







TECHNOLOGIE POLYMERE & KOMPOSITE

MC07, UdS WS 2019/2020

Chapter 3: Polymer blends

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Increasing strength while maintaining stiffness





How to create impact strength / toughness? (...without too much negative influence on stiffness...)

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e.g. mixture PS + rubber



conventional impact resistant PS

impact resistant PS with high stability against stress cracking impact resistant PS with high surface gloss

H. Jenne





e.g. mixture PS + rubber



impact resistant PS
with elastomer
capsules (increased
transparency)

impact resistant PS with finely distributed rubber phase (fully transparent)

H. Jenne

Influence of morphology on stress-strain behaviour



e.g. ABS with small rubber particles



F. Haaf

Influence of morphology on stress-strain behaviour





e.g. ABS with bigger rubber particles

F. Haaf

Influence of morphology on stress-strain behaviour





F. Haaf

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How does the dispersion process works?



- melt mixing process (kneader, extruder)
- flow behaviour of components
- external forces acting on the components
- theory for suspensions after Taylor (as a first approach)





- droplet that is dispersed in a newtonian liquid by shear forces
- no slip between matrix and droplet



difference in normal stress acts against capillary pressure from interfacial tension

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- balance of forces at the interface
- deformation droplet towards an ellipsoid
- ellipsoid oriented along the shear field •

$$\delta P_N$$
 = -4G η_M / f(λ)

maximum δP_N at $\lambda = 1$

with

 δP_{N} : difference in normal stress G: shear rate η_M : viscosity of the matrix $\lambda = \eta_D / \eta_M$: viscosity ratio $\eta_{\rm D}$: viscosity of the disperse phase



Taylor theory III



- deformation of ellipsoid acts against interfacial tension
- interfacial tension prefers the spherical shape

$$\delta P_{L} = 4\sigma / d$$

with

 δP_L : capillary pressure σ : interfacial tension d : diameter of droplet

breakup of droplet if $-\delta P_N > \delta P_L$



- domain size decreases with decreasing interfacial tension and with shear rate and matrix viscosity
- smallest domains at λ = 1

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Breakup of droplets in non-newtonian media



- polymer melts have also elastic properties!
- unknown if droplet breakup criterion is valuable in viscoelastic polymer melts
 - elongated particles can also be stable
- dispersion not proportional over whole range of shear rate τ
 - elongated morphology at $\tau = G\eta > 10^4 Pa$
 - extrusion systems with high shear rates can promote formation of elongated particles
- influence of extensional flow
 - low molecular weight systems: almost no dependence of droplet size on $\boldsymbol{\lambda}$
- coalescence
 - dynamic equilibrium assumed, but no quantitative prediction

2-phase morphology











PE shows shrinkage due to crystallisation

D.J. Meier

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VASILE FALLER AND 10µm 40001 SES 0.5% #0047 ×5000

blend from 30 % PE and 70 % PS

addition of 0.5 % SES as compatibiliser (styrene-*block*-ethylene-*block*-styrene copolymer)

D.J. Meier

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Compatibilisation reactions in the polymer melt



PP / PA-6 70 / 30







reactive compatibilisation with 2% Bisethoxybisphenol-A-diacrylate

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Disperse phases for polymers with matched yield stress





PA-12 yield stress adapted by use of plastisizer

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2-phase morphology





Formation of disperse phases with core shell structure





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3-phase morphology









PP / PA-6 blends

0% PPMSA



5% PPMSA

⊢3 µm –|

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|- 3 µm -|





PP / PA-6 blends

20% PPMSA

10% PPMSA



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PP / PA-6 70 / 30



|-10 µm-|

no compatibiliser

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PP / PA-6 70 / 30



|- 5 µm -|



2.5 % PPMSA

10 % PPMSA

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Core-shell-type disperse phases



PP / PA-6 70 / 30





|−1,5 µm-|

|-,0,3 µm-|

20 % EPM-g-MSA

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Young's modulus of isolated PA-particle

PA-particle with elastomer inclusions

Core-shell or PA with elastomer inclusions?

PP / PA-6 / EPM-g-MSA 60 / 30 / 10

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Possibilities to influence stiffness / toughness relation

small homogeneous domains

stiff elastomeric shells

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PP / PA-6 70 / 30

⊢0,5 µm–∣ 5% SEBS-g-MSA

⊢0,5 µm⊣ 5% SEBS-g-MSA

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PP / SEBS-g-MSA / PA-6 50 / 20 / 30

|−0,2 µm -|

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|- 3 µm -|

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What is determining toughness in rubber toughend INM polymers? 25 strength(Jm 1200 20 Notched Izod impact strength (ft-lb/in) 25 wt.-% impact 5 800 15 wt.-% С Notched Izod 10 В 400 10 wt.-% 5 П

rubber particle diameter d / μ m

0

∩.2

0.5

0

5

4

2

3

How can the results be explained?

