

Polymeric Nanocomposites

Theory and Practice

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1. Auflage 2007. Buch. XIV, 384 S. Hardcover

ISBN 978 3 446 40270 6

Format (B x L): 17,5 x 25,1 cm

Gewicht: 853 g

Weitere Fachgebiete > Technik > Verfahrenstechnik, Chemieingenieurwesen,
Lebensmitteltechnik > Technologie der Kunststoffe und Polymere

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ISBN-10: 3-446-40270-5

ISBN-13: 978-3-446-40270-6

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3.2.2 Multi-Component Systems

3.2.2.1 Chemical Potential

If the system incorporates a number of components:

$$dG = Vdp - SdT + \sum_i \mu_i dn_i \quad (3.11)$$

where n_i is the mole fraction of component i . The chemical potential for component i , μ_i , is defined as follows:

$$\mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{T, P, n_j} \quad (3.12)$$

The subscript j refers to all components in the system, except i . At equilibrium, the chemical potential of each component must be equal in all parts of the system. At constant P and T , Equation 3.12 becomes:

$$dG = \mu_1 dn_1 + \dots + \mu_i dn_i = dW'_i \quad (3.13)$$

Equation 3.13 shows that non-expansion work variation can arise from changes in the composition of the system. Chemical potential is an intensive property, and it can be regarded as the driving force of chemical systems to equilibrium. For multi-component systems, in which the chemical composition changes:

$$U = TS - PV + \sum_i \mu_i N_i \quad (3.14)$$

where N_i is the number of moles of component i in the system.

The configurational contribution to the entropy of mixing in a binary system containing mole fractions X_A and X_B of species A and B , respectively, is given by:

$$\Delta S = -\psi R(X_A \ln X_A + X_B \ln X_B) \quad (3.15)$$

where ψ is the number of sites per mole.

3.2.2.2 Phase Equilibria and Phase Diagrams

3.2.2.2.1 One Component Systems

Figure 3.2 shows the evolution of the Gibbs free energy as a function of temperature at constant pressure [Smith (2004)]. The two changes in the slope of the $(G - T)$ curve correspond to the two-phase transitions: solid-liquid and liquid-gas. Since $(\partial G / \partial T)_P = -S$, the slopes of the curves reflect the entropies of the phases. The gas phase has the largest negative slope and, accordingly, the highest entropies. Its free energy is lower at higher temperatures. It is the most stable phase at high temperatures.

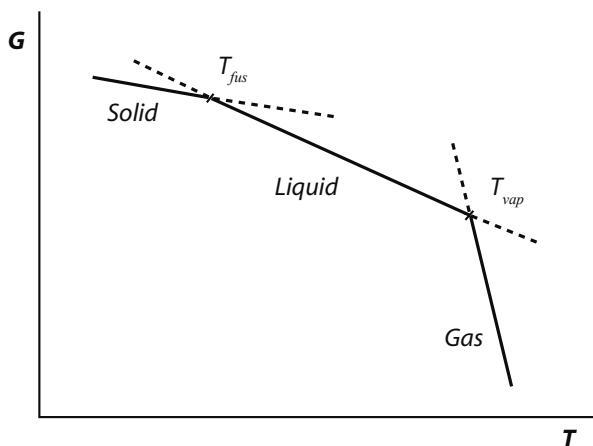


Figure 3.2: Gibbs free energy as a function of temperature for a pure substance

The lines intersect at points, where the free energies of the corresponding phases are equal:

$$G(s) = G(l) \quad \text{and} \quad G(l) = G(g) \quad (3.16)$$

where s , l , and g refer to the solid, liquid, and gas phases, respectively. Thus, at these points, $\Delta G = 0$ and $\Delta H = T\Delta S$. Moreover, $\Delta S_{fus} = \Delta H_{fus}/T_{fus}$, and $\Delta S_{vap} = \Delta H_{vap}/T_{vap}$. Subscripts fus and vap refer to fusion and vaporization, respectively.

The phase diagram of the substance may be obtained by combining data at different pressure levels (isobars), similar to those shown in Figure 3.2. According to the relation $(\partial G/\partial p)_T = V$, the variation of the Gibbs free energy is related to the system volume at constant temperature and variable pressure. Thus, shifts in the equilibrium position, as a result of phase transitions, depend on the volume change associated with the phase transition.

3.2.2.2 Phase Equilibrium in Multi-Component Systems

The Gibbs free energy is a function of pressure, temperature, and the composition of the mixture, represented by the mole fractions of the components: The free energy is an extensive property of the system. Therefore,

$$G_{mix} = \sum_i G_i \quad (3.17)$$

where G_i is the free energy of component i .

