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Physical properties of polymer blends and their theoretical consideration

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The physical properties of polymer blends and their theoretical consideration based on the double-lattice model (DLM) and a simple rheological equation of state were investigated. Cloud points of poly(ϵ-caprolactone) (PCL)/polystyrene (PS) blends were determined using the thermooptical analysis (t.o.a.) technique. PCL ($M_w = 125\,000$)/PS($M_w = 6200$) blends exhibit an upper critical solution temperature (UCST). The adjustable parameter values are $r_2 = 844.859$, $\epsilon/k = -313.092$ K, and $\delta\epsilon/k = 1381.824$ K. For PCL ($M_w = 15\,000$)/PS ($M_w = 840$) blends, $r_2 = 177.560$, $\epsilon/k = -254.163$ K, and $\delta\epsilon/k = 1195.827$ K. The DLM successfully describes and predicts the phase behaviour of polymer blends. Steady-state shear viscosity of PCL/linear low-density polyethylene (LLDPE) blends was also investigated. D.s.c. results showed that there is no miscibility between PCL and LLDPE. A simple rheological equation of state successfully describes and predicts the flow behaviour of the proposed polymer blend. © 1997 Elsevier Science Ltd.

(Keywords: polymer blend; double-lattice model; rheological equation of state)

INTRODUCTION

The phase behaviour of binary polymer/solvent mixtures differs from that of ordinary liquid mixtures because of the large molecular size difference of the components. Quantitative understanding of the phase behaviour of polymeric liquids is important for the development, production and processing of advanced polymer materials.

A variety of theories of polymer solutions and blends has developed during the last half-century. Most of them are revised forms of the classical theory proposed by Flory[1] and Huggins[2].

To account for compressibility and density changes upon isothermal mixing, Sanchez and Lacombe[3,4] and Kleintjens and Koningsveld[5] have derived different forms of a lattice-fluid model based on Flory–Huggins theory. Sanchez and Balazs[6] introduced corrections for oriented interactions between dissimilar components. On the other hand, free-volume theories for polymer solutions were developed by numerous investigators, notably by Flory[7] and by Patterson and Delmas[8]. Heil and Prausnitz[9], and later Brandani[10] and Vera[11], developed a theory taking local composition into account; however, these researchers were not able to predict a lower critical solution temperature (LCST). Bae *et al.*[12–16] reported the extended Flory–Huggins theory for both polymer solutions and phase transition of a hydrogel.

Many research groups have also sought to express the rheological behaviour of polymeric materials through suitable stress and deformation variables. Bae *et al.*[17–21] reported rheological properties of polymeric liquids and proposed a simple rheological equation of state.

Plastics have created problems for disposal, resulting in programs to reuse, incinerate or convert these wastes[22]. Therefore a need has been created, based on environmental considerations, for the development and study of biodegradable polymers.

Much work has been reported on the properties of biodegradable polymers. Bastioli and co-workers[23,24] reported the biodegradability, morphology and physical properties of starch-based polymer. Chapman[25] reported new applications and product improvements for biodegradable materials. Narayan[26] reported the advantages of using plasticized starch instead of granular starch in starch–poly(ϵ-caprolactone) (PCL) alloy. Doi and co-workers[27,28] reported the production and properties of poly(3-hydroxybutyrate). Suter and co-workers[29] reported the biodegradation of short-chain poly(3-hydroxybutyric acid).

In this study, we investigated the phase behaviour of blends of biodegradable polymer (PCL) and synthetic polymer (PS) and the flow behaviour of a PCL/LLDPE blend. The experimental technique to determine cloud-points of PCL/PS blends was the TOA technique, and a capillary rheometer was used to measure viscosities of the PCL/LLDPE blend. We used the DLM to predict the phase behaviour of PCL/PS blends, and a simple rheological equation of state to describe the flow behaviour of the PCL/LLDPE blend.

THEORETICAL CONSIDERATIONS

Double-lattice model (DLM)[30,31]

Freed and co-workers[32–34] developed a complicated lattice-field theory for polymer solutions which is formally an exact mathematical solution of the Flory–Huggins lattice. Good agreement was found between

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predicted results and the computer simulation data by Dickman and Hall[35] for the chain insertion probability and for pressures in a system of athermal chains and voids.

