UNESCO/IUPAC Postgraduate Course in Polymer Science

Lecture:

Polymer Blends

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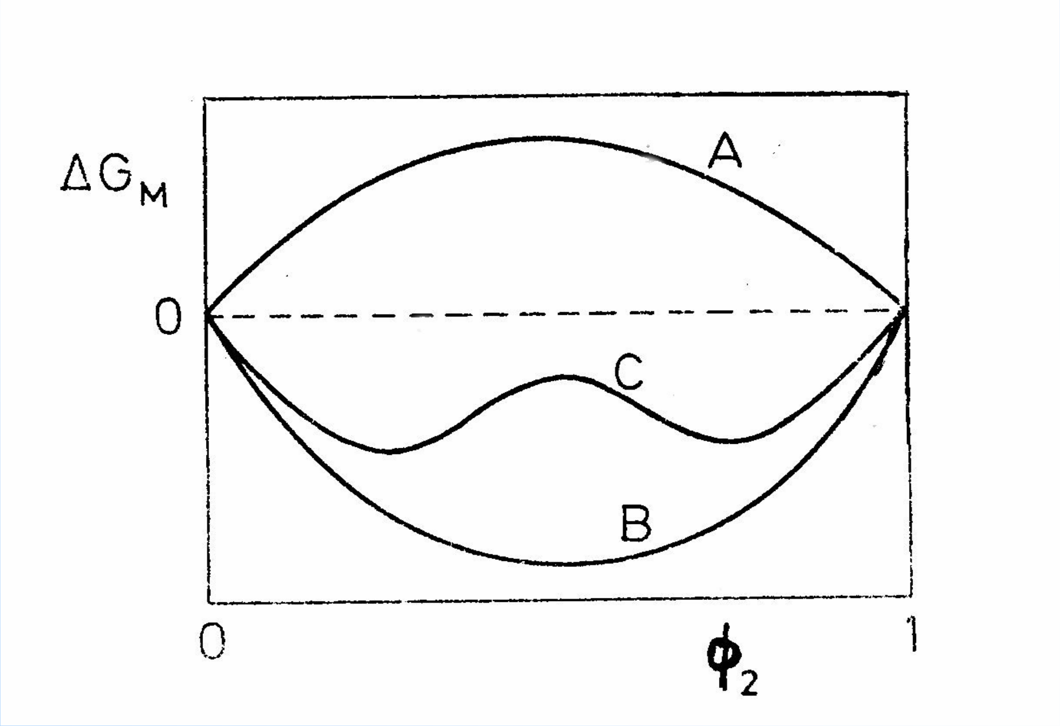
- **Content**
- Miscibility and compatibility
- Interface, compatibilizers
- Preparation of polymer blends
- Evolution of the phase structure at rest
- Properties of polymer blends
- Commercially important blends

Miscibility of polymers

- Miscible polymers – one phase system, miscibility on segmental level.
- Miscibility is controlled by Gibbs' energy of mixing ΔG_M
- $\Delta G_M = \Delta H_M - T\Delta S_M$
- Decisive role of the enthalpy of mixing
- Necessary condition for miscibility:
- $\Delta G_M \leq 0$

- Condition for full miscibility:

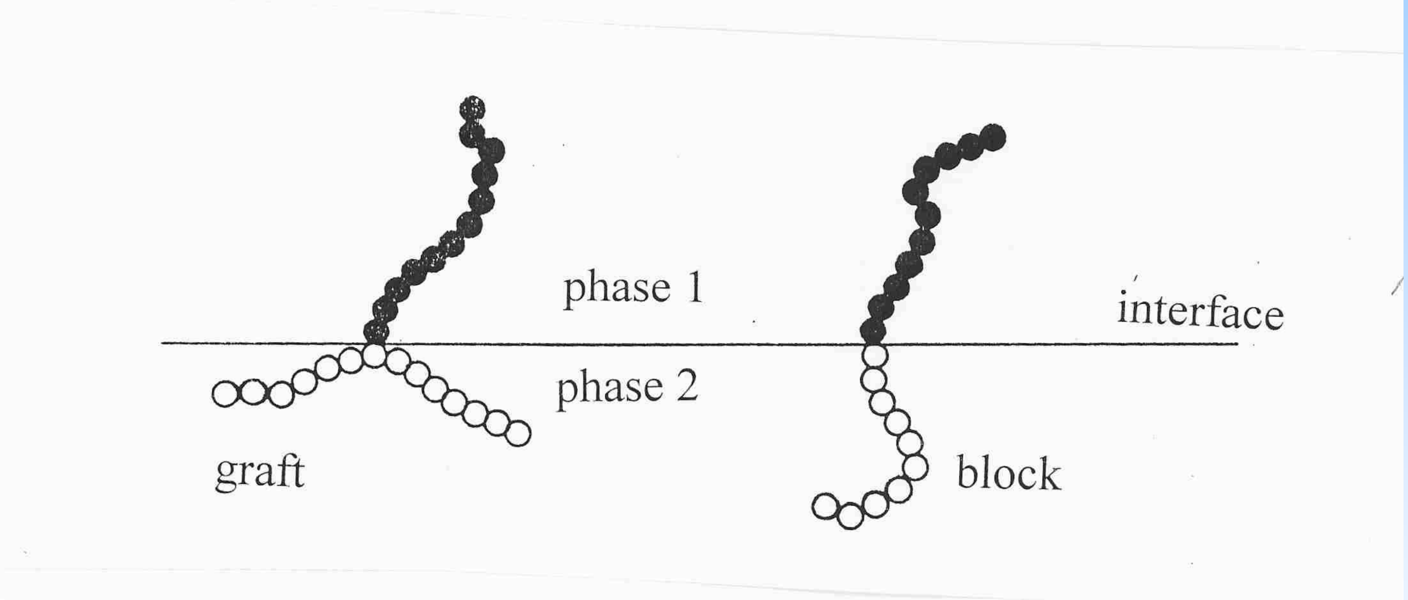
$$\left(\frac{\partial^2 \Delta G_M}{\partial \phi^2}\right)_{T,P} > 0$$