3.2.2.2.3 Binary Mixtures

The product of a mechanical mixture contains several non-interacting phases, each phase maintaining its individual characteristics. The Gibbs free energy is proportional to the quantities of the phases present in the mechanical mixture, as indicated in Eq. 3.17. As a result, the Gibbs free energy of a binary mechanical mixture varies linearly with composition. Figure 3.3 illustrates this situation [Richet (2001)].

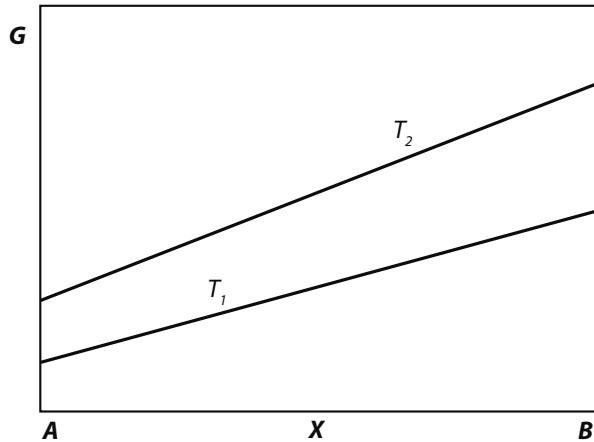


Figure 3.3: Gibbs free energy of a mechanical mixture, at two temperatures

The Gibbs free energy-composition curve, for a real solution, is not linear, and the shape of the curve depends on the miscibility of the two components of the solution: solvent and solute. Figure 3.4 shows the composition dependence of G for a stable solution. The two

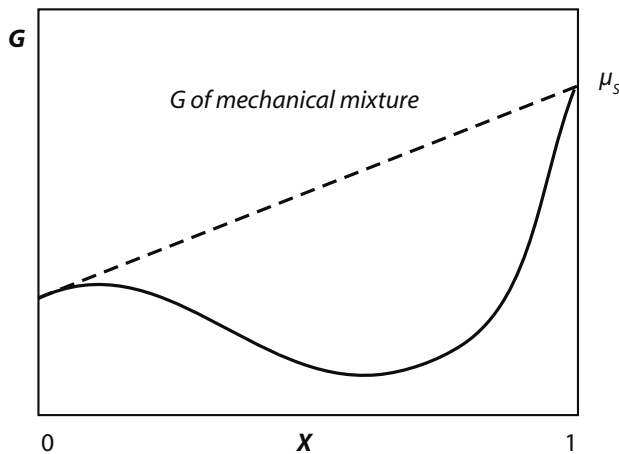


Figure 3.4: Gibbs free energy of a stable binary solution

components A and B are perfectly miscible over the whole range of the binary system. Thus, the Gibbs free energy shows a minimum with the solution composition or mole fraction X . At any point of the curve, $G_{\text{Solution}} < G_{\text{Mechanical mixture}}$.

For a mixture of two immiscible components, the solution is unstable at all concentrations, except in the immediate vicinity of the pure components. In this case, the curve $G - X$ is characterized by a maximum of G , as illustrated in Figure 3.5. For any composition, the Gibbs free energy of the solution would be higher than that of a mechanical mixture of the two pure components.

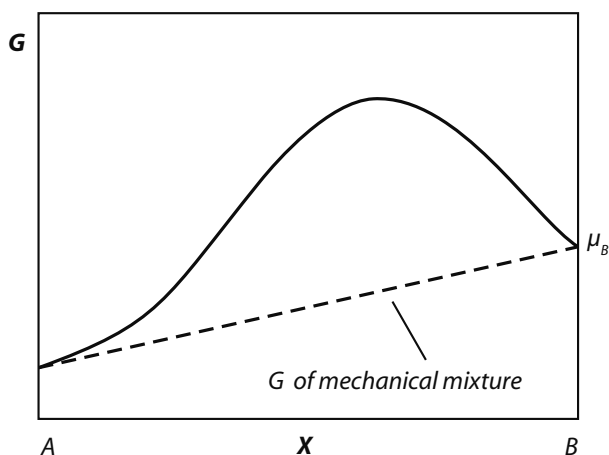


Figure 3.5: Gibbs free energy of a binary mixture, unstable at any point except the immediate vicinity of the pure components

Figure 3.6 shows the $G - X$ diagram for a real solution for which, over a wide composition interval, the stable state corresponds to a separation of the system into two phases. In this case, the relationship $G_{\text{Solution}} < G_{\text{Mechanical mixture}}$ holds for all compositions of the solution. Near the pure points of both A and B , the free energy G of the solution first decreases when the other component is added. Then, after reaching a minimum (points Q and Q'), it begins to increase with the addition of the second component. For a certain composition (M), the Gibbs free energy displays a maximum. The inflection points of the curve (P and P') mark the change in the concavity of the $G - X$ curve. Q , P , M , P' , and Q' divide the $G - X$ curve into three regions: stable, unstable, and metastable.