Freed's theory is the basis of the double-lattice model. Ordinary polymer solutions are described by the Flory–Huggins lattice, defined as the primary lattice, and a secondary lattice is introduced as a perturbation to account for oriented interactions originating from hydrogen bonding, donor–acceptor electron transfer or strong dipole–dipole interactions. These interactions cause the phase behaviour of systems with an LCST or with closed-miscibility loops. This secondary lattice requires an additional parameter ($\delta\epsilon/k$) related to the energy of the oriented interaction and one empirical parameter c_{10}. In this study, we briefly summarize the double-lattice theory as modified by Freed's lattice-field theory.

The total partition function of the double lattice for a binary mixture is given by

$$Q = \sum_{N_{12}} g(N_1, r_1, N_2, r_2, N_{12}) \times \left[\exp\left(\frac{\epsilon_{11} - \Delta A_{\text{sec},11}/N_{11}}{kT}\right)\right]^{N_{11}} \times \left[\exp\left(\frac{\epsilon_{22} - \Delta A_{\text{sec},22}/N_{22}}{kT}\right)\right]^{N_{22}} \times \left[\exp\left(\frac{\epsilon_{12} - \Delta A_{\text{sec},12}N_{12}}{kT}\right)\right]^{N_{12}} \tag{1}$$

where N_1 and N_2 are the numbers of molecules of solvent (1) and polymer (2), respectively; N_{11}, N_{22}, and N_{12} are the numbers of 1–1, 2–2 and 1–2 nearest-neighbour (nonbonded) segment–segment pairs; r_2 is the number of segments in the polymer molecule relative to $r_1 = 1$ for the solvent; and $g(N_1, r_1, N_2, r_2, N_{12})$ is the combinatorial factor which depends on the number of 1–2 segment–segment pairs. The positive energy parameters, $\epsilon_{11}, \epsilon_{22}$ and ϵ_{12}, are for the corresponding nearest-neighbour segment–segment interactions; k is Boltzmann's constant; $\Delta A_{\text{sec},ij}$ is the Helmholtz energy of the secondary lattice for each i–j segment–segment pair.

To obtain an analytical expression for the Helmholtz energy of mixing for the secondary lattice as an Ising model based on Freed's theory, Hu *et al.*[30,31] expand the Helmholtz energy of mixing to second order in reduced energy, introducing the adjustable parameters; Hu *et al.* then obtain a solution

$$\frac{\Delta A}{N_r kT} = x_1 \ln x_1 + x_2 \ln x_2 + \frac{z\tilde{\epsilon}x_1x_2}{2} - \frac{z\tilde{\epsilon}^2 x_1^2 x_2^2}{4} \tag{2}$$

where z is the coordination number and $\tilde{\epsilon}$ is a reduced interaction parameter defined by

$$\tilde{\epsilon} = \frac{\epsilon}{kT} = \frac{\epsilon_{11} + \epsilon_{22} - z\epsilon_{12}}{kT} \tag{3}$$

Agreement between phase boundaries calculated by Freed's theory and the results from Scesney[36] is not complete, probably because equation (2) does not include higher order terms. Two ways of improving the coexistence curves are investigated. One way is to introduce an empirical coefficient c_2 to the $z\tilde{\epsilon}^2 x_1^2 x_2^2/4$ term. The best choice is $c_2 = 1.074$. The other way is to add to equation (2) an additional higher order term, $c_{10} z\tilde{\epsilon}^{10} x_1^{10} x_2^{10}$, arbitrarily taken to be of order 10. Therefore, a general expression for the Helmholtz energy of mixing for the Ising model is

$$\frac{\Delta A}{N_r kT} = x_1 \ln x_1 + x_2 \ln x_2 + \frac{z\tilde{\epsilon}x_1x_2}{2} - \frac{c_2 z\tilde{\epsilon}^2 x_1^2 x_2^2}{4} - c_{10} z\tilde{\epsilon}^{10} x_1^{10} x_2^{10} \tag{4}$$

where c_2 and c_{10} are related by

$$c_{10} = 5515.1 - 5135.1c_2 \tag{5}$$

The contribution to the Helmholtz energy of mixing for the secondary lattice is obtained directly from equation (4) with three changes. First, x is replaced by η; second, $\tilde{\epsilon}$ is replaced by $\delta\tilde{\epsilon}$; and third, Hu *et al.* add the additional energy of the reference state ($-z\eta\delta\tilde{\epsilon}_{ij}/2$), which accounts for the energy of the reference state where all the sites in the lattice are responsible for oriented interactions.