- A – immiscible system
- B – fully miscible system
- C – partially miscible system
- Methods of determination:
- Glass transition *T*g – calorimetry, dynamical mechanical spectroscopy
- Scattering methods – light, X-ray
- Microscopy – coarsening of the phase structure
- **Compatibility –** technological sense. It is determined by the blend properties.

Interfacial tension

- σ correlates with ΔG_M (ΔH_M, χ (interaction) parameter).
- Large σ - poor adhesion between the blend components, coarse phase structure $\Rightarrow$ poor properties of polymer blends.
- **Compatibilizers:** Block or graft copolymers with blocks miscible, identical or very similar to the blend components.



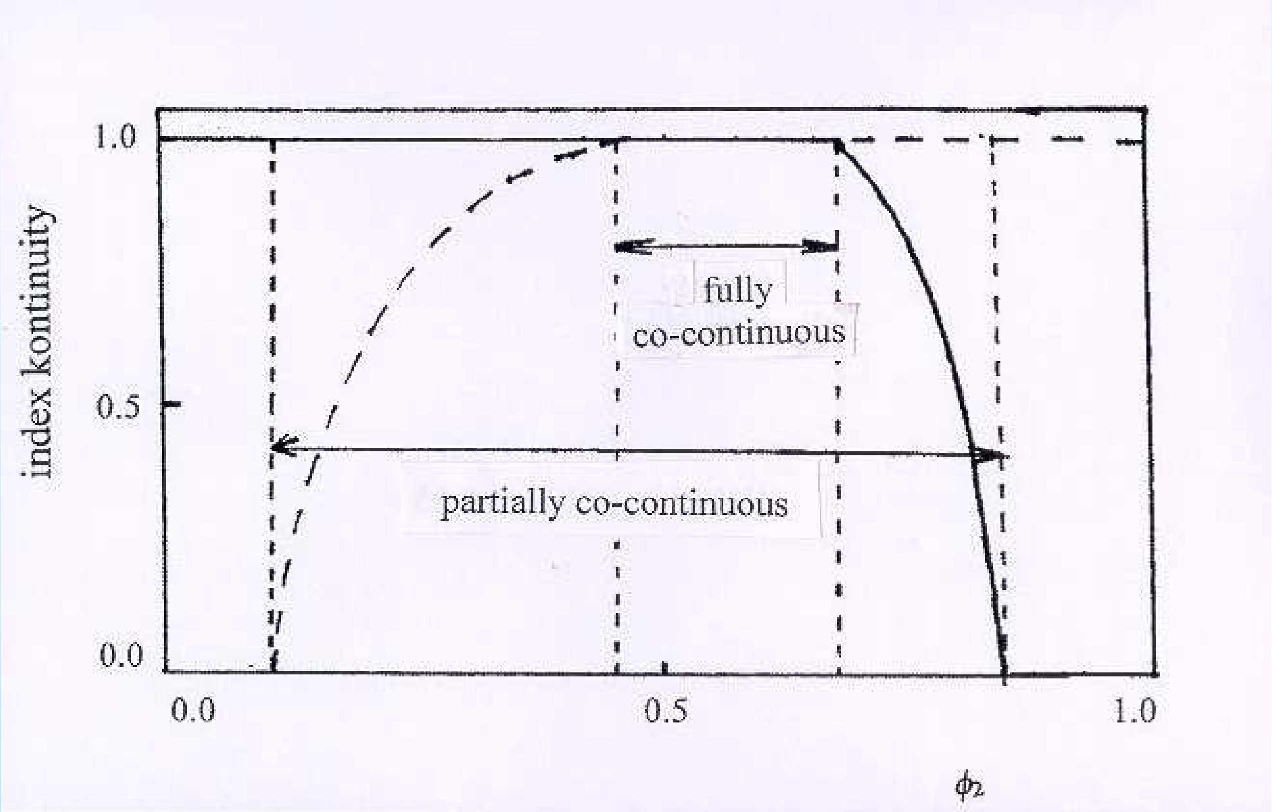
- Prediction of the distribution of a compatibilizer between the interface and bulk phases.
- Effects of statistical copolymers.