The Gibbs free energy and the separated phases change with pressure and temperature. As a result, the boundaries between the stable, metastable, and unstable regions also shift, when the pressure and temperature vary. In the pressure-temperature-composition space, the locus of the inflexion points of the $G - X$ curves, P and P' , is a surface called the “spinodal”.

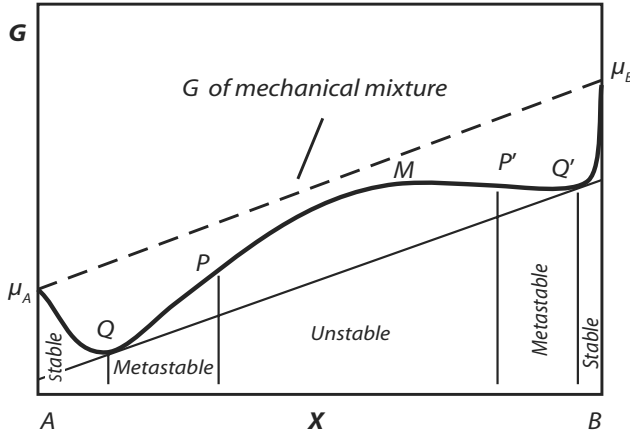


Figure 3.6: Gibbs free energy for a typical solution, which is stable at low concentrations of the components and unstable at intermediate concentrations

For a binary system at constant pressure (in $T - X$ coordinates), this surface reduces to a curve, as illustrated in Figure 3.7. The spinodal curve obeys the following relation:

$$\left(\frac{\partial^2 G}{\partial X^2} \right)_{P,T} = 0 \quad (3.18)$$

This partial derivative is negative in the unstable region and positive in the metastable region.

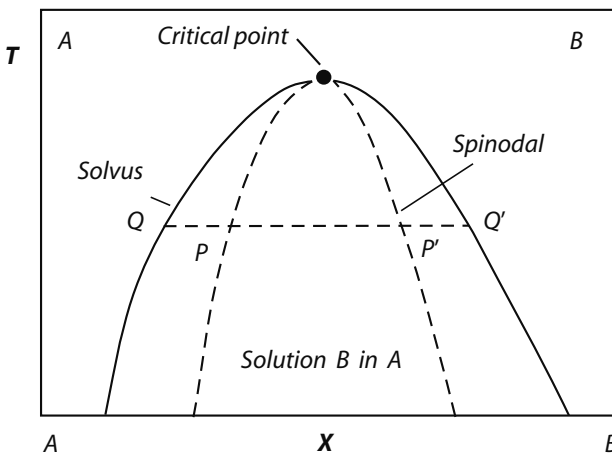


Figure 3.7: Component A – Component B phase separation; stability limit between A and B and the solution of B in A shown by solvus

In the pressure-temperature-composition space, the boundary between the metastability and stability defines another surface called *solvus* or bimodal. At the homogenization temperature, the solvus is tangential to the spinodal. At constant pressure, this surface (*solvus*) reduces to a curve, as shown in Figure 3.7. The point where the *solvus* is tangential to the *spinodal* is the critical point. At this point, the distinction between the two phases can no longer be made. This critical point is defined by:

$$\left(\frac{\partial^3 G}{\partial X^3} \right)_{p,T} = 0 \quad (3.19)$$

Equation 3.17 may be used to calculate the critical composition. Systems may exhibit a higher critical solution temperature (HCST), as in this case, or a lower solution critical temperature (LCST). In the latter case, the phase diagram will show a minimum.

The following relationships can be derived for an ideal solution containing mole fractions X_i of species i :

$$G = \sum_i \mu_i X_i \quad (3.20)$$

$$\Delta G_{mix} = RT \sum_i X_i \ln X_i \quad (3.21)$$

$$\Delta S_{mix} = -R \sum_i X_i \ln X_i \quad (3.22)$$

$$\Delta H_{mix} = \Delta G_{mix} + T \Delta S_{mix} = 0 \quad (3.23)$$

$$\Delta V_{mix} = - \left(\frac{\partial \Delta G_{mix}}{\partial p} \right)_T = - \left(\frac{\partial RT \sum_i X_i \ln X_i}{\partial p} \right)_T = 0 \quad (3.24)$$

The entropy of mixing given above is the ideal entropy of mixing. It applies to completely random mixing of the components and represents the limiting behavior for mixtures. The ideality condition implies that the molecules of all components interact in identical manner.

In real solutions, the entropies of mixing are positive.

