega A_T C_{p\omega} \cos(\omega t) + C \sin(\omega t) = [(C_{pg} - \text{Im}\{\phi\})\cos(\omega t) - \text{Re}\{\phi\}\sin(\omega t)] \quad (18)$$

Assuming $C_p' = A + BT + f(T)$ during the glass transition, according to Lacey et al. [13], C_p' and C_p'' can be obtained

$$C_p' = A + BT + \Delta C_p / (1 + \omega^2 \tau_g^2 \exp(-2\Delta h^*/(RT_g^2)(T - T_g))) \quad (19)$$

$$C_p'' = \Delta C_p \omega \tau_g \exp(-\Delta h^*/(RT_g^2)(T - T_g)) / (1 + \omega^2 \tau_g^2 \exp(-2\Delta h^*/(RT_g^2)(T - T_g))) \quad (20)$$

Figs. 1 and 2 show the C_p' , C_p'' and $\tan \delta$ vs. frequency for polystyrene. For this theoretical analysis, following parameters were used.

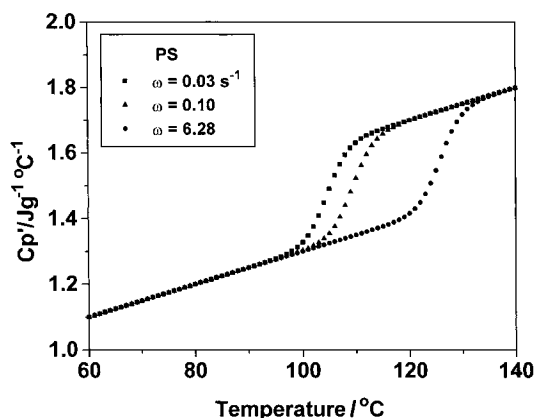


Fig. 1. Theoretical C_p' vs. temperature curves for polystyrene at different frequencies.

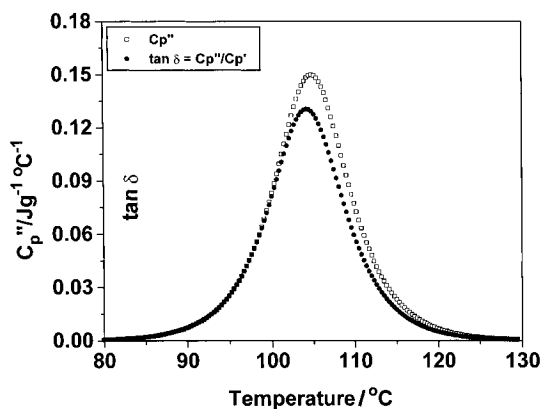


Fig. 2. Theoretical C_p'' and $\tan\delta$ vs. temperature curves during glass transition for polystyrene.

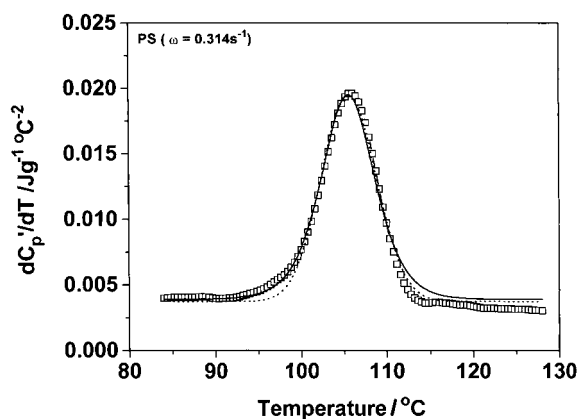


Fig. 3. Comparison of the dC_p'/dT vs. temperature data for experimental (□), theoretical (—) and a Gaussian function (···) for polystyrene.

$$\Delta C_p = 0.3 \text{ Jg}^{-1}\text{C}^{-1} \text{ (from [12])}$$

$$\Delta h^* = 300 \text{ kJ mol}^{-1} \text{ (assumed value)}$$

$$A = 0.8 \text{ Jg}^{-1}\text{C}^{-1} \text{ (assumed value)}$$

$$B = 0.002 \text{ Jg}^{-1}\text{C}^{-2} \text{ (assumed value)}$$

$$\tau_g = 100 \text{ s (from [12])}$$

Figs. 3 and 4 give the comparison of the dC_p'/dT vs. temperature data for experimental (square points), theoretical (solid line) and a Gaussian function (dots) for polystyrene and a (50/50) by weight miscible blend of poly(methyl methacrylate) and poly(styrene-co-acrylonitrile) [11]. Obviously, the experimental data can be well described by the theory and also by a