Preparation of polymer blends

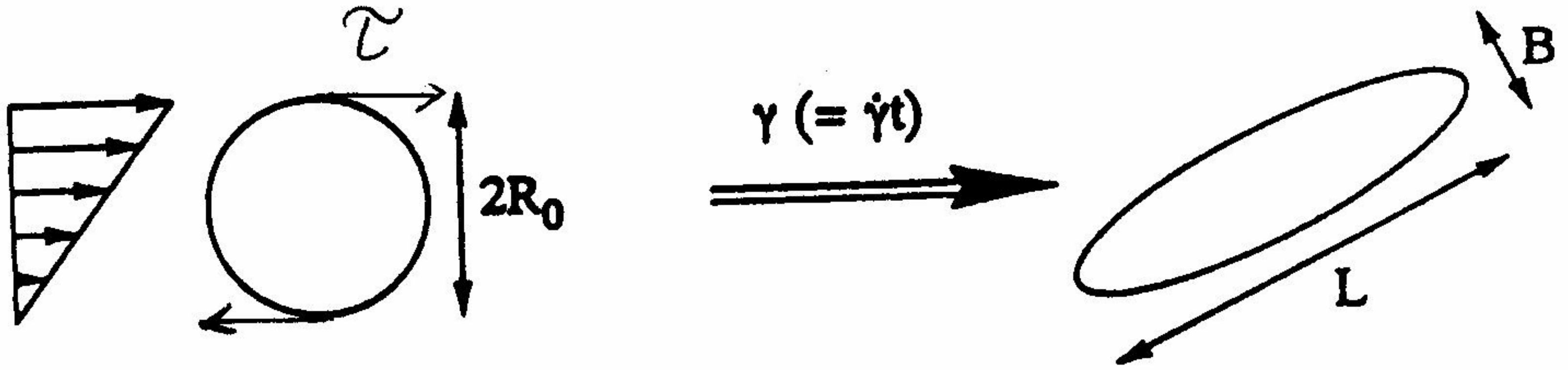
- Solution mixing – laboratory, paint industry. Problem is removing of a solvent.
- Mixing of lattices – saving energy, limited applicability.
- Interpenetrating networks – crosslinked materials.
- Partial copolymerization (HIPS, ABS) – special technologies for individual blends.
- Melt mixing (physical, reactive) – most important method in industry.

Melt mixing

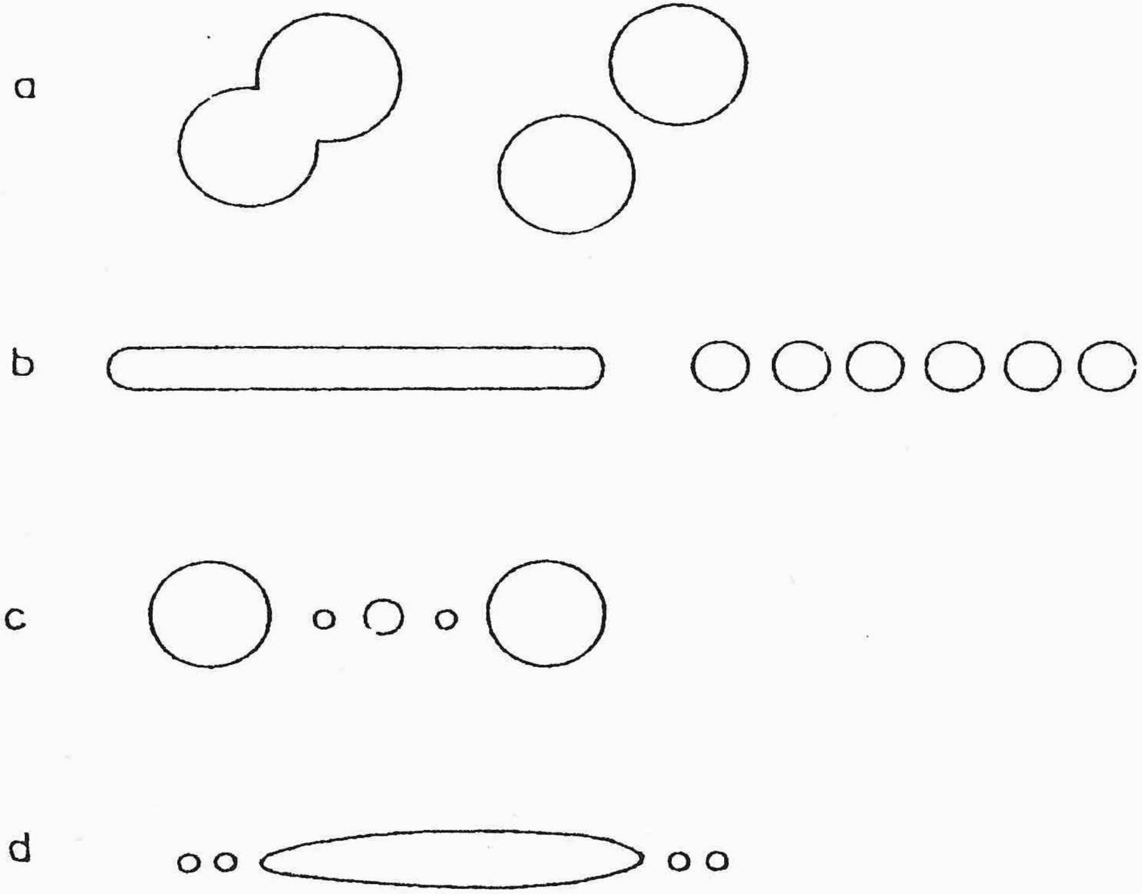
- Control of forming structure
- Type and fineness of the phase structure.



