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Effect of cure shrinkage on the miscibility of a rubber with a thermosetting polymer

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A theoretical simulation of the effect of cure shrinkage on the miscibility of a polydisperse rubber with a trifunctional monomer which undergoes a polycondensation reaction is presented. Both components contribute with an excess volume, calculated according to Simha and Boyer concepts. The free energy of mixing, stated in a lattice model, includes the contribution of holes in both entropic and enthalpic terms. The cure shrinkage is simulated through a decrease in the Van der Waals volume (and the associated excess volume) of the thermosetting polymer with conversion. This leads to a decrease in the absolute value of the entropic contribution and an increase in the value of the term associated with interaction energies. Both factors act against rubber miscibility, thus leading to demixing at lower conversions (compared to the case where cure shrinkage is excluded). The effect is, however, relatively small. © 1997 Elsevier Science Ltd.

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INTRODUCTION

Rubber modification of thermosetting polymers is extensively used for toughening purposes. A usual method of developing the required morphology of dispersed rubbery domains in the polymer network is to select an oligomer that is miscible in the initial formulation and that phase-separates during cure. This reaction-induced phase separation process is primarily driven by the decrease in the entropic contribution to the free energy of mixing, arising from the size increase of the oligomeric species[1,2]. A secondary effect, that may act in favour of or against demixing, is the variation of the effective interaction parameter with conversion[3,4].

We have recently presented a thermodynamic analysis of phase separation for a rubber-modified cyanate ester system[3]. The use of a Flory–Huggins (FH) equation, taking polydispersity of both components into account, led to the conclusion that experimental cloud-point conversions could be fitted only by accepting that the FH interaction parameter decreased with conversion. This was explained by the reduction of the gap between the solubility parameters of both components due to the conversion of polar cyanate ester units into less-polar triazine rings (it must be taken into account, however, that the mean-field approximation of the FH model constitutes a simplified thermodynamic description; in this regard, the interaction parameter plays the role of a fitting function[5–7]).

On the other hand, during the polycondensation of cyanate esters, a significant decrease in the specific volume at constant cure temperature has been reported[8]. For the uncatalysed cure of bisphenol A dicyanate at 200°C, the cure shrinkage attained a value of[8]

$\Delta V = 0.119 \, \mathrm{ml \, g^{-1}}$ or $\%\Delta V = 12.3$. Our attention has been drawn to the question of whether this volume change during reaction has a bearing on rubber miscibility. To get an answer to this question is the aim of the present paper.

A polydisperse polybutadiene oligomer dissolved in a trifunctional monomer undergoing an ideal polycondensation reaction will be considered in the following analysis. The system will be regarded as a blend of three constituents: a rubber, a thermosetting polymer and holes, the latter being present in an amount equal to the addition of the excess free volume contributed by the other two constituents. The effect of the decrease in the excess free volume due to polycondensation will be accounted for by a lattice model including the presence of holes[9,10].

SELECTED SYSTEM

The selected rubber is an oligomeric polybutadiene with $\bar{x}_n = 51.3$ and $\bar{x}_w = 98.5$, which are typical values for rubber modifiers[3]. Its molecular-mass distribution is described by the Schulz–Zimm equation[11]:

$$w_x = 3.09 \times 10^{-4} x^{1.087} \exp(-0.0212x) \qquad (1)$$

where w_x is the mass fraction of the x-mer.

In order to determine the excess volume contributed by x-mers, Simha and Boyer concepts for the thermal expansion of polymers will be applied (*Figure 1*)[12]. The Van der Waals molar volume for the constitutive repeating unit of polybutadiene is equal to[12] $V_w = 37.4 \, \mathrm{cm^3 \, mol^{-1}}$. Therefore, the Van der Waals volume of an x-mer is given by

