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Publisher's version / Version de l'éditeur:

https://doi.org/10.1007/978-94-011-4421-6_81

Polypropylene, pp. 601-605, 1999

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POLYMER BLENDS — Fundamentals

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Introduction

Polymer blend is a mixture of at least two macromolecular substances, polymers or copolymers, in which the concentration of each polymeric ingredient is above 2 wt%. Blends are either miscible or immiscible. *The miscible polymer blends* are homogenous down to the molecular level. Their free energy and heat of mixing, $\Delta G_m \cong \Delta H_m \leq 0$ and $\partial^2 \Delta G_m / \partial \phi^2 > 0$, where ϕ is the volume fraction. In these blends, the domain size is comparable to the dimension of the macromolecular statistical segment, $d < 20$ nm. *The immiscible polymer blends* are those where $\Delta G_m > 0$, and/or $\partial^2 \Delta G_m / \partial \phi^2 < 0$. Most polymer blends are immiscible.

Polymer alloy is an immiscible, compatibilized blend with modified interface and tailored morphology. *Compatibilization* is either a chemical or physical modification of the interfacial properties. *The interphase* is the third phase in binary blends, formed in between domains of the two polymeric components — its thickness is $\Delta l = 2$ to 60 nm.

Thermodynamics — miscibility and phase separation

It is customary to discuss blend miscibility starting with the Huggins-Flory relation:

$$\Delta G_m = \Delta H_m - T\Delta S_m; \quad \Delta H_m = RTV\chi_{12}\phi_1\phi_2; \quad \Delta S_m = RTV\sum_{i=1}^2(\phi_i \ln \phi_i) / V_i \quad (1)$$

where ΔS_m is the configurational entropy of mixing, R is the gas constant, T is temperature, V_i its molar volume, $V = \sum V_i$, and χ_{ij} is the binary interaction parameter, usually a complex function of ϕ , T and pressure, P . In polymer blends $\Delta S_m \rightarrow 0$, thus miscibility originates mainly from the enthalpic effects, $\Delta H_m < 0$, viz. specific

interactions (hydrogen bonding, ionic, or dipole interactions). It may also be caused by the interactions between two macromolecules that reduce the internal steric stresses in at least one polymeric chain.

Owing to the presence of specific interactions, most blends have phase separation diagram with the lower critical solution temperature, LCST, i.e., phase separation occurs upon heating. Two separation mechanisms are known: spinodal decomposition, SD, and nucleation-and-growth, NG. The morphology generated in NG is dispersed, whereas that in SD is co-continuous. Cahn and Hilliard's theory describes the SD kinetics.

Interphase and compatibilization

The interphase is a separate phase with its own characteristics and two interfacial tension coefficients, $\gamma_1 + \gamma_2 = \gamma_{12}$, with γ_{12} being the experimental quantity. The lattice theories predict that in binary blends: (i) there is a reciprocity between γ_{12} and the interphase thickness, $\gamma_{12}\Delta l = \text{constant}$, (ii) the surface energy is proportional to $\chi_{12}^{1/2}$, (iii) polymer chain-ends concentrate at the interface, (iv) and any low molecular weight components migrate to the interface, thus low entanglement density and viscosity.

Compatibilization must: (1) reduce γ_{12} and parallel with it the size of the dispersed phase; (2) stabilize the morphology against changes during processing; and (3) ascertain good interaction between domains in the solid state. Compatibilization involves either addition of a compatibilizer (e.g., a block or graft copolymer), or reaction between the principal blend components during the compounding or processing. The latter method is more advantageous and economic, thus it dominates commercial blending.

Morphology

Performance of an immiscible blend depends on the composition, interphase, and morphology. At equilibrium, for $\phi < \phi_c \cong 0.16$ droplets are expected, while at higher concentrations fibers and lamellae are found. Further increase of concentration leads to phase inversion at $\phi = \phi_{II}$:

$$\lambda = [(1 - \phi_c - \phi_{2I}) / (\phi_{2I} - \phi_c)]^{[\eta]_{\text{disp}}} ; \quad \phi_{II} + \phi_{2I} = 1 \quad (2)$$

where λ is the viscosity ratio, and $[\eta]$ is the intrinsic viscosity.