- The relations between a type of the phase structure, blend composition and rheological properties of the components are not well understood so far.
- Fineness of the phase structure (particle size for blends with dispersed structure).
- Competition between the breakup and coalescence of droplets.
- Droplet breakup – competition between the stress in flow, τ, and interfacial stress, σ/R. Capillary number, *Ca*
- $Ca = \tau R/\sigma$ ($= \eta_m \dot{\gamma} R/\sigma$ for shear flow)

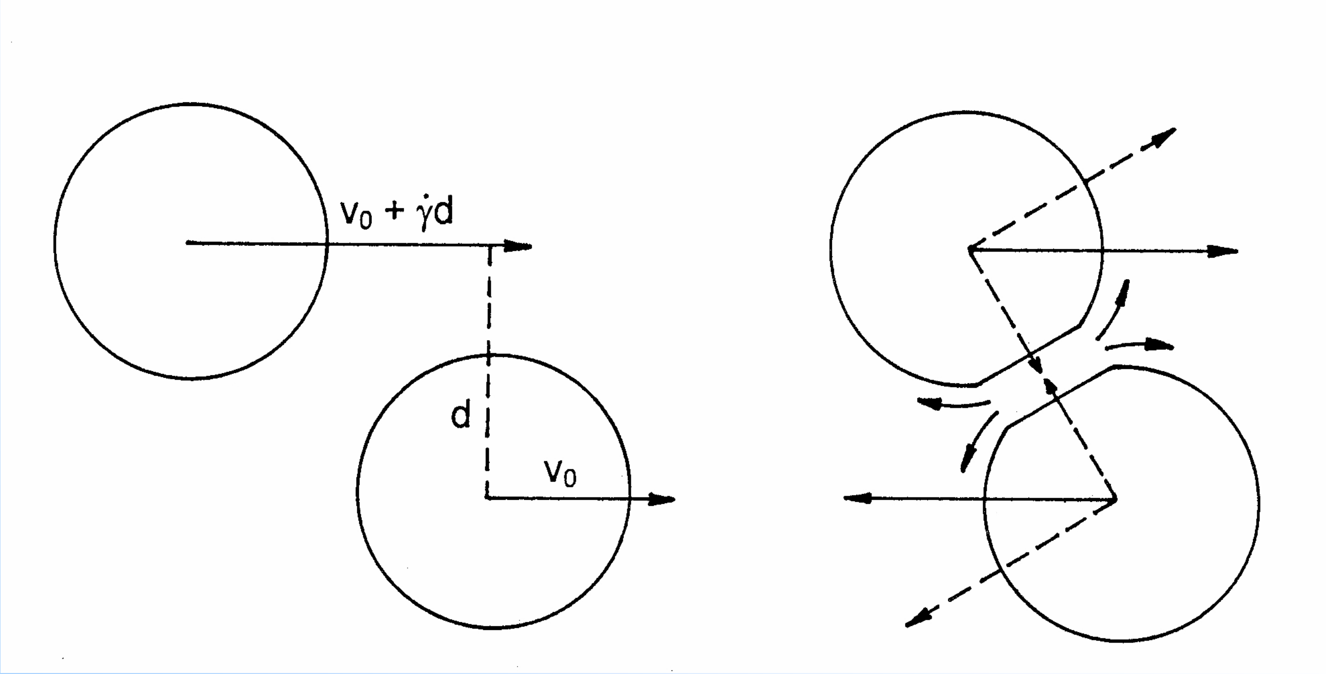


- Breakup for $Ca > Ca_{\text{crit}}$
- Ca_{crit} is a function of rheological properties of the components.
- Breakup mechanisms


a
b
c
d

Coalescence

- Collision of the droplets. Competition between rotation of the droplet pair and approach of the droplets (drainage of the matrix trapped between them).