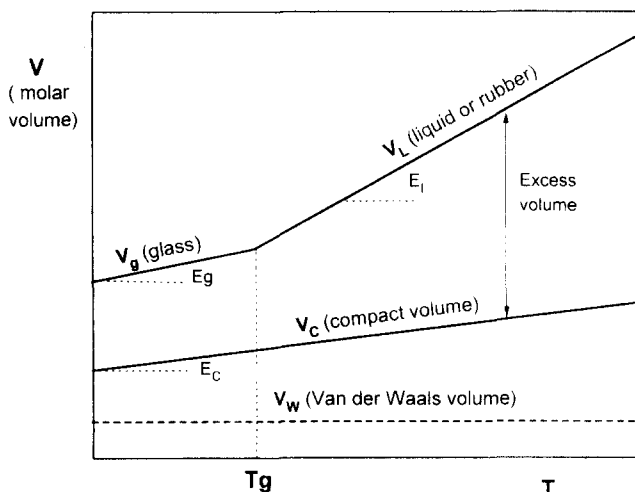$$V_w(x) = 37.4x \, \mathrm{cm^3 \, mol^{-1}} \qquad (2)$$

Figure 1 Molar volume as a function of temperature

Values of molar thermal expansivities are taken as[12]

$$E_c = 0.45 \times 10^{-3} V_w \, \text{cm}^3 \, \text{mol}^{-1} \, \text{K}^{-1} \qquad (3)$$

$$E_L = 1.00 \times 10^{-3} V_w \, \text{cm}^3 \, \text{mol}^{-1} \, \text{K}^{-1} \qquad (4)$$

The compact volume at $T = 0$ K is related to the Van der Waals volume by[12]

$$V_c(0) = V_L(0) = 1.30 V_w \qquad (5)$$

Therefore, molar volumes for an x-mer at any temperature T above T_g are given by

$$V_L(x) = (1.3 + 10^{-3}T)37.4x \qquad (6)$$

$$V_c(x) = (1.3 + 0.45 \times 10^{-3}T)37.4x \qquad (7)$$

The associated volume of holes (excess volume) is given by

$$V_H(x) = V_L(x) - V_c(x) = 2.057 \times 10^{-2} Tx \qquad (8)$$

The selected trifunctional monomer has the following arbitrary values of molar mass and Van der Waals volume: $M = 300 \, \text{g mol}^{-1}$ and $V_w = 160 \, \text{cm}^3 \, \text{mol}^{-1}$. The Flory–Stockmayer distribution gives mass fractions of y-mers for any conversion, $p < p_{gel} = 0.5$:

$$w_y = \frac{(2y)!3}{(y-1)!(2+y)!} p^{y-1}(1-p)^{y+2} \qquad (9)$$

The Van der Waals volume of the y-mer is expressed as

$$V_w(y) = 160y - (y-1)\Delta V_w = (160 - \Delta V_w)y + \Delta V_w \qquad (10)$$

where ΔW_w is the decrease in V_w per mol of covalent bonds (cure shrinkage). At full conversion ($p = 1$), there are 3/2 covalent bonds per mol of initial monomer. Therefore,

$$V_w(p = 1) = V_w(p = 0) - 1.5\Delta V_w \qquad (11)$$

Assuming a 12% volume contraction in the course of polymerization, i.e. $V_w(p = 1)/V_w(p = 0) = 0.88$, leads to $\Delta V_w = 12.8 \, \text{cm}^3 \, \text{mol}^{-1}$.

The molar volumes of the y-mer at any temperature T (above T_g) may be obtained by similar arguments as those used to derive equations (6) to (8):

$$V_L(y) = (1.3 + 10^{-3}T)(12.8 + 147.2y) \qquad (12)$$

$$V_c(y) = (1.3 + 0.45 \times 10^{-3}T)(12.8 + 147.2y) \qquad (13)$$

The associated molar volume of holes (excess volume) is given by

$$V_H(y) = V_L(y) - V_c(y) = 0.55 \times 10^{-3}T(12.8 + 147.2y) \qquad (14)$$

VOLUME FRACTIONS

In order to calculate the volume occupied by each one of the three constituents, i.e. compact rubber, compact thermosetting polymer and holes, it is necessary to define a calculation basis independent of conversion. The mass fraction of rubber in the initial formulation, w_R, is selected.

