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An application of modulated-temperature differential scanning calorimetry to the study of crystallisation kinetics in poly(ϵ-caprolactone)-poly(styrene-*co*-acrylonitrile) blends

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Abstract

In order to evaluate the application of modulated-temperature differential scanning calorimetry (M-TDSC) to the study of the crystallisation kinetics of semi-crystalline polymers, isothermal crystallisation kinetics in poly(ϵ-caprolactone)-poly(styrene-*co*-acrylonitrile) blends have been investigated. M-TDSC data were analysed according to the method suggested by Toda et al. [Toda A, Oda T, Hikosaka M, Saruyama Y. Polymer Communications 1997;38:231]. The temperature dependence of d ln G/dT (G is the crystal growth rate), determined by M-TDSC agreed approximately with the experimental data and theoretical values reported by Wang and Jiang [Wang Z, Jiang BZ. Macromolecules 1997;30:6223]. Their experimental data were obtained from direct measurements of spherulite growth rate by optical microscopy. Our theoretical and M-TDSC experimental results showed that the d ln G/dT versus temperature plots are not sensitive to the non-crystalline component in the poly(ϵ-caprolactone)-poly(styrene-*co*-acrylonitrile) blends. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Modulated-temperature DSC; Crystallisation; Polymer blends

1. Introduction

Since its recent invention, modulated-temperature differential scanning calorimetry (M-TDSC) has already been used widely to study polymer materials, such as polymer blends [1], structured lattices [2], interpenetrating polymer networks [3] and semi-crystalline polymers [4,5]. It has been shown that M-TDSC can be readily used to study the glass transition [6,7] of polymers. However, it has been found that the sample mass and thickness have clear influences on the measured heat capacity during the melting transition in semi-crystalline polymers [8]. Recently, Toda et al. [4] have developed a new M-TDSC method to measure the dependence of spherulite growth rate on crystallisation temperature. Their M-TDSC results were in good agreement with data determined by means of optical microscopy.

The question arises as to whether the M-TDSC method developed by Toda et al. [4] can be used to study crystallisation kinetics in polymer blends. From the study of poly(ϵ-caprolactone)-poly(styrene-*co*-acrylonitrile) (PCL-SAN) blends by means of optical microscopy [9], it is known that the non-crystalline component concentration influences the spherulite growth rate. The question is whether d ln(G/G_o)/dT versus crystallisation temperature plots from M-TDSC data are also sensitive to the non-crystalline component composition in non-crystalline-crystalline polymer blends.

This paper attempts to answer this question. In this study, the temperature dependence of the spherulite growth rate of PCL-SAN blends is reported.

2. Model suggested by Toda et al. [4]

M-TDSC [10] utilises the response in heat flow, dQ/dt, to a sinusoidal modulation in sample temperature, T_s. T_s and dQ/dt can be expressed as follows [4]:

$$T_s = \bar{T}_s(\text{the underlying signal}) + \tilde{T}_s \exp\{i(\omega t + \epsilon)\}(\text{the cyclic signal}) \quad (1)$$

$$\frac{dQ}{dt} = \frac{d\bar{Q}}{dt}(\text{the underlying signal}) + \frac{d\tilde{Q}}{dt} \exp\{i(\omega t + \delta)\}(\text{the cyclic signal}) \quad (2)$$

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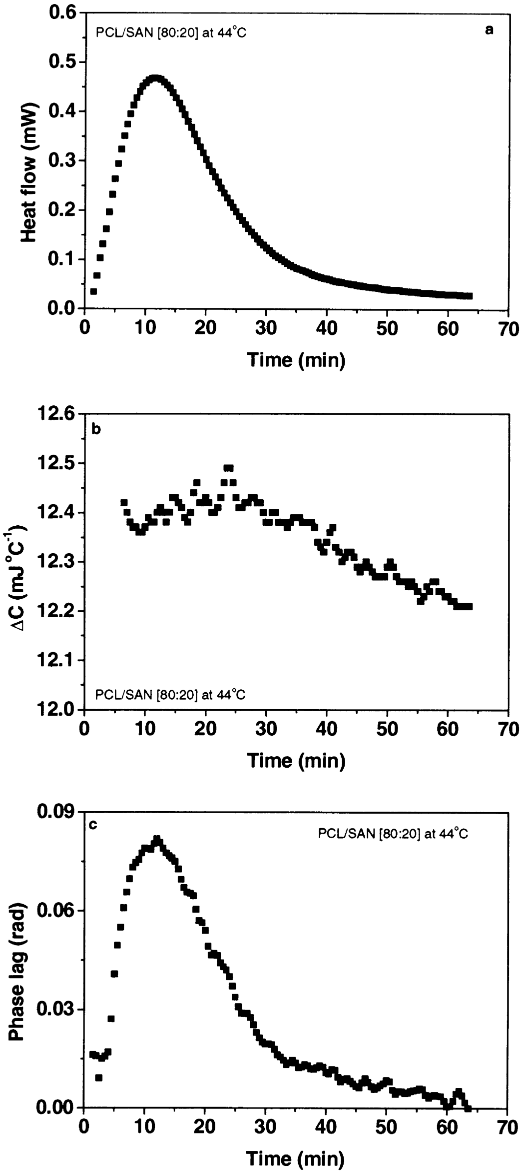