$$\Delta A_{\text{sec},ij} = N_l kT \left[\eta \ln \eta + (1 - \eta)\ln(1 - \eta) - \frac{z\delta\tilde{\epsilon}_{ij}\eta^2}{2} - \frac{c_2 z(\delta\tilde{\epsilon}_{ij})^2 \eta^2 (1 - \eta)^2}{4} - c_{10} z(\delta\tilde{\epsilon}_{ij})^{10} \eta^{10} (1 - \eta)^{10}\right] \tag{6}$$

where N_l is the total number of lattice sites.

In Freed's theory, there are three contributions to the Helmholtz energy of mixing for a Flory–Huggins lattice: the mean-field contribution plus two corrections for deviations from mean-field behaviour, one energetic and the other entropic. After rearrangement, the general form for the Helmholtz energy of mixing can be expressed as

$$\frac{\Delta A}{N_r kT} = \left(\frac{\phi_1}{r_1}\right) \ln \phi_1 + \left(\frac{\phi_2}{r_2}\right) \ln \phi_2 + \sum_m \sum_n a_{mn} \phi_1^m \phi_2^n \tag{7}$$

where coefficients a_{mn} are functions of z, r_1, r_2 and $\tilde{\epsilon}$.

Hu *et al.* revise the entropy correction term by dropping all the higher order terms and retaining only the first-order term but multiplied by an empirical coefficient c_s; then a_{mn} are given by

$$a_{11} = \left(\frac{4}{9}\right) c_s \left(\frac{1}{r_1} - \frac{1}{r_2}\right)^2 + 2\tilde{\epsilon} \tag{8}$$

$$a_{21} = \frac{\tilde{\epsilon}}{r_2}, \quad a_{12} = \frac{\tilde{\epsilon}}{r_1}, \quad a_{22} = \frac{-3c_2\tilde{\epsilon}^2}{2}$$

where c_s is an empirical coefficient (we fix $c_s = 0.3$ in this study) for the entropic correlation, and $c_2 = 1.074$.

The second term for a_{11} is the original Flory–Huggins term; the first term for a_{11} corrects the entropy for deviations from mean-field behaviour. Coefficients a_{12} and a_{21} are (essentially) equivalent to the effect that concerned Orofino and Flory[37] and Koningsveld and Kleintjens[38]. Coefficient a_{22} corrects for the Flory–Huggins mean-field energy.

For calculating the binary coexistence curve, we need the chemical potential for components 1 and 2. They are found from

$$\mu_1 - \mu_1^0 = \frac{\partial \Delta A}{\partial N_1}$$

$$\mu_1 - \mu_1^0 = kT\left[\ln \phi_1 + \phi_2\left(1 - \frac{r_1}{r_2}\right) + r_1 \sum_m \sum_n a_{mn}\left(m\phi_1^{m-1}\phi_2^{n+1} + (1-n)\phi_1^m\phi_2^n\right)\right] \tag{9}$$

$$\mu_2 - \mu_2^0 = \frac{\partial \Delta A}{\partial N_2}$$

$$\mu_2 - \mu_2^0 = kT\left[\ln \phi_{21} + \phi_1\left(1 - \frac{r_1}{r_2}\right) + r_2 \sum_m \sum_n a_{mn}\left(n\phi_1^{m+1}\phi_2^{n-1} + (1-m)\phi_1^m\phi_2^n\right)\right] \tag{10}$$

where the superscript '0' refers to the standard state (pure close-packed liquid at system temperature T).

