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Binary interaction parameters from blends of SMA copolymers with TMPC–PC copolycarbonates

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Miscibility maps for blends of copolycarbonates based on various proportions of tetramethyl bisphenol-A and bisphenol-A (TMPC–PC) with copolymers of styrene–maleic anhydride (SMA) have been established and interaction energies have been calculated from the data using a binary interaction model combined with the Flory–Huggins theory. This analysis provides an independent assessment of all six interaction energies between the various repeat unit pairs. These include the first reported estimates for the binary interaction energies of MA with TMPC and with PC. The other four interaction energy values found here are in excellent agreement with earlier reports. LCST-type phase separation temperatures were determined and compared with values predicted by the Sanchez–Lacombe equation-of-state theory. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: blends; polycarbonates; styrene/maleic anhydride copolymer)

INTRODUCTION

Commercial blends of polycarbonate (PC) with acrylonitrile–butadiene–styrene (ABS) materials generally have adequate properties without the use of a compatibilizer owing to the nature of the thermodynamic interactions between PC and the styrene–acrylonitrile (SAN) matrix of ABS. Extensive research has accurately quantified the PC/SAN interaction, and the results may be used to optimize blend performance[1–11]. There has been recent interest in blends of PC with styrene–maleic anhydride (SMA) copolymers[12]. To rationally evaluate the opportunities afforded by such blends, it is useful to determine the PC/SMA interaction. Blends of PC with SMA copolymers are completely immiscible; however, prior work has shown that tetramethyl polycarbonate (TMPC) is miscible with SMA copolymers containing limited amounts of MA[13]. With this knowledge, a strategy to probe polymer interactions can be devised through the use of copolymers to dilute the unfavourable PC/SMA interactions employing the repeat-unit-based accounting procedures of a binary interaction model[14–16]. This will create an envelope of miscibility in the isothermal phase map of SMA copolymer composition *versus* TMPC–PC copolycarbonate composition. The boundary separating miscible and immiscible blend compositions can then be used to extract interaction energy estimates, thus allowing the verification or refinement of previously determined interaction energies and the evaluation of unknown interaction energies. Furthermore, once binary interaction energies for the blend system are known, equation-of-state theory can be used to predict phase separation behaviour for comparison with experimental observations.

POLYMER BLEND THERMODYNAMICS

The Gibbs free energy of mixing per unit volume for a binary system of monodisperse polymers can be modelled by the Flory–Huggins theory[17,18]

$$\Delta g_{\mathrm{mix}} = RT\left(\frac{\rho_A\phi_A \ln\phi_A}{M_A} + \frac{\rho_B\phi_B \ln\phi_B}{M_B}\right) + B\phi_A\phi_B \qquad (1)$$

where R is the gas constant, T is the absolute temperature, and ρ_i, ϕ_i, and M_i are the density, volume fraction and molecular weight of component i, respectively. The interaction energy density B includes the heat of mixing plus other non-combinatorial effects. An expression for the spinodal condition can be derived from equation (1) if it is assumed that B is not a function of composition

$$\frac{\mathrm{d}^2\Delta g_{\mathrm{mix}}}{\mathrm{d}\phi_1^2} = RT\left(\frac{\rho_A}{\phi_A M_A} + \frac{\rho_B}{\phi_B M_B}\right) - 2B_{\mathrm{sc}} = 0 \qquad (2)$$

However, if B is dependent on composition, a new interaction energy at the spinodal condition, denoted B_{sc}, is defined by equation (2). At the critical conditions of temperature and blend composition, where the third derivative of Δg_{mix} with respect to composition is exactly zero and the system lies on the boundary between miscible and immiscible, the balance between the combinatorial entropy and component interactions is described by

$$B_{\mathrm{crit}} = \frac{RT}{2}\left[\sqrt{\frac{\rho_A}{(\bar{M}_{\mathrm{W}})_A}} + \sqrt{\frac{\rho_B}{(\bar{M}_{\mathrm{W}})_B}}\right]^2 \qquad (3)$$

where $(\bar{M}_{\mathrm{W}})_i$ is the weight-average molecular weight[19–22]. At a given temperature, miscibility is predicted when the net interaction energy for a blend is more favourable than B_{crit}.

For a blend of two homopolymers, B is simply the interaction energy between the two repeat units involved. However, for blends of homopolymers with copolymers or for blends of two copolymers, a model must be invoked to

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account for the multiple intramolecular and intermolecular interactions that contribute to the net interaction energy density B in equation (1). The binary interaction model accounts for such interactions and has been used with considerable success for interpreting the phase behaviour of blends involving copolymers[14–16]. It has the following form for a blend of two copolymers

$$B=B_{13}\phi_1'\phi_3''+B_{14}\phi_1'\phi_4''+B_{23}\phi_2'\phi_3''+B_{24}\phi_2'\phi_4'' - B_{12}\phi_1'\phi_2'-B_{34}\phi_3''\phi_4'' \qquad (4)$$

where repeat units 1 and 2 are randomly incorporated with volume fractions ϕ_1' and ϕ_2' in the first copolymer, and repeat units 3 and 4 are likewise incorporated in the second copolymer with volume fractions ϕ_3'' and ϕ_4''. The binary interaction model simplifies to the following expression

$$B=B_{12}(\phi_2'')^2 \qquad (5)$$

for a homopolymer/copolymer blend where repeat units of type 1 are common to both polymers and where ϕ_2'' is the volume fraction of type 2 repeat units in the copolymer. Clearly, when the homopolymer and copolymer share a common repeat unit, there is only one binary interaction and it may be determined independently of previously evaluated interaction energies.