Fig. 1. Quasi-isothermal crystallisation of the PCL-SAN blend (80:20 by weight) at 44°C: (a) Heat flow; (b) apparent heat capacity and (c) the phase lag.

where ω is the frequency, ϵ and δ are the phase of T_s and dQ/dt, respectively. An apparent complex heat capacity, $\Delta C \exp(-i\alpha)$, is defined as follows [4].

$$\Delta C \exp(-i\alpha) \equiv \Delta C' - i\Delta C'' \tag{3}$$

$$\Delta C = \frac{d\tilde{Q}/dT}{\omega \tilde{T}_s} \tag{4}$$

$$\alpha = (\epsilon - \delta) \tag{5}$$

where $\Delta C'$ and $\Delta C''$ are the real and imaginary parts of the apparent complex heat capacity, and α is the phase angle which can be obtained directly from a M-DSC experiment. Toda et al. [4] have suggested that the apparent heat capacity for transformation processes such as crystallisation should be expressed as

$$\Delta C \exp(-i\alpha) = mc_p + iF'_T/\omega \tag{6}$$

where mc_p is the true heat capacity of the sample and F'_T represents the response of the transformation process.

In the case of polymer crystallisation, the apparent heat capacity is given by the following expression [4].

$$\Delta C \exp(-i\alpha) = mc_p + \frac{iF_{\text{cryst}}}{\omega} \frac{d \ln(G/G_o)}{dT} \tag{7}$$

where F_{cryst} is the exothermic crystallisation heat flow. The $d \ln(G/G_o)/dT$ is the temperature dependence of the linear spherulite growth rate. Combining Eqs. (3), (6) and (7), the following equation can be obtained [4]:

$$\frac{d \ln(G/G_o)}{dT} = -\frac{\omega \Delta C \sin \alpha}{F_{\text{cryst}}} \tag{8}$$

Here Eq. (8) is the model established for the M-TDSC studies by Toda et al. [4].

3. Experimental

Samples: The PCL sample was obtained from Polysciences Inc. Its M_w and M_n values, determined by gel permeation chromatography, (GPC) were 22,000 and 11,300, respectively. The melting temperature of the PCL was approximately 60°C. SAN with a 25 wt.% acrylonitrile (AN) content was supplied by Polysciences Inc. The M_w and M_n values were 197,000 and 106,000 by GPC. The T_g of the SAN was 105°C as determined by DSC. PCL/SAN blends with compositions of 80/20 and 70/30 were prepared by solution blending in $CHCl_3$. The solution (6% wt/wt) was stirred continuously for 24 h at room temperature before casting. Cast films were dried in a vacuum oven at 40°C for three weeks.

Instrumentation: A DSC 2920 Module controlled with Thermal Analyst 2200 (TA Instruments) was used for all measurements. A nitrogen gas purge was used. With the latest version of Thermal Analysis 2200, the phase angle, $(\epsilon - \delta)$, can be obtained directly using Graphware software from TA Instruments. Baselines for the apparent heat capacity, heat flow and phase angle data were considered according to the method used by Toda et al. [4]. The M-TDSC run was used in the isothermal mode. The observed phase angle is equal to the real phase angle plus the baseline. It is assumed the baseline is linear with time. The baseline for the transition was drawn as follows. The on-set and the off-set temperatures were taken from the heat flow vs. time data and were used directly as the on-set and off-set temperatures for the phase angle vs. time curve. A straight line was drawn between these points to give the baseline. The modulation period was 80 s and the amplitude was ±0.2°C.

