4. Thermodynamics of Polymer Blends

Polymeric materials find growing applications in various fields of everyday life because they offer a wide range of application relevant properties. Blending of polymers is a technological way for providing materials with full set of desired specific properties at the lowest price, e.g. a combination of strength and toughness, strength and solvent resistance, etc. Blending also benefits the manufacturer by offering improved processability, product uniformity, quick formulation changes, plant flexibility and high productivity.[56]

If two polymers are mixed, the most frequent result is a system that exhibits a complete phase separation due to the repulsive interaction between the components (i.e. the chemical incompatibility between the polymers).[57, 58] Complete miscibility in a mixture of two polymers requires that the following condition is fulfilled:

$$\Delta G_m = \Delta H_m - T\Delta S_m < 0 \qquad\qquad (4.1)$$

where ΔG_m, ΔH_m, and ΔS_m are the Gibb's free energy, the enthalpy and entropy of mixing at temperature T, respectively.

For a stable one-phase system, criteria for phase stability of binary mixtures of composition ϕ at fixed temperature T and pressure p are:

$$\Delta G_m < 0 \quad , \quad \left(\frac{\partial^2 \Delta G_m}{\partial \phi^2} \right)_{p,T} > 0 \qquad\qquad (4.2)$$

Miscible polymer blend is a polymer blend which is homogeneous down to the molecular level and associated with the negative value of the free energy of mixing and the domain size is comparable to the dimensions of the macromolecular statistical segment. The value of $T\Delta S_m$ is always positive since there is an increase in the entropy on mixing. Therefore, the sign of ΔG_m always depends on the value of the enthalpy of mixing ΔH_m. The polymer pairs mix to form a single phase only if the entropic contribution to free energy exceeds the enthalpic contribution, i.e.,

$$\Delta H_m < T\Delta S_m \qquad\qquad (4.3)$$

For most polymer blends the miscibility increases with increasing the pressure. The effect depends on the magnitude of the heat of mixing ΔH_m. For $\Delta H_m < 0$ the miscibility is enhanced by compression, whereas for those with $\Delta H_m > 0$ it is reduced.

A schematic phase diagram is shown in Figure 4.1. There are three regions of different degree of miscibility: 1. The single-phase miscible region between the two binodals, 2. The four fragmented metastable regions between binodals and spinodals, and 3. The two-phase separated regions of immiscibility, bordered by the spinodals. The diagram also shows two critical solution temperatures, the lower, LCST (at higher temperature), and the upper, UCST (at lower temperature). The phase diagram with two critical points is a rule for mixtures of low molar mass components, whereas the polymer blends usually show either LCST (most) or UCST.
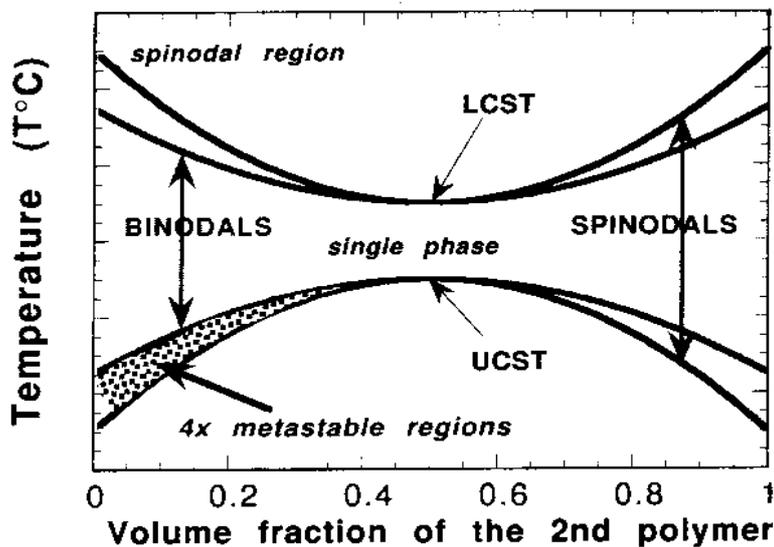

Figure 4.1 Phase diagram for liquid mixtures with the upper and the lower critical solution temperature, UCST and LCST, respectively.[59]

The binodals (Figure 4.1) separate miscible (one-phase) and metastable region, the spinodals separate metastable and two-phase region. The thermodynamic conditions for phase separations are given by[59]:

spinodal:
$$\left(\frac{\partial^2 \Delta G_m}{\partial \phi^2} \right)_{p,T} = 0 \qquad (4.4)$$

critical point:

$$\left(\frac{\partial^2 \Delta G_m}{\partial \phi^2}\right)_{p,T} = \left(\frac{\partial^3 \Delta G_m}{\partial \phi^3}\right)_{p,T} = 0 \qquad (4.5)$$

The phase separation takes place when a single-phase system suffers a change of either composition, temperature or pressure that forces it to enter either the metastable or the spinodal region. When the system enters from single-phase region into the metastable region, the phase separation occurs by the mechanism resembling crystallization – slow nucleation followed by growth of the phase separated domains.[59] By contrast, when the system is forced to jump from a single-phase into the spinodal region of immiscibility the phases separate spontaneously by a mechanism called spinodal decomposition.