For phase equilibrium calculations, we require the experimental coordinates of the critical point. We find these coordinates using

$$\frac{\partial^2\left(\dfrac{\Delta A}{N_r kT}\right)}{\partial \phi_2^2} = 0$$

which leads to

$$\frac{\partial^2\left(\dfrac{\Delta A}{N_r kT}\right)}{\partial \phi_2^2} = \frac{1}{r_1\phi_1} + \frac{1}{r_2\phi_2} + \sum_m \sum_n a_{mn}\left[m(m-1)\phi_1^{m-2}\phi_2^n - 2mn\phi_1^{m-1}\phi_2^{n-1} + n(n-1)\phi_1^m\phi_2^{n-2}\right] \tag{11}$$

$$\frac{\partial^3\left(\dfrac{\Delta A}{N_r kT}\right)}{\partial \phi_2^3} = 0$$

which leads to

$$\frac{\partial^3\left(\dfrac{\Delta A}{N_r kT}\right)}{\partial \phi_2^3} = \frac{1}{r_1\phi_1^2} - \frac{1}{r_2\phi_2^2} + \sum_m \sum_n a_{mn} \times \left[-m(m-1)(m-2)\phi_1^{m-3}\phi_2^n + 3mn(m-1)\phi_1^{m-2}\phi_2^{n-1} - 3mn(n-1)\phi_1^{m-1}\phi_2^{n-2} + n(n-1)(n-2)\phi_1^m\phi_2^{n-3}\right] \tag{12}$$

Using the experimental upper (or lower) critical coordinates, equations (11) and (12) are solved to yield energy and size parameters ϵ/k and r_2.

For polymer blends, r_1 is defined as

$$r_1 = \frac{M_{\text{p}1}}{M_{\text{m}1}} \tag{13}$$

where $M_{\text{p}1}$ and $M_{\text{m}1}$ are the molecular weight of polymer (1) and monomer (1), respectively.

For hydrogen bonding systems, or for systems whose components differ appreciably in molecular size, the primary lattice alone always yields a narrower coexistence curve. Hu *et al.* have to introduce the secondary lattice to obtain a satisfactory fit.

For systems having only a UCST, we set $c_2 = 1.074$ and $c_{10} = 0$. The results are not sensitive to η, which can be arbitrarily set within a reasonable range from 0.3 to 0.5. Hu *et al.* set $\eta = 0.3$ in this study. The only additional adjustable parameter is $\delta\epsilon/k$, the extra energy contributed by an oriented interaction. This parameter is obtained from fitting data for one tie line.

For systems having an LCST or closed-miscibility loops (both UCST and LCST), c_{10} cannot be set to zero; c_{10} or c_2 must be adjusted to obtain a good fit with the restraint shown by equation (5). In these cases, altogether four parameters are needed. Besides ϵ/k and r_2 obtained from one critical point, Hu *et al.* have to use another two, viz. $\delta\epsilon/k$ for special interactions and c_{10}. They can be obtained by fitting another set of experimental (upper or lower) critical coordinates and one tie line, giving the equilibrium compositions for a pair of conjugated phases.

A rheological equation of state[20,21]

If the steady-state shear viscosity (η), which is a state function, and shear rate ($\dot\gamma$) and temperature ($1/T$) are the chosen independent variables for a chosen system of fixed composition,

$$\eta = \bar{K}\dot\gamma^{n-1}\exp\left(\frac{Q}{RT}\right) \tag{14}$$

where $\bar{K}$ is a material constant, n is the power-law index, Q is the activation energy for the given flow, and R is the gas constant.

Taking the natural log of both sides of equation (14) gives

$$\ln\eta = \ln\bar{K} + \left(\alpha + \frac{\beta}{T}\right)\ln\dot\gamma + \frac{Q}{RT} \tag{15}$$

where $n - 1$ is related by

$$n - 1 = \alpha + \frac{\beta}{T} \tag{16}$$

To satisfy equation (15) to be a thermodynamic equation of state,

$$\operatorname{curl}\ln\vec{\eta} = \vec{0} \tag{17}$$

the above condition is for the criterion for exactness and independence of path,

$$\begin{vmatrix} \dfrac{\partial}{\partial\ln\dot\gamma} & \dfrac{\partial}{\partial\left(\dfrac{1}{T}\right)} \\ \dfrac{\partial\ln\eta}{\partial\ln\dot\gamma} & \dfrac{\partial\ln\eta}{\partial\left(\dfrac{1}{T}\right)} \end{vmatrix} = 0 \rightarrow J \equiv \frac{\partial^2\ln\eta}{\partial\left(\dfrac{1}{T}\right)\partial\ln\dot\gamma} = \frac{\partial^2\ln\eta}{\partial\ln\dot\gamma\,\partial\left(\dfrac{1}{T}\right)} \equiv D \tag{18}$$

In this study, we proved experimentally that equation (15) is a state function by using this relation of equation (18).