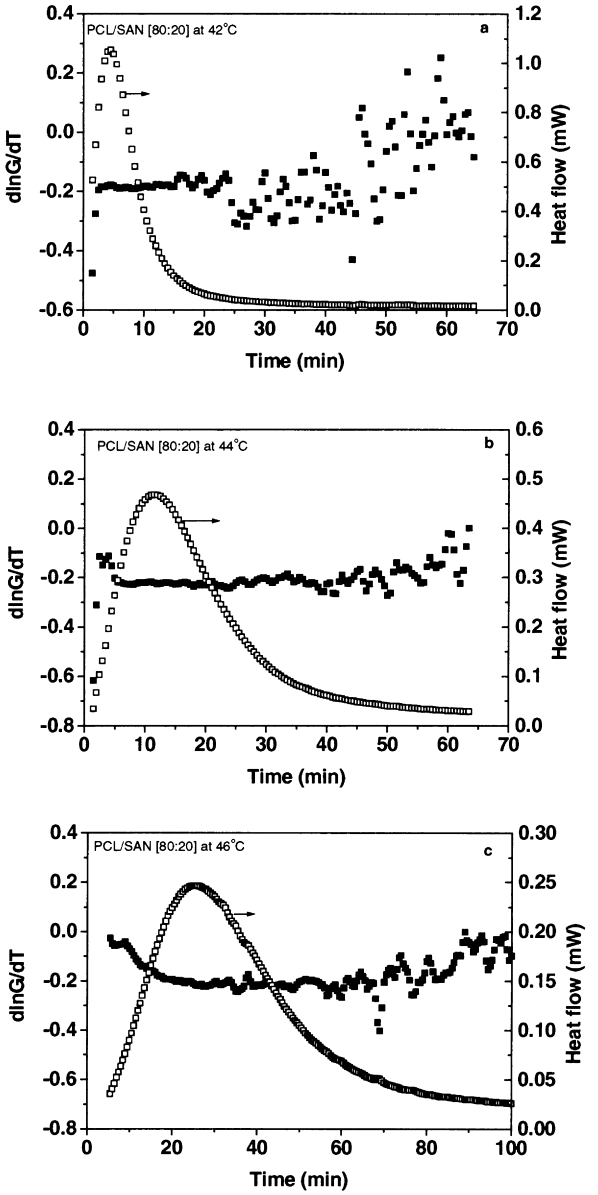

Fig. 2. d ln G/dT versus crystallisation time for the PCL-SAN (80:20 by weight) blend: (a) 42°C; (b) 44°C and (c) 46°C.