Starting point for most of the theoretical interpretations of polymer solutions and blends is the Flory-Huggins lattice theory. It is basically an extension of the concept of regular solutions on polymer solutions. Thus the model restrictions are no change of volume during mixing (incompressible model), the entropy of mixing is entirely given by the number of rearrangements during mixing (combinatorial entropy) and the enthalpy of mixing is caused by interactions of different segments after the dissolution of interactions of the same type of segments. It is a mean-field model, i.e. only average interactions are taken into consideration. The main problem was to find an expression for the entropy of mixing because it was found experimentally that polymer solutions show significant deviations from values expected for ideal solutions. Assuming a rigid cubic lattice model, this problem was independently solved for polymer solutions by Huggins and Flory.

The lattice theory for the enthalpy of mixing in polymer solutions, developed by Flory and Huggins, can be formally applied to polymer mixtures, which provides a rough estimation of the miscibility of the polymers.[60, 61] Assuming random mixing of two polymers and $\Delta V_m = 0$ yields the well-known expression for the combinatorial entropy of mixing ΔS_m of the Flory-Huggins theory:

$$\Delta S_m = -R\left[\frac{\phi_1}{r_1}\ln\phi_1 + \frac{\phi_2}{r_2}\ln\phi_2\right] \qquad (4.6)$$

where ϕ_i is the volume fraction of the component i and r_i is the number of polymer segments, R is the gas constant. It can be seen that the entropy of mixing decreases with increasing molar mass (r_i is proportional to the degree of polymerization) and vanishes for infinite molar

masses. Applying the concept of regular solutions and assuming all pair interactions in the framework of a mean-field theory yields for the enthalpy of mixing ΔH_m:

$$\Delta H_m = RT\chi\phi_1\phi_2 \qquad (4.7)$$

For binary systems the Flory-Huggins equation can be expressed in the following form [62, 63]:

$$\Delta G_m = RT\left[\frac{\phi_1}{r_1}\ln\phi_1 + \frac{\phi_2}{r_2}\ln\phi_2 + \chi\phi_1\phi_2\right] \qquad (4.8)$$

where χ is the so called Flory-Huggins binary interaction parameter. R is the universal gas constant, and T is the absolute temperature. The first two terms of the right hand side in Equation 4.8 are related to the entropy of mixing and the third term is originally assigned to the enthalpy of mixing.

For polymers having infinite molar mass (i.e. r_i is infinite) the entropic contribution is very small and the miscibility or immiscibility of the system mainly depends on the value of the enthalpy of mixing (Equation 4.7). Miscibility can only be achieved when χ is negative.

The term 'parameter' is widely used to describe χ but it is definitively better characterized by the term 'function', because χ depends on such quantities as temperature, concentration, pressure, molar mass, molar mass distribution and even on model parameters as the coordination number of the lattice and segment length.[56]

For polymers, the miscibility can only be achieved when $\chi < \chi_{cr}$. The χ parameter at the critical point χ_{cr} can be obtained from the definition of the critical point (Figure 4.1) and Equation 4.8 as follows:

$$\chi_{cr} = \frac{1}{2}\left(\frac{1}{\sqrt{r_1}} + \frac{1}{\sqrt{r_2}}\right)^2 \qquad (4.9)$$

where r_i is the number of polymer segments (which is proportional to the degree of polymerization).

It should be mentioned that the Equations 4.8 and 4.9 are based on the assumption that χ is not a function of composition, χ_{cr} is only a function of the molar masses.

PE/EVA blends under investigations in this work are blends of a homopolymer and a copolymer (PE/E_xVA_{1-x}). The effective interaction parameter χ between the homopolymer and the copolymer is given by:

$$\chi = x\chi_{EE} + (1-x)\,\chi_{EV} - x(1-x)\,\chi_{EV} \qquad (4.10)$$

where χ_{ij} are the segmental interaction parameters and x is the copolymer composition in mol.-%. $\chi_{EE} = 0$ in the case of PE/EVA blends and therefore the effective interaction parameter χ is equal to:

$$\chi = (1-x)\,\chi_{EV} - x(1-x)\,\chi_{EV} \qquad (4.11)$$

And as already mentioned, the polymers are miscible when $\chi < \chi_{cr}$.