The number of moles of the rubber x-mer, per unit mass, is given by

$$n_x = w_R w_x/(54.1x) \qquad (15)$$

where $54.1x$ is the molar mass of the x-mer.

The compact volume occupied by the rubber x-mer, per unit mass of system, is obtained from

$$V_R(x) = n_x V_c(x) \qquad (16)$$

The total compact volume occupied by the rubber, per unit mass, is given by

$$V_R = \sum V_R(x) \qquad (17)$$

Values for the thermosetting polymer y-mer are calculated in an anologous way:

$$n_y = (1 - w_R)w_y/(300y) \qquad (18)$$

$$V_P(y) = n_y V_c(y) \qquad (19)$$

$$V_P = \sum V_P(y) \qquad (20)$$

The volume of holes per unit mass is calculated from

$$V_H = \sum n_x V_H(x) + \sum n_y V_H(y) \qquad (21)$$

The total volume per unit mass, is then given by

$$V_T = V_R + V_P + V_H \qquad (22)$$

Corresponding volume fractions are defined by

$$\phi_x = V_R(x)/V_T \qquad (23)$$

$$\phi_R = \sum \phi_x \qquad (24)$$

$$\phi_y = V_P(y)/V_T \qquad (25)$$

$$\phi_P = \sum \phi_y \qquad (26)$$

$$\phi_H = 1 - \phi_R - \phi_P \qquad (27)$$

FREE ENERGY OF MIXING

In order to derive expressions for the free energy of mixing, ΔG_{mix}, a lattice with a mesh equal to the compact volume of the rubber repeating unit will be defined.

$$V_{cell} = (1.3 + 0.45 \times 10^{-3}T)37.4 \, \text{cm}^3 \, \text{mol}^{-1} \qquad (28)$$

The number of moles of cells occupied by x-mers and y-mers, per unit mass, is given by

$$V_c(x)/V_{cell} = x \qquad (29)$$

$$V_c(y)/V_{cell} = (12.8 + 147.2y)/37.4 = Y(y) \qquad (30)$$

The number-average degrees of polymerization of both components, referred to the lattice size, are calculated as

$$\sum n_x x / \sum n_x = \bar{x}_n \qquad (31)$$

$$\sum n_y Y(y) / \sum n_y = \bar{Y} \qquad (32)$$

While $\bar{x}_n$ remains constant, $\bar{Y}$ increases with conversion.

The number of moles of cells, per unit mass, occupied by the different constituents are

$$N_R = V_R / V_{cell} \qquad (33)$$

$$N_P = V_P / V_{cell} \qquad (34)$$

$$N_H = V_H / V_{cell} \qquad (35)$$

and

$$N_T = N_R + N_P + N_H \qquad (36)$$

Both N_P and N_H decrease with conversion due to cure shrinkage.

The number of moles of holes in the system is determined by the size distribution. If a uniform distribution equal to the cell size is set, the number of moles of holes is given by

$$n_H = N_H \qquad (37)$$

The free energy of mixing may be expressed in terms of the variations of internal energy, the volume change upon mixing and the entropic contribution:

$$\Delta G_{mix} = \Delta U_{mix} + P_T \Delta V_{mix} - T \Delta S_{mix} \qquad (38)$$

where P_T is the total pressure. It has already been assumed that $\Delta V_{mix} = 0$, i.e. the total volume of holes is the sum of the volume of holes associated with the rubber and that associated with the thermosetting polymer.

The entropic contribution is calculated by assuming a random occupation of cells by the different constituents. This gives the usual combinatorial expression:

$$-\Delta S_{mix} / R = \sum n_x \ln \phi_x + \sum n_y \ln \phi_y + n_H \ln \phi_H \qquad (39)$$

The internal energy of the mixture is calculated by assuming that it depends only on nearest-neighbour interactions[9],

$$U_{mix} = (z/2)(N_R P_{RR} E_{RR} + 2 N_R P_{RP} E_{RP} + N_P P_{PP} E_{PP}) \qquad (40)$$

where z is the coordination number, P_{ij} is the probability that component i at a particular lattice site interacts with j (if $i = j$, then P_{ij} is calculated taking into account only the segments that are not covalently bonded), and E_{ij} is the energy per interaction pair (all the interaction energies involving holes are assumed to be zero).