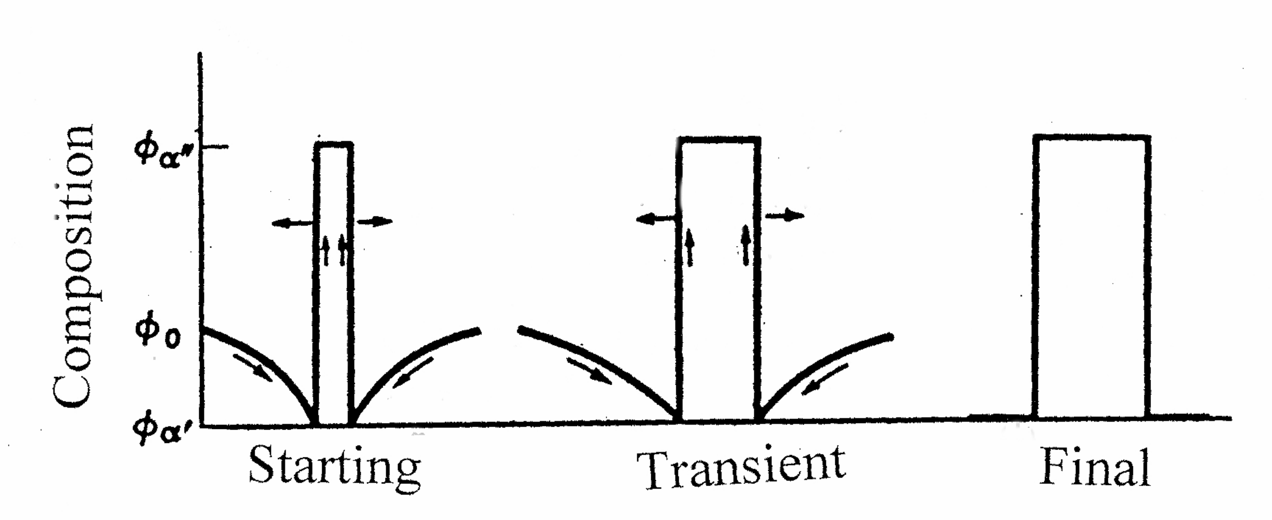


- Effect of a compatibilizer on the droplet breakup and coalescence.
- The competition between the droplet breakup and coalescence. In first approximation: the breakup frequency is independent of ϕ, the coalescence frequency is proportional to ϕ. As a consequence, the size of dispersed particles increases with ϕ.

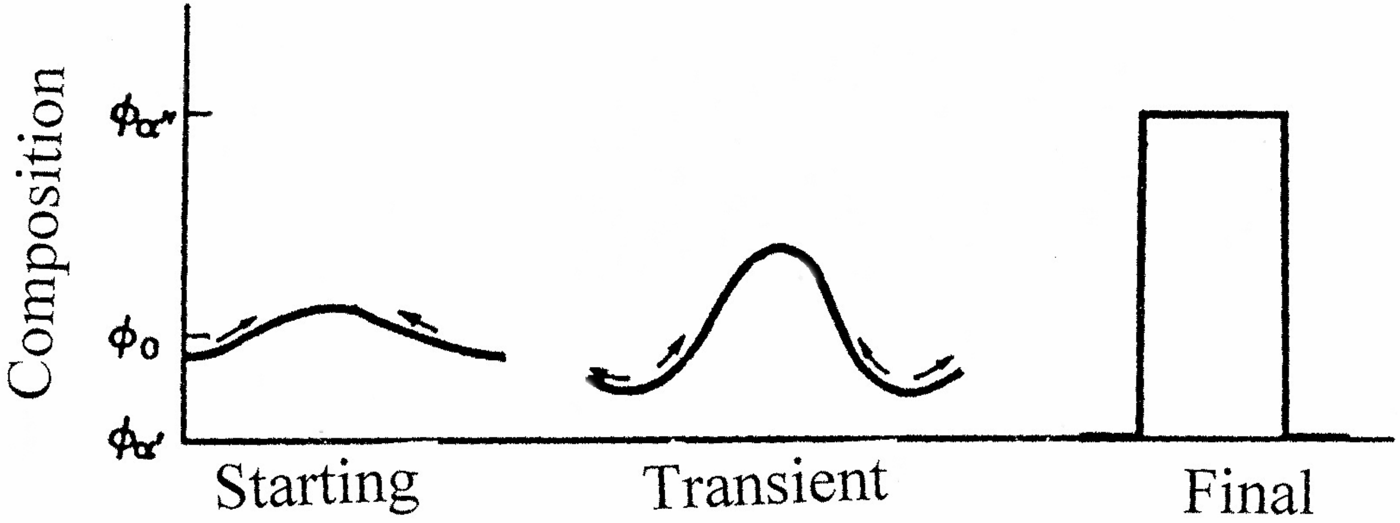
$$\frac{\mathrm{d}n}{\mathrm{d}t} = \left(\frac{\mathrm{d}n}{\mathrm{d}t}\right)_B + \left(\frac{\mathrm{d}n}{\mathrm{d}t}\right)_C$$

Evolution of the phase structure at rest

- Phase separation induced by a change in miscibility – nucleation and growth, spinodal decomposition. Mechanism is controlled by position in the phase diagram.
- Nucleation and growth