Microrheology and flow

In a steady state, uniform shear flow at low concentrations and stresses, the drop deformation can be expressed using the three dimensionless parameters: the capillary number, κ , the viscosity ratio, λ , and the reduced deformation time, t^* :

$$\kappa = \sigma_{ij} \mathbf{d} / v_{12} ; \quad \lambda = \eta_{\text{dispersed}} / \eta_{\text{matrix}} ; \quad t^* = t \gamma / \kappa \quad (3)$$

where σ_{ij} is the local stress (shear: $ij = 12$; elongation: $ij = 11$), \mathbf{d} is the drop diameter, t is the deformation time, and γ is the deformation rate. In shear flow, for $\lambda > 3.8$, drops deform but do not break, while in extensional flow this limitation does not exist. Drop break-up occurs for $\kappa \geq \kappa_{\text{crit}} \cong 1$. However, the equilibrium drop deformation or break may occur only when t^* exceeds the required time: $t^* \geq t_s^* \cong 25$, or $t^* \geq t_b^* \cong 160$, respectively. When $\kappa > 2$, drops deform affinely with matrix into fibers that disintegrate by the capillary instability mechanism into mini-drops when $\kappa < 2$.

To describe polymer blending the microrheology must be supplemented by coalescence effects. Coalescence can be driven by either the thermodynamics (i.e., minimization of the interfacial energy), or by flow. During compounding the latter dominates. It has been shown that the dynamic coalescence increases with γ^2 and $\phi^{4/3}$, thus at equilibrium between dispersion and coalescence the drop diameter can be expressed as:

$$d_{\text{equilibrium}} = d_{\text{equilibrium}}^{\phi=0} + \left(6C\kappa_{\text{crit}} t_{\text{break}}^* \phi^{8/3}\right)^{1/2} \quad (4)$$

where C is an experimentally determined constant.

Flow may change local and global blend's morphology, e.g., local: the degree and type of dispersion by shear coalescence, interlayer slip, encapsulation, etc., and global: skin-core structures, gradient composition, etc. The effects depend on the imposed stresses.

The concentration dependence of blends' viscosity (at constant T and σ) can be classified in reference to the log-additivity rule, $\ln \eta = \sum \phi_i \ln \eta_i$, as showing a positive deviation, PDB, negative, NDB, or mixed, PNDB or NPDB. Considering blends to be emulsions of viscoelastic liquids, leads to prediction of PDB, (found in 60% of blends). The mechanism that explains NDB is the interlayer slip, caused by thermodynamically driven low entanglement density at the interface. In non-compatibilized, immiscible blends the interphase viscosity was calculated as being two to three orders of magnitude smaller than viscosities of component polymers.

In polymer blends, both the morphology and flow behavior depend on the deformation field — under different flow conditions it may have different structures, hence behave as *different materials*. Note that in multiphase systems, the relationships between the steady state, dynamic, and elongational viscosities (known for simple fluids) are not observed. Similarly, the time-temperature (t - T) superposition principle that has been a cornerstone of viscoelastometry is not valid.

Performance

Performance of polymer blends is controlled by morphology. For example, the optimum toughening of a brittle resin is usually obtained by dispersing $\phi \leq 0.1$ of an elastomer. The optimum drop size derived from the cavitation mechanism, $d_{opt} = 0.3 \mu\text{m}$ for ABS, $> 1 \mu\text{m}$ for PS, $< 0.1 \mu\text{m}$ for PVC, and $0.5 \mu\text{m}$ for PP/EPDM. One of the three compatibilization tasks is to ascertain the required d_{opt} value.

The phase co-continuity provides the best balance of properties, e.g., maximum ductility, high rigidity, and large elongation. Two basic methods are used to generate this structure: (1) SD by control of T, P, and solvent evaporation rate, and (2) rheologically controlled phase inversion. Compatibilization is used to optimize the degree of dispersion.

In blends developed to improve the barrier properties against permeability by gases, vapors, or liquids, the lamellar morphology is required. To create this structure, biaxial extensional flow is required in molding or extrusion. Best results are obtained pre-blending a low permeability resin (e.g., $d = 50 \mu\text{m}$ drops of PA or PVAI) in a matrix, then processing it in a biaxial flow field.

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Keywords

Blends, alloys, miscibility, interphase, phase inversion, compatibilization, phase diagram, spinodal decomposition, nucleation and growth, coalescence, rheology, mixing, compounding, blending, microrheology, morphology, performance.