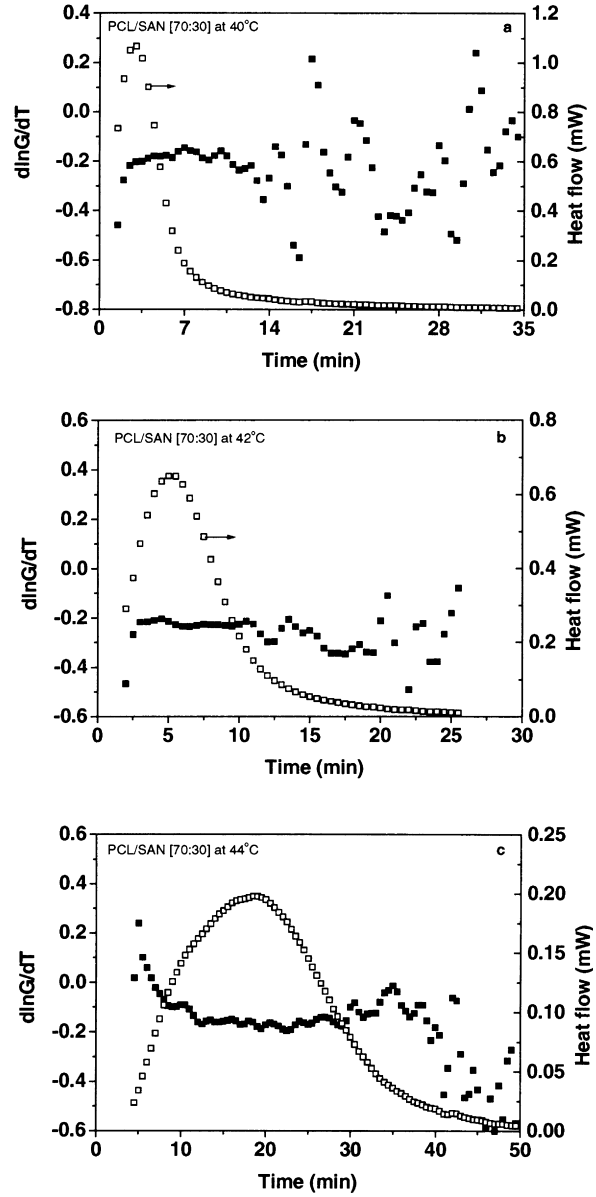

Fig. 3. d ln G/dT versus crystallisation time for the PCL-SAN (70:30 by weight) blend: (a) 40°C; (b) 42°C and (c) 44°C.

For the M-TDSC measurements of isothermal crystallisation, the samples were annealed in the instrument for 10 min at 100°C, and then rapidly quenched to the crystallisation temperature.

4. Results and discussion

Fig. 1(a)–(c) show, respectively, typical M-TDSC total heat flow, apparent heat capacity, ΔC, and phase lag versus time plots for the 80/20 by weight PCL-SAN blend at 44°C. Figs. 2(a)–(c) and 3(a)–(c) show the temperature dependence of crystal growth rate calculated by Eq. (8) for the quasi-isothermal crystallisation of the PCL-SAN blends (80:20 and 70:30 systems, respectively) for different crystallisation temperatures above $T(G_{\max})$. During the crystallisation, a peak in the phase lag was confirmed for these blends. It was found that in the early stages of growth, an accurate determination of d ln G/dT could not be obtained because the system is in an unstable state. Subsequently, d ln G/dT had an essentially constant value. Thus, it is possible that M-TDSC measurements can be used to estimate the temperature dependence of crystal growth rate. In the late stages of crystallisation, the d ln G/dT values are very scattered. It was also found that the time period over which d ln G/dT has a constant value becomes longer with increasing crystalline temperature above $T(G_{\max})$ (Figs. 2(a)–(c) and 3(a)–(c)). This result observed by M-TDSC is similar to that observed by means of optical microscopy [9].

Fig. 4 gives a comparison of d ln G/dT versus

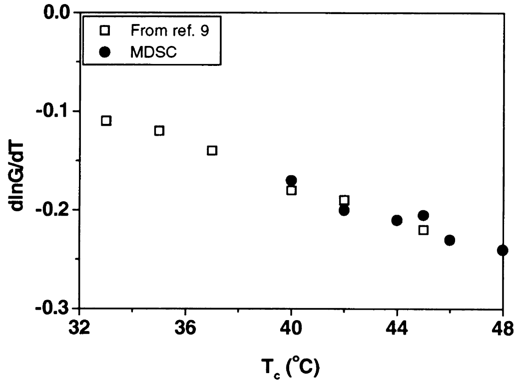

Fig. 4. d ln *G*/d*T* versus crystallisation temperature plot. The data (□) were determined by optical microscopy [9]. The M-TDSC results (●) were calculated using Eq. (8).

crystallisation temperature data determined by M-TDSC and literature [9] values measured by optical microscopy. These M-TDSC data are in good agreement with literature values.

There are numerous reports [9,11–13] on studies of crystallisation kinetics in miscible blends of non-crystalline with crystalline polymers, as determined from measurements of spherulite growth rates. All the previous reports have indicated that with increasing non-crystalline component, the growth rate of the crystalline component is depressed. The depression in growth rate is due to the dilution of the crystallisable component at the growth front and changes in free energy of nucleation due to specific interactions [9,11–13]. In a very recent report [9], Wang and Jiang have discussed the effects of the glass transition temperature, the non-crystalline component and specific interactions on crystallisation kinetics. Their results indicated that the effects of the glass transition temperature of the amorphous component and specific interactions on crystallisation kinetics cannot be observed by means of optical microscopy. They indicated, therefore, that the Flory–Huggins interaction parameter obtained by fitting the kinetic equation with experimental data [14,15] measured by means of optical microscopy is questionable. What new information can d ln *G*/d*T* versus crystallisation temperature plots provide for the study of crystallisation kinetics in polymer blends?