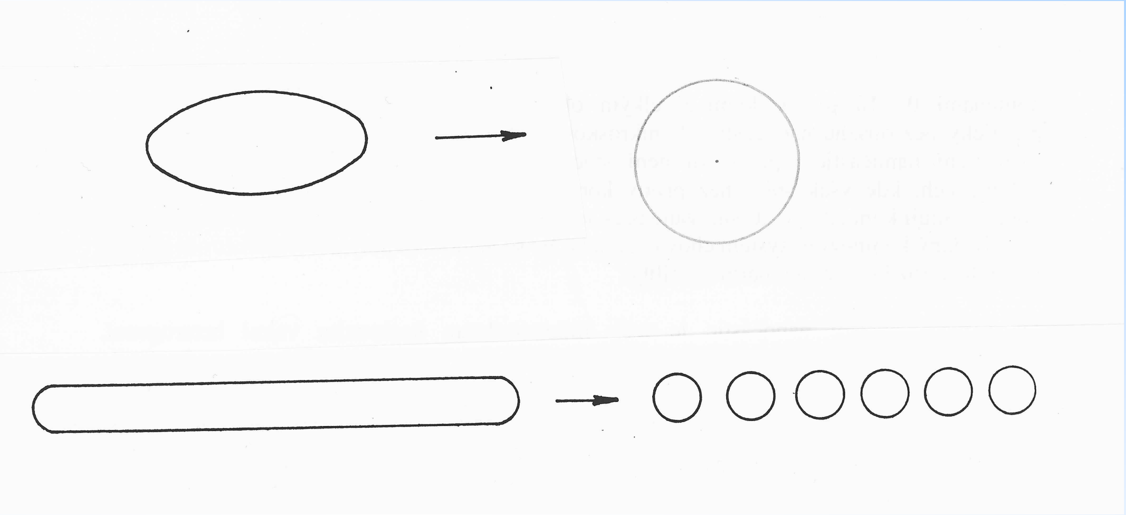


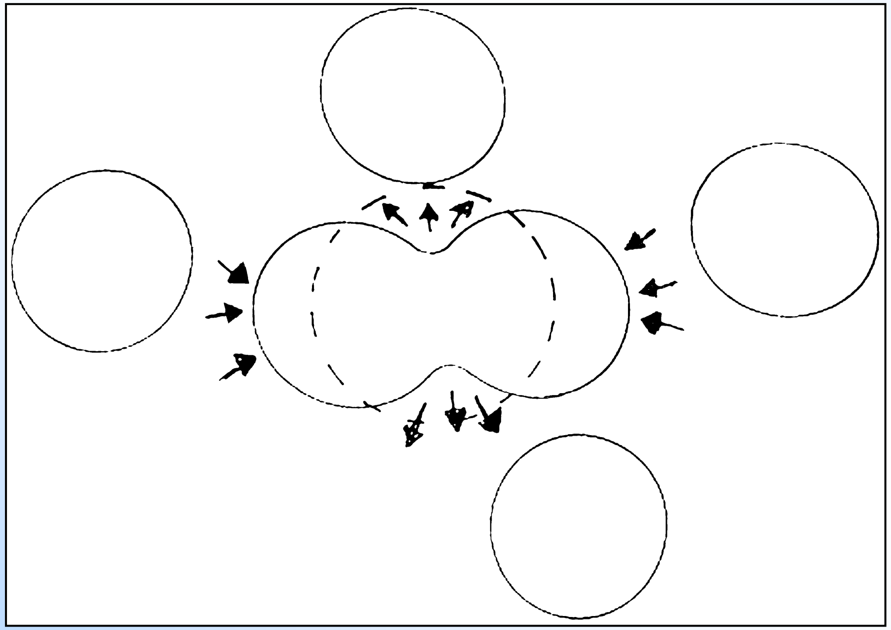
- Spinodal decomposition

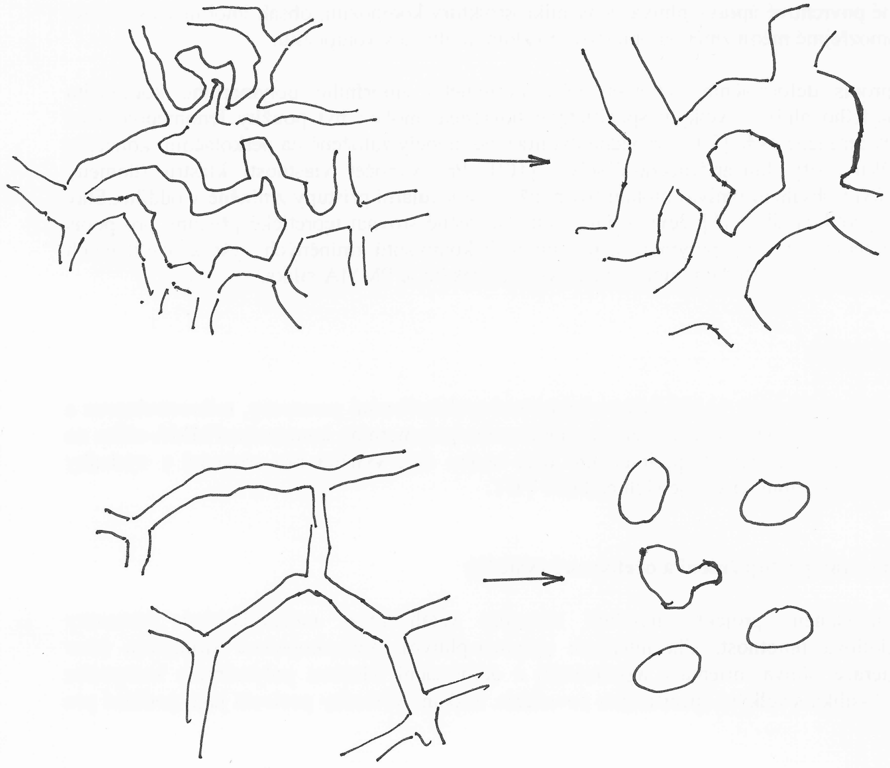


Evolution of the phase structure in immiscible polymer blends:

- General feature – reduction of interfacial area
- Breakup of long thin fibers and co-continuous structures in blends with a low content of the minor phase.
- Retraction of the shape of deformed droplets.
- Coarsening of co-continuous structures in blends with a high content of the minor phase.
- Coalescence, Ostwald ripening.