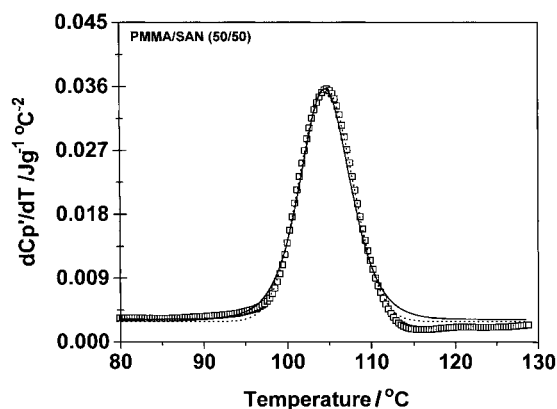


Fig. 4. Comparison of the dC_p'/dT vs. temperature data for experimental (□), theoretical (—) and a Gaussian function (···) for a miscible blend of poly(methyl methacrylate) and poly(styrene-co-acrylonitrile) (50/50 by weight).

Gaussian function at the glass transition. For simplicity, in this paper, we use a Gaussian function to describe the change of dC_p'/dT vs. temperature at the glass transition.

3. Experimental

3.1. Polystyrene/polyurethane interpenetrating polymer networks

The polyurethane component comprised a tertiary diisocyanate, 1,1,3,3-tetramethylxylene diisocyanate (m-TMXDI, kindly donated by Cytec Industries), a polyoxypropylene glycol with a molar mass of 1025 (PPG1025, BDH) and the crosslinker, trimethylol propane (TMP, Aldrich). Benzene-1-(1-isocyanato-1-methyl ethyl)-3-(1-methylethenyl) (TMI, Cytec) was used as a grafting agent. Stannous octoate (SnOC, Sigma) was used as the PUR catalyst. The other monomer used was styrene (S, Aldrich). Divinylbenzene (DVB, Aldrich) was used to crosslink the polystyrene network. The reaction was initiated with azoisobutyronitrile (AIBN, Aldrich). The required amount of AIBN was dissolved in the monomer (S) and crosslinker divinylbenzene (DVB). In a separate receptacle, the triol (TMP) was dissolved in the PPG1025 at 60°C. Both components were combined at room temperature and the polyurethane catalyst was added. A nitrogen blanket was applied. On addition of the TMXDI, the components were mixed for 5 min at

high speed. Degassing for 1 min under vacuum was conducted to remove the entrapped air. The mixture was cast into stainless-steel spring-loaded O-ring moulds, which had been pre-treated with CIL Release 1771 E release agent. The curing cycle consisted of three stages of 24 h each at 60, 80 and 90°C.

3.2. Instrumentation M-TDSC

A TA instruments M-TDSC calorimeter was used. An oscillation amplitude of 1.5°C, an oscillation period of 60 s and a heating rate of 3°C/min were used. The calorimeter was calibrated with a standard indium sample.

4. Results and discussion

Fig. 5 shows the dC'_p/dT vs. temperature plots for the PUR/PS IPN with 2.5% of TMI and a 40% PS +60% PUR physical blend. From Fig. 5, it can be seen that dC'_p/dT (the PUR/PS IPN) > dC'_p/dT (40% PS+60% PUR) from -20 to 85°C. The value of the dC'_p/dT signal is greater than that of the physical blend in this temperature range. This is expected as IPN materials often form multiple phases which have different compositions.

To analyse the morphology of the PUR/PS IPN with 2.5% of TMI, it is necessary to know the change of the dC'_p/dT with temperature signal for a diffuse interface. Fig. 6 shows the change of the dC'_p/dT with temperature signal for a diffuse interface between

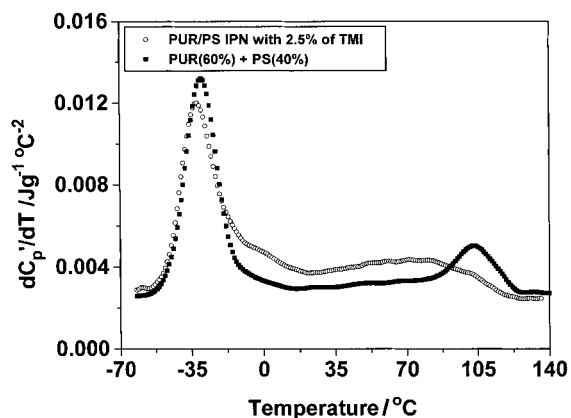


Fig. 5. dC'_p/dT vs. temperature for the PUR/PS(60/40) IPN with 2.5% of TMI and for a 40% PS+60% PUR physical blend.