In the mean-field approximation, P_{ij} values are given by[9]

$$P_{RP} = N_P / N_T = \phi_P \qquad (41)$$

$$P_{RR} = f_R N_R / N_T = f_R \phi_R \qquad (42)$$

$$P_{PP} = f_P N_P / N_T = f_P \phi_P \qquad (43)$$

$$f_R = (z - 2)/z + 2/(z \bar{x}_n) \qquad (44)$$

$$f_P = (z - 2)/z + 2/(z \bar{Y}) \qquad (45)$$

The factors f_R and f_P give the fraction of coordination sites that are not covalently bonded with the selected site. If $z \rightarrow \infty$, $f_R = f_P = 1$.

For the pure compact components, the corresponding internal energies are given by

$$U^R = (z/2) N_R f_R E_{RR} \qquad (46)$$

$$U^P = (z/2) N_P f_P E_{PP} \qquad (47)$$

Then,

$$\Delta U_{mix} = U_{mix} - U^R - U^P = (z/2)(N_R N_P / N_T)$$
$$\times \{ 2 E_{RP} - [(N_T - N_R)/N_P] f_R E_{RR} \qquad (48)$$
$$- [(N_T - N_P)/N_R] f_P E_{PP} \}$$

By calling $\alpha = z E_{RP}/RT$, $\beta = z f_R E_{RR}/2RT$ and $\gamma = z f_P E_{PP}/2RT$, and using volume fractions, equation (48) becomes

$$\Delta U_{mix} / N_T RT = \chi \phi_R \phi_P \qquad (49)$$

where

$$\chi = \alpha - \beta(\phi_P + \phi_H)/\phi_P - \gamma(\phi_R + \phi_H)/\phi_R \qquad (50)$$

From equations (38), (39) and (49), and taking into account that $x n_x / N_T = \phi_x$ and $Y(y) n_y / N_T = \phi_y$, the free energy of mixing per mole of cells may be written as

$$\Delta G_{mix} / N_T RT = \sum (\phi_x / x) \ln \phi_x + \sum [\phi_y / Y(y)] \ln \phi_y + \phi_H \ln \phi_H + \chi \phi_R \phi_P \qquad (51)$$

CLOUD-POINT CURVES (CPC)

Chemical potentials arise from the partial derivatives of ΔG_{mix} with respect to n_x, n_y and n_H. The following equations were obtained:

$$\Delta \mu_x / RT = 1 + \ln \phi_x - Ax + \chi(\phi_P)^2 x + x \gamma \phi_P \phi_H / \phi_R \qquad (52)$$

$$\Delta \mu_y / RT = 1 + \ln \phi_y - A Y(y) + \chi(\phi_R)^2 Y(y) + Y(y) \beta \phi_R \phi_H / \phi_P \qquad (53)$$

$$\Delta \mu_H / RT = 1 + \ln \phi_H - A - \chi \phi_R \phi_P - \beta \phi_R - \gamma \phi_P \qquad (54)$$

where

$$A = (\phi_R / \bar{x}_n) + (\phi_P / \bar{Y}) + \phi_H \qquad (55)$$

Cloud-point curves (CPC) were obtained by equating the chemical potentials in both phases and using typical procedures to solve the resulting equations[13,14].