3.2.3 Surface Free Energy

A typical molecule in a solid or liquid sample is completely surrounded by other molecules. Thus, the intermolecular forces (cohesive forces) are balanced, and the net internal force is zero. This is not true at the surface, because there is an imbalance as the local chemical environment changes and the net internal force is not zero. The net effect is the presence of an excess energy at the surface, called “surface free energy”. The imbalance generates a surface tension (σ) which acts to minimize the surface area. The surface (free) energy is

defined as the work required to increase the area of a surface by a unit area or to create a new surface of a unit area. The magnitude of this work is proportional to the area of the new surface:

$$dW = \sigma dA \quad (3.25)$$

where σ is the surface tension. Typical units of surface tension are joules per square meter ($\text{J} \cdot \text{m}^{-2}$) (surface energy) or $\text{N} \cdot \text{m}^{-1}$ (surface tension). At constant pressure and temperature, the work of creating surfaces is related to the Gibbs free energy:

$$\sigma = \left(\frac{\partial G}{\partial A} \right)_{P, T, n} \quad (3.26)$$

Since σ is positive, surfaces spontaneously contract, $dA < 0$, then $dG < 0$.

When two immiscible phases (i and j) meet, the interaction between the substances involved occurs at their interfaces. At the interface, the net internal force of each phase is not zero and will lead to the appearance of a tension called interfacial tension (σ_{ij} or γ_{ij}). Interfacial tension is somewhat similar to surface tension in that cohesive forces are also involved. However, the main forces involved in interfacial tension are adhesive forces, i.e., tension between phases.

The work required to separate two immiscible liquids α and β , in contact, is related to the surface tension at the interface by the equation:

$$W_{adh} = W_{coh}^{\alpha} + W_{coh}^{\beta} - \sigma_{\alpha\beta} \quad (3.27)$$

where W_{adh} is the work of adhesion, W_{coh}^{α} is the work of cohesion of phase α , W_{coh}^{β} is the work of cohesion of phase β , and $\sigma_{\alpha\beta}$ is the interfacial tension at the interface between the phases α and β .

At a liquid-solid interface, if the liquid-solid adhesive forces are stronger than the liquid-liquid cohesive forces, the liquid will tend to spread over or wet the solid surface. If the liquid-liquid cohesive forces are stronger than the liquid-solid adhesive forces, then the liquid does not wet the solid surface. The liquid will tend to form a droplet. Wetting ability of a liquid is a function of the surface energies of the solid-gas interface, the liquid-gas interface, and the solid-liquid interface. One way to quantify the liquid surface wetting characteristics is to measure the contact angle of a drop of liquid placed on the surface of the solid. As shown in Figure 3.8, the contact angle (ϕ), is the angle formed by the solid/liquid interface and the liquid/vapor interface, measured from the side of the liquid. The contact angle should be less than 90 degrees for the liquids to wet a given surface.

The fundamental thermodynamics equation for mixtures, including surface effects, becomes:

$$dG = VdP - SdT + \sum_i \mu_i dn_i + \sigma dA \quad (3.28)$$

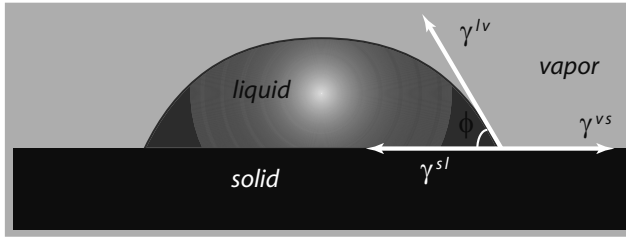


Figure 3.8: Contact angle between a liquid and a solid

If we consider the surface “s”, at constant temperature and pressure, the surface free energy G_s relation takes the following forms:

$$dG_s = \sigma_s dA_s + \sum_i \mu_{si} dn_{si} \quad (3.29)$$

$$G_s = \sigma_s A_s + \sum_i \mu_{si} n_{si} \quad (3.30)$$

where n_{si} represents the moles of component i at the surface, μ_{si} is the surface chemical potential, and A_s is the surface area. Equation 3.30 is the Gibbs-Duhem equation for the free energy of the surface [Lewis and Randall (1961)]. The following relationship may be derived:

$$d\sigma_s = - \sum_i \Gamma_{si} d\mu_{si} \quad (3.31)$$

where Γ_{si} is the number of moles of component i adsorbed per unit area of the surface.

3.2.4 Types of Interfacial Interactions

3.2.4.1 Intermolecular Interactions – Van Der Waals Forces

Van der Waals [van Oss (1994)] showed that the ideal gas law does not apply to real gases or liquids, due to interatomic or intermolecular forces that are non-covalent and non-electrostatic. The van der Waals forces may be generated by:

- randomly orienting dipole-dipole interactions, described by [Keesom (1921)],
- randomly orienting dipole-induced dipole interactions, described by [Debye (1920)], and
- fluctuating dipole-induced dipole interactions, described by [London (1930, 1937)].