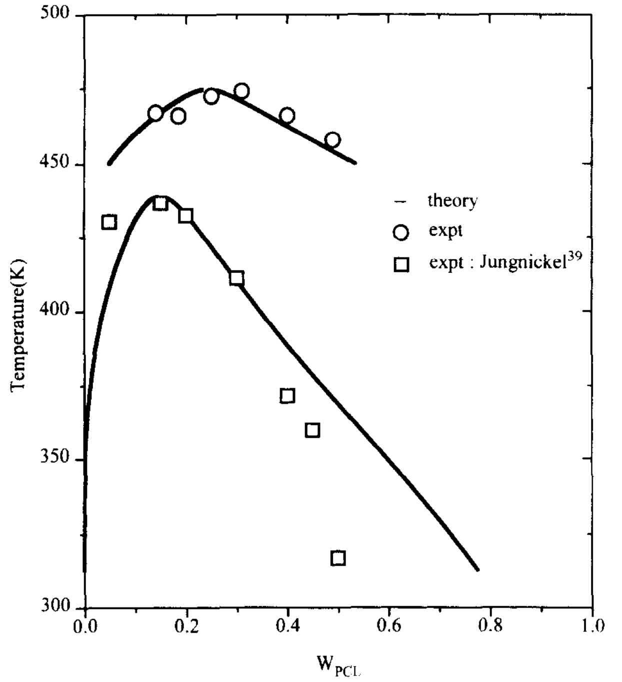

Figure 1 Cloud point curves for PCL/PS

EXPERIMENTAL

Materials

The PCL used in this study was supplied by Union Carbide Corp. (TONE p-787). The weight-average molecular weight (M_w) is 125 000. PS was from Toyo Soda Mfg Co., Ltd; M_w and polydispersity are 6200 and 1.04, respectively. LLDPE was from Hanyang Chemical Co. and its melt index is 20.

Sample preparation

The solvent-casting method was employed to prepare PCL/PS blends with various W_{PCL} values ranging from 0.1 to 0.5. PCL/PS dissolved in methylene chloride was cast on a glass plate, and the solvent was evaporated under vacuum for 48 h.

PCL and LLDPE were manually mixed with PCL/LLDPE at a composition of 30% PCL by volume and then blended in a two-roll mixer at 100°C for 5 min.

Apparatus and measurements

Thermooptical analysis (t.o.a.) apparatus consisted of a heating-cooling stage, a photodiode (Mettler FP80) and a microprocessor (Mettler FP90). An IBM PC was used for data acquisition. Cloud points of PCL/PS blends were determined using t.o.a. apparatus with a scan rate of 0.2°C min^{-1}.

Melting temperatures (T_m) of PCL, LLDPE and PCL/LLDPE blend were measured using d.s.c. (Perkin-Elmer). The steady-state shear viscosity of PCL/LLDPE blend was measured using a capillary rheometer (Instron Co., Model 3211). Test temperatures were 160°C, 180°C and 200°C.

RESULTS AND DISCUSSION

Figure 1 shows cloud point curves for PCL (M_w = 125 000)/PS (M_w = 6200) blends and PCL (M_w = 15 000)/PS (M_w = 840) blends. This system exhibits a UCST. The solid line is predicted by DLM. Open circles are experimental data for PCL (M_w = 125 000)/PS (M_w = 6200) blends. The adjustable parameter values are $r_2 = 844.859$, $\epsilon/k = -313.092$ K, and $\delta\epsilon/k = 1381.824$ K. Open squares are experimental data for PCL (M_w = 15 000)/PS (M_w = 840) blends by Jungnickel *et al.*[39]. The adjustable parameter values are $r_2 = 177.560$, $\epsilon/k = -254.163$ K, and $\delta\epsilon/k = 1195.827$ K. Experimental results show that the energy parameters are dependent on the chain length. In this study, we could not quantitatively correlate the energy parameters with the chain length of the polymer. This is because our polymer samples used in this study are different from those of Jungnickel *et al.*'s.