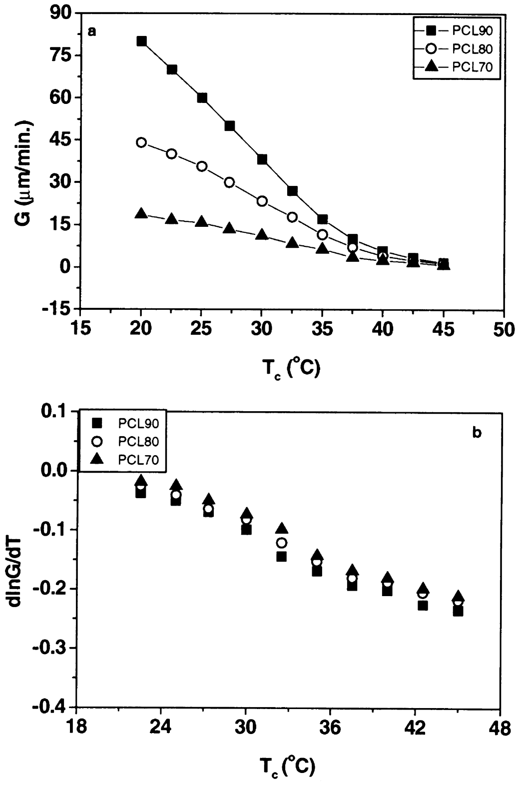

Fig. 5. Temperature dependence of spherulite growth rate for different non-crystalline component compositions. (a) *G* versus temperature of crystallisation. (b) d ln *G*/d*T* versus temperature of crystallisation.

Fig. 5(a) and (b) show the calculated results for *G* and d ln *G*/d*T* versus crystallisation temperature for 90:10, 80:20 and 70:30 PCL/SAN blends, respectively. The following equation [9] was used for this calculation:

$$G_{\mathrm{m}} = \phi_2 G_{\mathrm{o}} \exp\left[-\frac{\Delta E}{\mathrm{R}(T - T_{\mathrm{g}} + C)}\right] \times \exp\left[\frac{-2b\sigma\sigma_{\mathrm{e}}}{\mathrm{k_B} T \Delta h_{\mathrm{u}} f(1 - T/T_{\mathrm{m}}^{\mathrm{o}} - \mathrm{R}TV_{2\mathrm{u}}/(\Delta h_{\mathrm{u}} f V_{1\mathrm{u}})\chi(1 - \phi_2)^2)}\right]$$

where $f = 2T/(T + T_{\mathrm{m}}^{\mathrm{o}})$, G_{o} is a constant that depends upon the regime of crystallisation, R is the gas constant, T_{g} is the glass transition temperature of the amorphous phase in the blend system, T is the temperature of crystallisation, $\mathrm{k_B}$ is the Boltzmann constant, ΔE is the energy necessary to achieve the transport of segments across the liquid-solid interface, Δh_{u} is the heat of fusion per mole of monomer of the crystallisation component with volume fraction ϕ_2 at temperature T, $T_{\mathrm{m}}^{\mathrm{o}}$ is the equilibrium melting point of the pure material, $V_{i\mathrm{u}}$ is the molar volume of component i, χ is the Flory–Huggins interaction parameter, b is the thickness of the critical nucleus and $\sigma\sigma_{\mathrm{e}}$ is the product of the lateral and fold surface free energies. The related parameters required were obtained from Ref. [9]. The non-crystalline component has an obvious influence on growth rate, *G* [9]. However, the d ln *G*/d*T* versus crystallisation temperature plots is not sensitive to the non-crystalline component in non-crystalline-crystalline polymer blends. This conclusion can also be drawn from Fig. 2(a)–(c) and 3(a)–(c).

5. Conclusions

1. The temperature dependence of d ln *G*/d*T* (*G* is the crystal growth rate) can be investigated in non-crystalline–crystalline polymer blends by the M-TDSC model suggested by Toda et al. [4]. Observations by optical microscopy and theoretical results are in good agreement with M-TDSC data for these SAN-PCL blends.

2. The theoretical and experimental results showed that the d ln G/dT versus crystallisation temperature plots are not sensitive to the amount of non-crystalline component in these polymer blends.

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