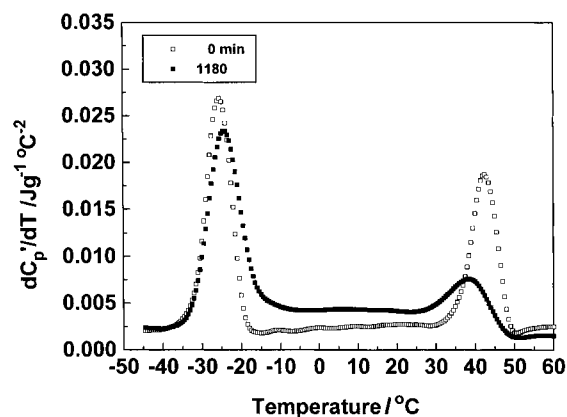


Fig. 6. dC'_p/dT vs. temperature for a diffuse interface between PECH and PVAc. See Ref. [15].

polyepichlorohydrin (PECH) and polyvinyl acetate (PVAc) [15]. Here, two polymer films were put together in a DSC pan and annealed at 100°C for 1180 min. The diffuse interface results in an increase of the dC'_p/dT with temperature signal between the two glass-transition temperatures of PECH and PVAc.

Now, on comparing Figs. 5 and 6, it is clear that diffuse interfaces are formed in the PUR/PS IPN with 2.5% of TMI. There is also a significant shoulder on the high temperature side of the PUR glass transition. The glass-transition temperature of the PUR phase in the PUR/PS IPN with 2.5% of TMI is the same as that of the pure PUR network. In this case, the pure PS transition disappeared.

Figs. 7–9 show the dC'_p/dT vs. temperature plots for the PUR/PS IPNs with different TMI contents (open square symbols). With increasing TMI contents, the transition peaks shift inwards and broaden. This can be interpreted in terms of the degree of component mixing. The fact that transition peaks shift inwards and broaden indicates that the degree of mixing has increased, i.e. degree of network interpenetration has increased.

For polymers and miscible polymer blends, the dC'_p/dT with temperature signal can be described in term of Gaussian function, G , of temperature; increment of heat capacity, ΔC_p ; glass-transition temperature, T_g ; and half width, ω_d , of the glass transition.

$$G = \Delta C_p / [\omega_d (\pi/2)^{1/2}] \exp[-2(T - T_g)^2 / \omega_d^2] \quad (21)$$

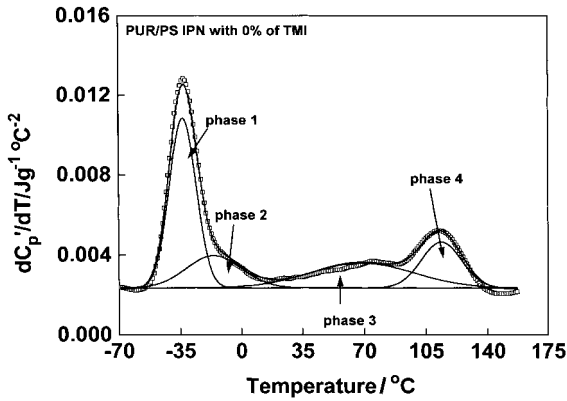


Fig. 7. dC_p'/dT vs. temperature curves for the PUR/PS(60/40) IPN with 0% of TMI (\square). The solid lines (—) are peak resolution results.

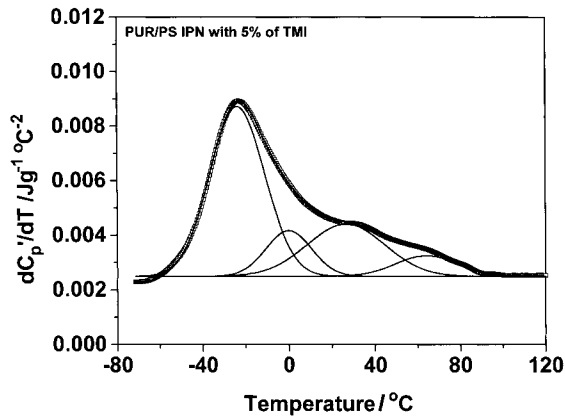


Fig. 8. dC_p'/dT vs. temperature curves for the PUR/PS(60/40) IPN with 5% of TMI (\square). The solid lines (—) are peak resolution results.