The Flory–Huggins theory as presented here can predict only UCST-type phase boundaries unless an empirical temperature dependence is introduced into the interaction energy B. However, most polymer blends, including those investigated in this study, show LCST-type phase behaviour. Equation-of-state theories account for the compressible nature of polymer mixtures and can predict LCST-type phase separation. The lattice-fluid theory of Sanchez and Lacombe[23–29] is used in this work; however, only a brief overview is given here. More detailed discussion and a review of its application to polymer blends can be found elsewhere[30,31]. The Sanchez–Lacombe equation of state is given by

$$\tilde{\rho}^2+\tilde{P}+\tilde{T}\left[\ln(1-\tilde{\rho})+\left(1-\frac{1}{r}\right)\tilde{\rho}\right]=0 \qquad (6)$$

in terms of the reduced variables $\tilde{P}=P/P^*$, $\tilde{T}=T/T^*$, $\tilde{\rho}=\rho/\rho^*=v^*/v$, where P and v are pressure and specific volume, respectively, and r is the chain length defined as

$$r=\frac{MP^*}{kT^*\rho^*}=\frac{M}{v^*\rho^*} \qquad (7)$$

Variables with asterisks denote equation-of-state characteristic parameters with mixing rules as given by Sanchez and Lacombe[25]. The spinodal condition has been derived as

$$\frac{d^2G}{d\phi_1^2}=\frac{1}{2}\left(\frac{1}{r_1\phi_1}+\frac{1}{r_2\phi_2}\right)-\tilde{\rho}\left(\frac{\Delta P^*v^*}{kT}+\frac{1}{2}\psi^2\tilde{T}P^*\beta\right)=0 \qquad (8)$$

where ψ is a dimensionless function reviewed elsewhere[25] and β is the isothermal compressibility. In the Sanchez–Lacombe theory, the bare interaction energy density, ΔP^*, is analogous to B of the Flory–Huggins theory stripped of equation-of-state effects. The binary interaction model shown in equation (4) for B may also be expressed in terms of ΔP^* as

$$\Delta P^*\Delta P^*_{13}\phi_1'\phi_3''+\Delta P^*_{14}\phi_1'\phi_4''+\Delta P^*_{23}\phi_2'\phi_3''+\Delta P^*_{24}\phi_2'\phi_4'' - \Delta P^*_{12}\phi_1'\phi_2'-\Delta P^*_{34}\phi_3''\phi_4'' \qquad (9)$$

where volume fractions are based on hard core volumes. Furthermore, if the volume fractions used in the Flory–Huggins theory are assumed to be equivalent to those used in the Sanchez–Lacombe theory, the Flory–Huggins interaction energy and the bare interaction energy can be related[30,32]

$$B_{sc}=\tilde{\rho}\Delta P^*+\left\{[P_2^*-P_1^*+(\phi_2-\phi_1)\Delta P^*] + \frac{RT}{\tilde{\rho}}\left(\frac{1}{r_1^0v_1^*}-\frac{1}{r_2^0v_2^*}\right)-RT\left[\frac{\ln(1-\tilde{\rho})}{\tilde{\rho}^2}+\frac{1}{\tilde{\rho}}\right] \times\left(\frac{1}{v_1^*}-\frac{1}{v_2^*}\right)\right\}^2 \times\left\{\frac{2RT}{v^*}\left[\frac{2\ln(1-\tilde{\rho})}{\tilde{\rho}^3}+\frac{1}{\tilde{\rho}^2(1-\tilde{\rho})}+\frac{(1-1/r)}{\tilde{\rho}^2}\right]\right\}^{-1} \qquad (10)$$

where r_i^0 is the number of sites occupied by molecule i in the pure close-packed state such that $r_i^0v_i^*=r_iv^*$.

MATERIALS AND PROCEDURES

The polymers used in this study are listed in *Table 1* and *Table 2* along with their physical properties. The polystyrene (PS), Cosden 550, was obtained from Cosden Oil and Chemical Co., while the SMA copolymers were obtained from Arco Chemical Co. and Dow Chemical Co. as indicated. The numerical suffix on the copolymer acronym indicates the weight per cent of MA. Three of the SMA copolymers, SMA9, SMA10.7 and SMA12.2, contain rubber particles added by the manufacturer to improve impact resistance. The PC is Lexan 131-111 from General Electric Co. and the TMPC is from Bayer AG. TMPC–PC copolycarbonates were synthesized in our laboratory using an interfacial polymerization technique described previously[4,33]. The suffix on the copolycarbonate code indicates the weight per cent of TMPC. Molecular weight information was determined by gel permeation chromatography calibrated with polystyrene standards.

Polymer blends of 50/50 composition by weight of TMPC–PC and SMA copolymers were cast from a common solvent, either dichloromethane, DCM, or tetrahydrofuran, THF. Blends containing SMA copolymers with rubber modifier were prepared on a rubber-free basis by subtracting the weight of the rubber from the actual SMA weight; thereby, the correct SMA to TMPC–PC blend ratio was maintained. Films from DCM solutions were cast at room temperature by evaporation from an open beaker, allowed to dry overnight, and then annealed for up to 96 h in a vacuum oven at 180°C. At room temperature, DCM solutions containing 2 wt.% of polymer dried into films within 2 h. Blends were also hot cast from DCM and THF by pouring 2 wt.% polymer solutions on to a glass plate maintained at 50°C and 60°C, respectively. The films were dry to the touch within 3 min but were allowed to remain on the glass plate for an additional 5 min before they were removed and annealed in a vacuum oven at 180°C for up to 96 h.

Glass transition temperatures were determined and blend miscibility was assessed with a Perkin-Elmer DSC-7 system using a scan rate of 20°C min^{-1}. Two scans were performed: the first to erase the thermal history and the second to evaluate the thermal characteristics. Both the onset and the