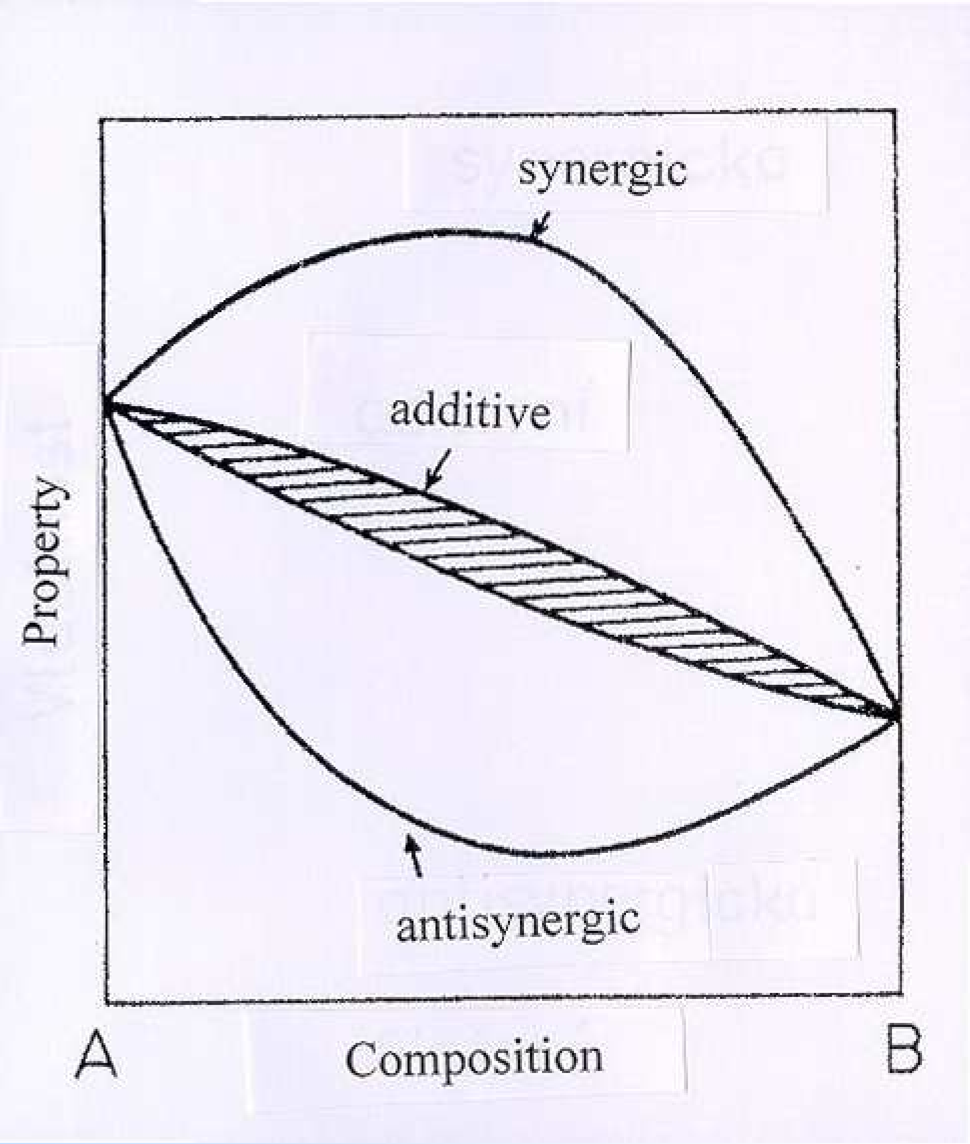




Properties of polymer blends

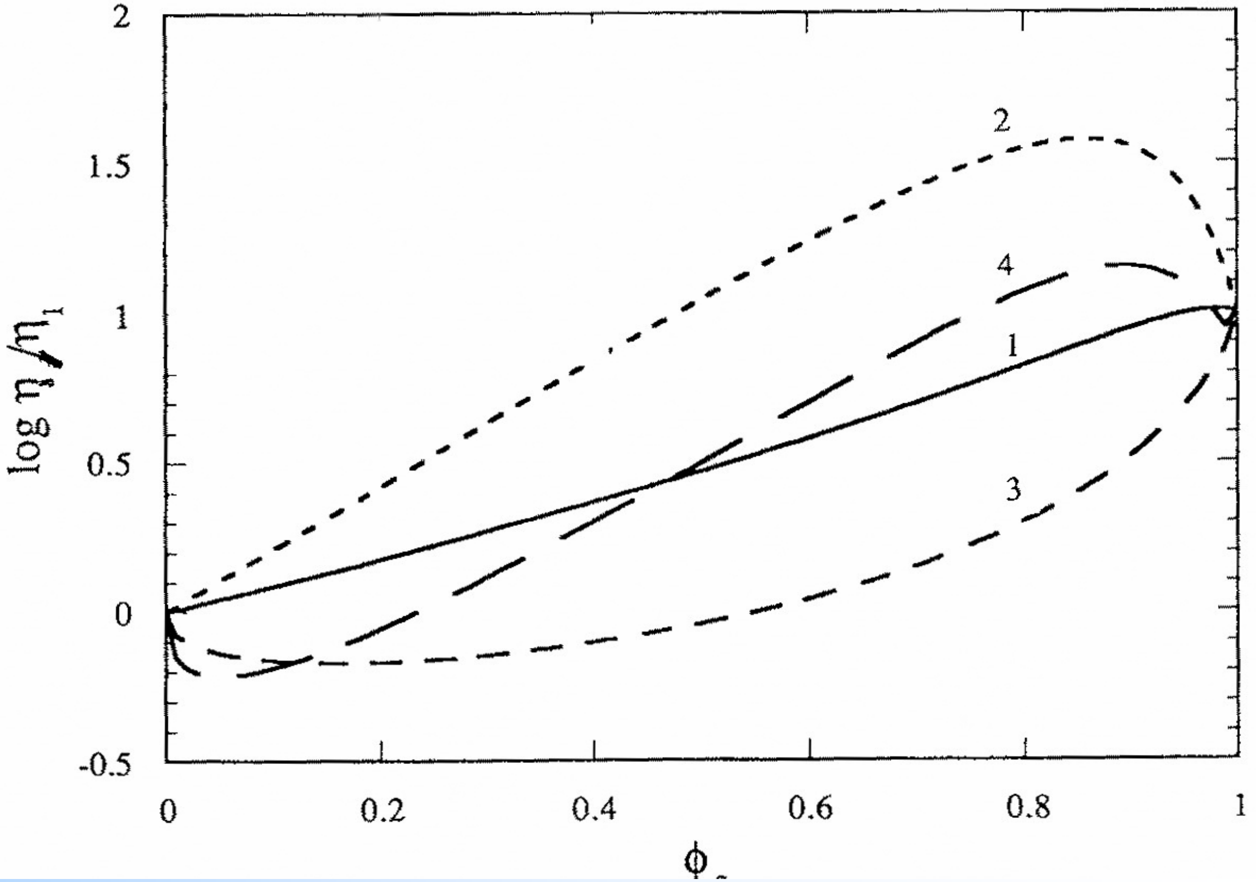
- Prediction of a blend property from the blend composition and related properties of the blend components – mixing rules (various sorts of additivity).

- Dependences on the blend composition:
- 1) Additive
- 2) Synergic
- 3) Antisynergic (incompatible)


synergic
additive
antisynergic
Property
A
Composition
B

- Mechanical properties – connectivity of the components must be considered. Properties insensitive to the details of morphology (e. g. modulus) – mixing rules are applicable. Properties sensitive to the details of morphology (e. g. impact strength) – detail model of a blend must be considered.

- Flow properties – complex shape of the curves. The competition between emulsion effect and slip at the interface.


2
1.5
1
0.5
0
-0.5
log η /η1
0
0.2
0.4
0.6
0.8
1
ϕ
1
2
3
4

Commercially important blends

- Impact resistant plastics – fine rubber particles dispersed in a thermoplastic matrix (PP/EP(D)M, HIPS, ABS, PA/EP(D)M-gMA, PA/SEBS-gMA).

- Thermoplastic elastomers – dynamically vulcanized blends (EP(D)M/PP). Mechanical properties of vulcanized rubber, processing by injection molding.

- Miscible blends with balanced processibility and mechanical properties (PPO/PS).

- Blends with balanced barrier properties (PE/PS and PP/PS compatibilized with SB or SEB block copolymers).

- Application of blending and compatibilization at recycling mixed plastic waste.

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Thank you for your attention

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