The deviation between the theory and experimental results in *Figure 1* occurs because the DLM is originally developed for the polymer/solvent system, so a slight deviation appears for polymer blend systems. Another possible explanation is that the PCL used in this study is a polydisperse polymer. It is well known that the phase diagram for a polydisperse solute is qualitatively different from that for a monodisperse sample. In the monodisperse case, the principal phase and the conjugate phase are located on the same cloud point curve and the maximum of that is the critical point. However, in the polydisperse case, the cloud point curve for principal phases does not coincide with the corresponding plot for conjugated phases. The latter is called the shadow curve. The chain length distribution for the principal phase is usually different from that of the conjugated phase[40,41]. One more possible explanation of this is that DLM does not take into account the free volume effects of polymers. Even then DLM successfully predicts phase behaviours of the given polymer blend systems.

The melting temperatures of PCL and LLDPE are 61.6°C and 125.5°C, respectively. *Figure 2* shows the melting temperature of PCL/LLDPE (PCL 30 vol%). The PCL/LLDPE blend shows two distinctive melting temperatures at 60.75°C and 126.0°C. It shows that the two polymers are immiscible.

As shown in *Figure 3*, steady-state viscosities of the PCL/LLDPE were plotted against temperature at various shear rates. The value of $Q/R + \beta \ln \dot{\gamma}$ was then determined from the slopes of the plot in *Figure 3*. The values of $Q/R + \beta \ln \dot{\gamma}$ at various logarithmic shear rates were determined and plotted against $\ln \dot{\gamma}$ in *Figure 4*.

From equation (18), the values of J for PCL/LLDPE were determined from the slope of the plot in *Figure 4*, and the calculated value was −520.37. *Figure 5* shows the steady-state shear viscosity vs logarithmic shear rate at various temperatures. The values of $\alpha + \beta/T$ were determined from the slopes of the plot in *Figure 5*. The values of $n - 1$ at various temperatures were determined and plotted in *Figure 6*.

From equation (18), D can be determined from the slope of the plot in *Figure 6*; the value of D was −513.05.

The difference between J and D is negligible. Therefore we have proved experimentally that equation (18) satisfies the thermodynamic criterion. It shows that the steady-state shear viscosity of the PCL/LLDPE blend can be described by the rheological equation of state expressed in equation (14). When β is chosen as the mean value (= −516.71), the values of Q/R and α can be calculated on the basis of the results shown in *Figures 4* and *6*, respectively.