RESULTS AND DISCUSSION

In order to generate a CPC with a maximum located close to room temperature and with an upper-critical-solution-temperature behaviour (UCST), the coordination number, z, was set equal to 10 and the following values were selected for the interaction energies: $E_{PP} = 235.3 \, J \, mol^{-1}$, $E_{RR} = 402.8 \, J \, mol^{-1}$ and $E_{RP} = (E_{RR} E_{PP})^{1/2} = 307.9 \, J \, mol^{-1}$. The resulting CPC for the initial mixture of monomer and rubber is shown in *Figure 2*. The location of the maximum threshold temperature at very low rubber concentrations, i.e. $w_R(max) = 0.075$, is typical of solutions of a polydisperse polymer (the rubber) in a solvent (the monomer). The critical point is located at $w_R(crit) = 0.163$.
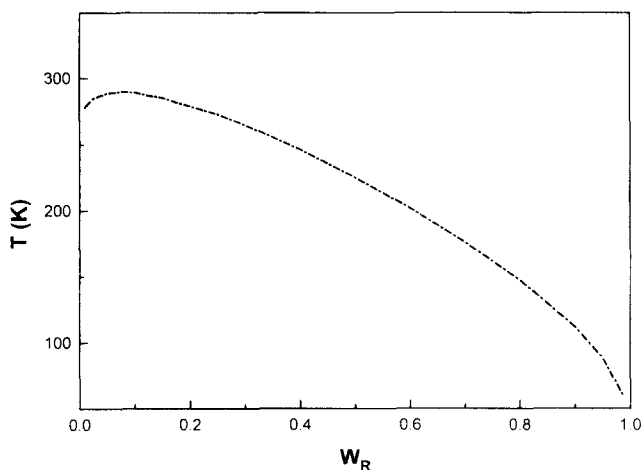
Figure 2 Cloud-point curve for the initial mixture of the monomer with the polydisperse rubber
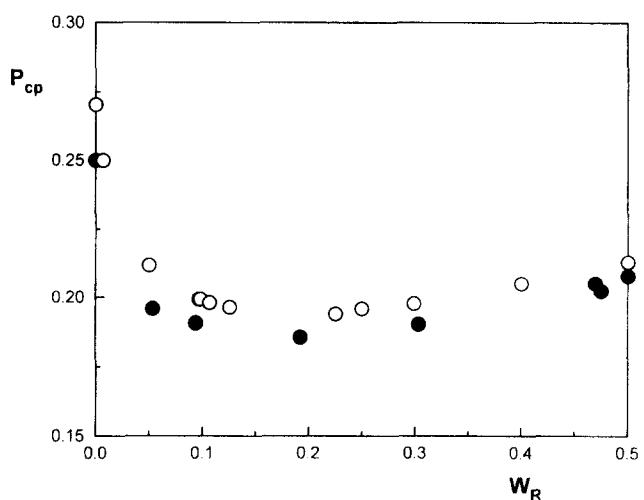

Figure 3 Cloud-point conversions (p_{cp}) as a function of the rubber mass fraction when the polycondensation is carried out at $T = 460$ K (O: $\Delta V_w = 0$; ●: $\Delta V_w = 12.8$ cm^3 mol^{-1})

Figure 3 shows the calculated cloud-point conversions when the polycondensation is carried out of 460 K. Points located at higher conversions represent the case where no cure shrinkage occurs ($\Delta V_w = 0$). Points located at lower conversions take the volume shrinkage into account ($\Delta V_w = 12.8$ cm^3 mol^{-1}). Simulations performed at different temperatures gave the same picture as *Figure 3*; i.e., cure shrinkage acts to decrease the cloud-point conversion but the effect is relatively small (it may

be contained within the experimental error involved in the measurement of conversion).

From equation (51), it is observed that a decrease in the volume fraction of holes decreases the entropic contribution to the free energy of mixing and increases the value of the energetic term. Both factors act against rubber miscibility in the thermosetting polymer. Therefore, cloud-point conversions are shifted to lower values.

CONCLUSIONS

The volume contraction during polymerization (cure shrinkage) produces a slight decrease in the miscibility of the rubber in the thermosetting polymer, leading to a shift of cloud-point conversions to lower values. The reason for this effect is the reduction in the volume fractions of holes. This produces a decrease in the entropic contribution to the free energy of mixing and an increase in the value of the energetic term. Both factors act in the sense of decreasing rubber miscibility in the thermosetting polymer.

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