For a heterogeneous IPN, such as the PUR/PS IPNs, it may be considered that G is a multiple Gaussian function in the transition region.

$$\begin{aligned}
 G &= \sum_i G_i(T, T_{gi}, \omega_{di}, \Delta C_{pi}) \\
 &= \Delta C_{p1} / [\omega_{d1} (\pi/2)^{1/2}] \exp[-2(T - T_{g1})^2 / \omega_{d1}^2] \\
 &\quad + \Delta C_{p2} / [\omega_{d2} (\pi/2)^{1/2}] \exp[-2(T - T_{g2})^2 / \omega_{d2}^2] \\
 &\quad + \Delta C_{p3} / [\omega_{d3} (\pi/2)^{1/2}] \exp[-2(T - T_{g3})^2 / \omega_{d3}^2] \\
 &\quad + \dots
 \end{aligned} \quad (22)$$

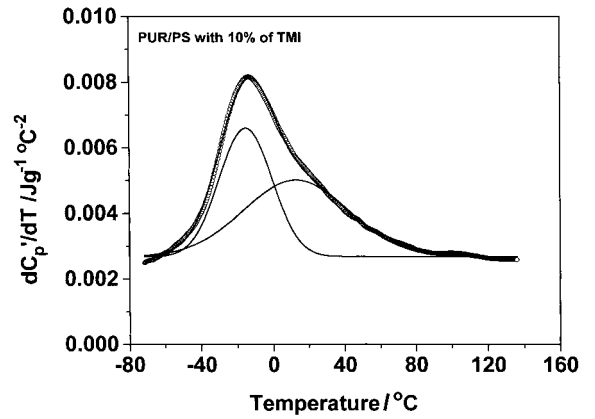


Fig. 9. dC_p'/dT vs. temperature curves for the PUR/PS(60/40) IPN with 10% of TMI (\square). The solid lines (—) are peak resolution results.

where $G_i(T)$ is related to i th phase of the multi-phase system. For a multi-phase IPN, the total ΔC_p is the linear addition of ΔC_{pi} of each phase.

$$\Delta C_p = \sum_i \Delta C_{pi} \quad (23)$$

By a peak resolution technique, the parameters, ω_{di} , ΔC_{pi} and T_{gi} can be obtained.

Consider the i th PS-rich phase. Its glass-transition temperature, $T_g^{(ie)}$, and the increment of heat capacity, $\Delta C_p^{(ie)}$, are theoretically as follows.

$$\begin{aligned}
 T_g^{(ie)} &= \omega_{ps}^{(i)} T_{gPS} + \omega_{PUR}^{(i)} T_{gPUR} \\
 \Delta C_p^{(ie)} &= \omega_{ps}^{(i)} \Delta C_{pPS} + \omega_{PUR}^{(i)} \Delta C_{pPUR}
 \end{aligned} \quad (24)$$

$\omega_{ps}^{(i)}$ and $\omega_{PUR}^{(i)}$ are the weight fractions of the PS and PUR networks in the i th phase, respectively.

ΔC_{pPS} and ΔC_{pPUR} are the increments of heat capacity of the PS and PUR networks, respectively. T_{gPS} and T_{gPUR} are the glass-transition temperatures of the PS and PUR networks, respectively. The weight fractions of i th phase is as follows

$$\begin{aligned}
 \omega_i &= \Delta C_{pi} / \Delta C_p^{(ie)} = \Delta C_{pi} (T_{gPS} - T_{gPUR}) / \\
 &\quad [(T_g^{(ie)} - T_{gPUR})(C_{pPS} - \Delta C_{pPUR}) \\
 &\quad + (T_{gPS} - T_{gPUR}) \Delta C_{pPUR}]
 \end{aligned} \quad (25)$$