Since the values of Q/R and material constant α are

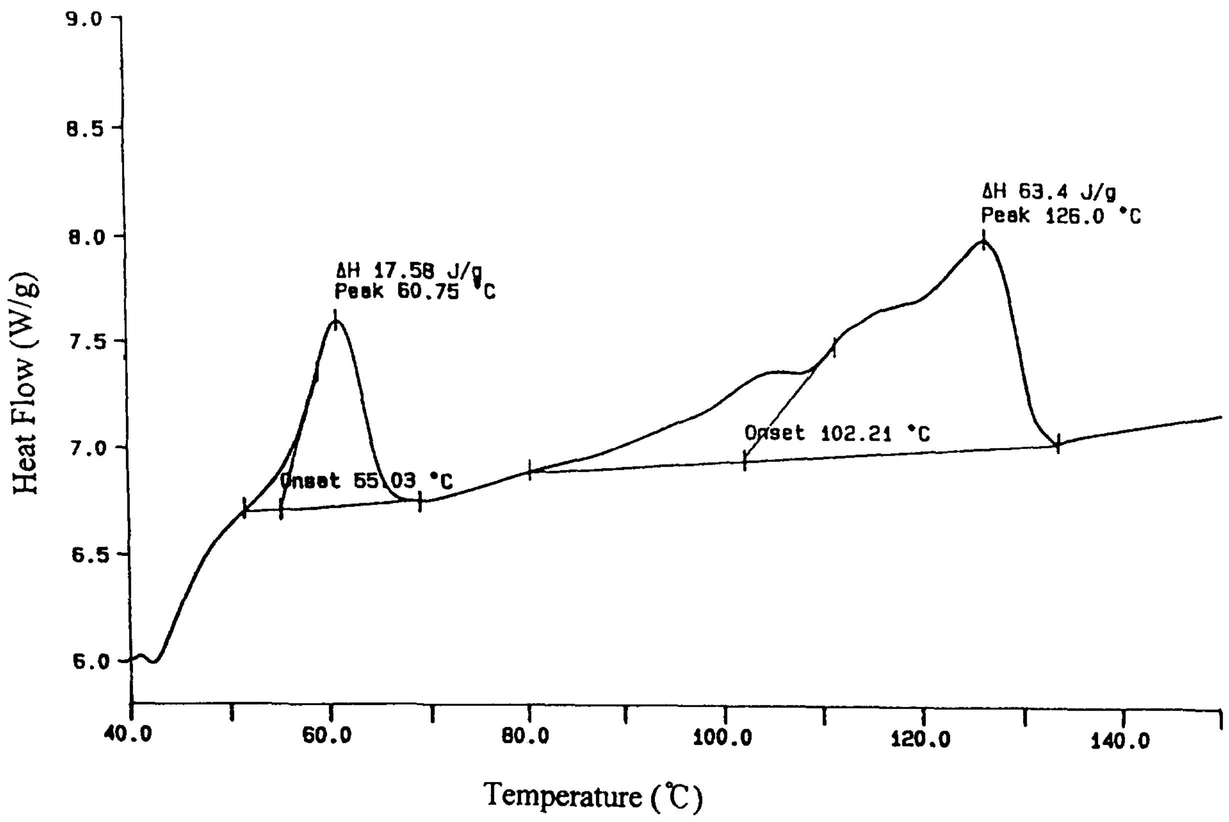

Figure 2 Melting temperature of PCL/LLDPE at composition of 30 vol% PCL

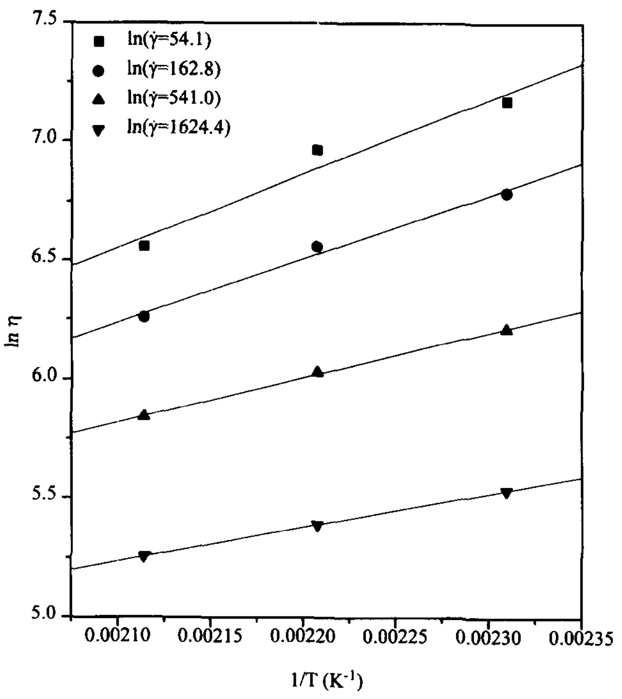

Figure 3 Ln η as a function of $1/T$

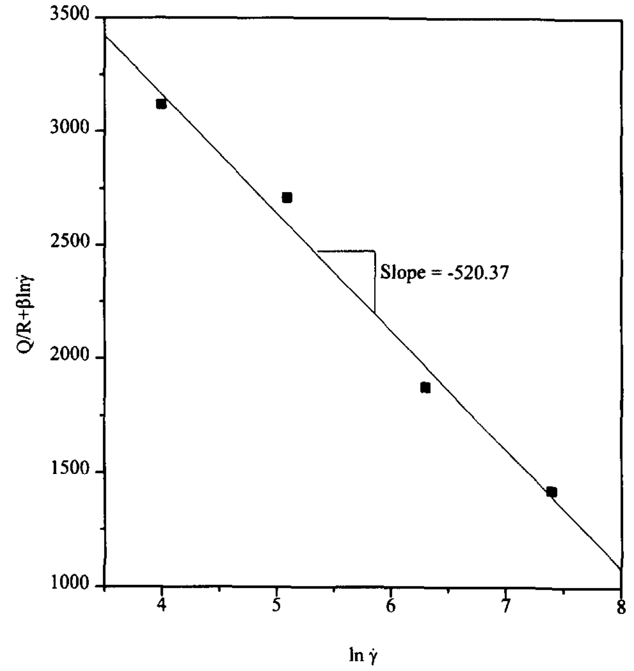

Figure 4 $Q/R + \beta \ln \dot{\gamma}$ as a function of $\ln \dot{\gamma}$

5241.14 K and 0.71, respectively, the value of $\ln \bar{K}$ can be calculated from equation (12); its value is −2.91.

From the previous results, equation (15) can be rewritten as:

$$\ln \eta = -2.91 + \left(0.71 - \frac{516.71}{T}\right) \ln \dot{\gamma} + \frac{5241.14 K}{T} \quad (19)$$

CONCLUSIONS

We have shown phase diagrams of PCL ($M_w = 125\,000$) and PS ($M_w = 6200$) blend systems. T.o.a. easily determined the cloud points of the given polymer systems. DLM successfully describes and predicts the phase behaviour of the polymer blend, but needs to take into account the free volume effects of polymers.

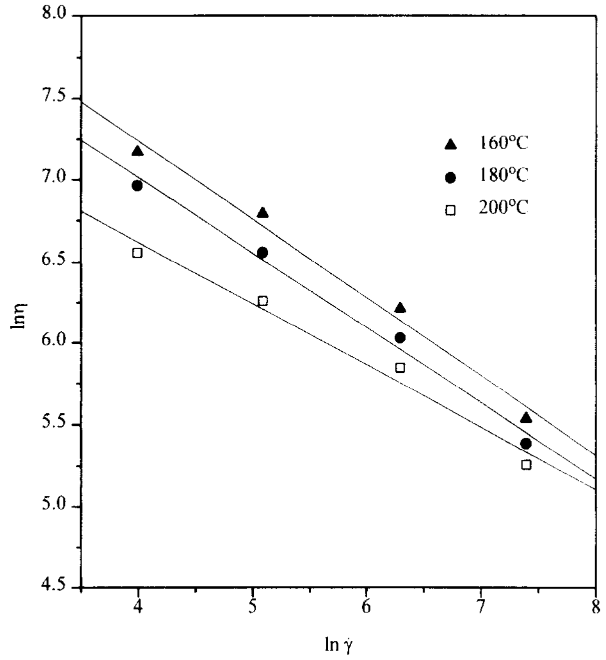

Figure 5 Ln η as a function of ln $\dot{\gamma}$

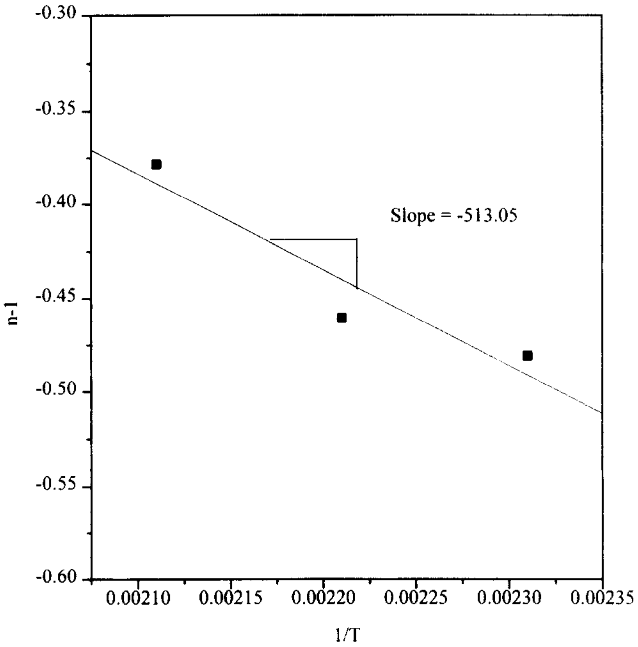

Figure 6 The value of $n - 1$ as a function of $1/T$

The rheological equation of state excellently describes and predicts the flow behaviour of the polymer blend.

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