Then, the weight fraction of PUR and PS in i th phase are as follows

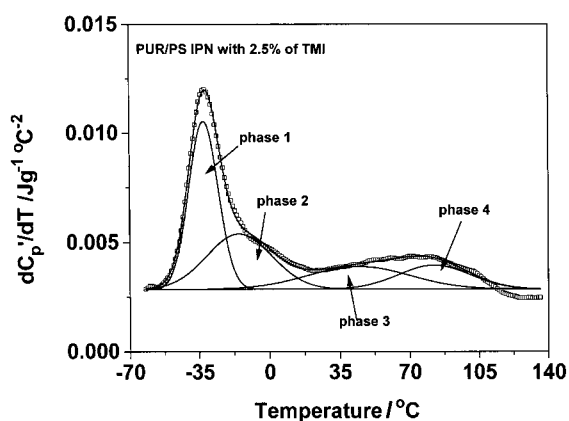


Fig. 10. dC_p'/dT vs. temperature curves for the PUR/PS(60/40) IPN with 2.5% of TMI (\square). The solid lines (—) are peak resolution results.

$$\omega_i(\text{PUR}) = \frac{\Delta C_{pi}(T_{gPS} - T_{gPUR})}{[(T_g^{(ie)} - T_{gPUR})(\Delta C_{pPS} - \Delta C_{pPUR}) + (T_{gPS} - T_{gPUR})\Delta C_{pPUR}] \times (T_g^{(ie)} - T_{gPS}) / (T_{gPUR} - T_{gPS})}$$

$$\omega_i(\text{PS}) = \frac{\Delta C_{pi}(T_{gPS} - T_{gPUR})}{[(T_g^{(ie)} - T_{gPUR})(\Delta C_{pPS} - \Delta C_{pPUR}) + (T_{gPS} - T_{gPUR})\Delta C_{pPUR}] \times (T_g^{(ie)} - T_{gPUR}) / (T_{gPS} - T_{gPUR})} \quad (26)$$

ΔC_{pPS} , ΔC_{pPUR} , T_{gPS} and T_{gPUR} are obtained from M-TDSC measurements. $T_g^{(ie)}$ and ΔC_{pi} are obtained from the peak resolution.

The solid lines shown in Figs. 7–10 show the peak resolution results for the PUR/PS IPN with 0, 5, 10 and 2.5 wt.% of TMI. For the PUR/PS IPN with 0% of TMI, phase 1 is a pure PUR phase because its T_g is the same as that of the pure PUR network. Phase 4 is the pure PS phase having the same T_g as that of the pure PS network. Phases 2 and 3 are the phases of PUR mixed with PS. For simplicity, consider them as diffuse interfaces. For the PUR/PS IPN with 5% of TMI, the pure PUR and PS phases disappear. Four transition peaks were separated from the overlapping dC_p'/dT signals. However, it is very difficult to say which transition peak results from diffuse interfaces. For the PUR/PS IPN with 10% of TMI, two-phase

Table 1

Phase T_g and weight fraction for the PUR/PS IPN with 2.5% of TMI

T_g ($^{\circ}\text{C}$)	Weight fraction (%)
-33	32
-17	23
50	30
90	19

information was obtained. In this IPN, there exists a high degree of mixing. From the above analysis, it is possible that by increasing the grafting agent content, the degree of mixing increases. For the calculation of the weight fraction of each phase in these PUR/PS IPNs, only the result for the PUR/PS IPN with 2.5% of TMI is shown (see Table 1).

Sperling et al. proposed a wall and cell model to describe IPN morphology on the segmental level 20 years ago [16]. This wall and cell model predicts that the dispersed phases are virtually interconnected by their own polymer chains, which interpenetrate through the continuous phase [1,16]. This will result in a continuous change of dC_p'/dT . Our experimental results support the wall and cell model.

Various approaches have been taken to study the degree of phase mixing in IPNs. Among the most powerful are solid-state NMR [5], direct non-radiative energy transfer [6] and X-ray and neutron scattering [2–4]. Although there have been various reports in the literature describing these measurements, the picture they provide is still far from complete. dC_p'/dT signal as an analysis tool may be a useful alternative or a powerful complement to NMR, scattering and direct non-radiative energy-transfer methods.

4.1. Summary

The dC_p'/dT vs. temperature profile of the PUR/PS IPN with different TMI contents obtained from M-TDSC are a multiple Gaussian function of temperature, increment of heat capacity, glass-transition temperature and half peak width of glass transition. From analysis of peak resolution of the dC_p'/dT vs. temperature signal, it is possible to obtain information on the phase structure, different compositions and glass-transition temperatures in IPNs. The T_g and weight fraction of each phase can be obtained quantitatively.

The dC_p'/dT signal can indicate degree of network mixing in IPNs.

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