Particle concentration model

$$d_{\rm c} = 6\phi_{\rm r}/A_{\rm c}$$

Interfacial area model

 $d_{c} = \left[\left(\frac{6\phi_{r}}{\pi N_{c}} \right)^{1/3} \right]$

Interparticle distance model

$$d_{c} = T_{c} \left[\left(\frac{\pi}{6\phi} \right)^{1/3} - 1 \right]^{-1}$$

$$\begin{array}{l} - \ \ T_c = 0.304 \ \mu m \\ - \ \ N_c = 0.831 \ \mu m \\ - \ \ A_c = 1.508 \ \mu m \end{array}$$

Interparticulate distance seems to be important

plot against matrix ligament thickness (derived from TEM analysis)

Estimation of the mean interparticulate distance τ

estimation for a simple cubic packing

Determining parameters

particle size: d = 2rfiller content: ϕ

Interparticulate distance as important dimension

S. Wu, J. Appl.Polym.Sci 35 (1988), 549-561 000

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k = 1,25 mm

large interface between nanoparticles and matrix

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Interfacial layers in nanocomposites

Volume fraction interfacial layer on overall matrix volume

 $[AIL] = [\phi/v(1-\phi)]^*(V-v)^*100$

 ϕ : filler volume fraction, d = 2*r: particle size, v = 4/3 π *r³: particle volume

 $V = 4/3\pi^*(r+i)^3$: volume particle + interfacial layer, r: particle radius, i: interfacial layer thickness

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Interfacial layers in polymer matrix composites

Example of a trans-crystalline layer on a fibre

PA-6.6 trans-crystalline layers (5-23 µm wide) on Kevlar fibres

R.H. Burton, M.J.Folkes

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Overlap of interfacial layers in dependence on filler aspect ratio

epitaxial growth of crystalline matrices

 $\phi_{\rm F} = 0,112$

 $\phi_{\rm F} = 0,112$

$\phi_{\rm F}\!\!:$ filler volume fraction

The attraction of nanoparticles

no light scattering if d < λ / 20

Solid state physical properties + polymer processing techniques

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► SiO₂ – nanoparticles used for following example

Nissan MA-ST d₉₀ < 15 nm colloidal SiO₂ in methanole

TEM – micrograph from the unmodified diluted dispersion primary particles separable particle synthesis bottom-up from liquids

- chemically controlled precipitation process
 - control of nucleation (ΔG_n , ΔG_D , σ_N)
 - control of particle growth ($\Delta G_{G}, \Delta G_{D}, \sigma_{S}$)

Adsorption of macromolecules on solid surfaces

Principle of steric stabilisation

diffusion of solvent overlap of segments of molecules stabilising polymer chains lead to: increase of osmotic pressure (= driving force) diffusion of solvent molecules stabilising ...solvent pushes them polymer chains apart... adsorbed on the surface of the particles

... if particles approach and tend to agglomerate...

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Interfacial adhesion with rigid particles

low interfacial interaction

PA-6/(GlasSi-OH) ⊣6,66µm⊣ Sprödbruch eines Polyamid-6-Blends mit unfunktionalisierten Glaskugeln

high interfacial interaction

PA-6/(Glas-NH₂) |-6,66µm-| Sprödbruch eines Polyamid-6-Blends mit 3-APS-Gkaskugeln

Interfacial adhesion with rigid particles

formation of thicker elastomeric interlayers

. PA-6/(Glas-NH₂)Desm ⊣6,66µm⊣ Sprödbruch eines Polyamid-6-Blends mit isocyanatfunktonalisierten Glaskugeln

PA-6/(Glas-NH2)PH1 |-6,66µm-| Sprödbruch eines Polyamid-6-Blends mit polyharnstoffbeschichteten Glaskugeln, 10 Mol% PTHF-(3000)-diamin

Interfacial adhesion with rigid particles

formation of thicker elastomeric interlayers

. PA-6/(Glas-NH₂)PH3 |-6,66µm-| Sprödbruch eines Polyamid-6-Blends mit polyharnstoffbeschichteten Glaskugeln, 50 Mol% PTHF-(3000)-diamin

PA-6/(Glas-NH₂)PH4 ⊣6,66µm⊣ Sprödbruch eines Polyamid-6-Blends mit polyharnstoffbeschichteten Glaskugeln, 70 Mol% PTHF-(3000)-diamin

Compatibilisation by surface modification

silanes

- acidic
- basic
- non reactive
- polymerisable
- polycondensable
- adhesion
- anti-adhesion
- hydrophilic
- hydrophobic
- β -di-ketones
- complexing agents
- chelating agents
- oligomers

INA

SMSM-principle: Small Molecule Surface Modification

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Thermodynamics in nanocomposites

<u>compatibilisation step</u> to overcome the interaction forces between the primary particles (by <u>smsm-principle</u>)

Specific surface modification of SiO₂ nanoparticles using alkoxysilanes

Compatibilisation by surface modification of the SiO₂

TEM – analysis on ultramicrotomed specimen from PMMA / SiO_2 nanocomposites 2 Vol.%

200 nm 200 nm 200 nm

unmodified SiO₂

APTS / SiO₂

MPTS / SiO₂

5 Vol.%

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morphology on ultramicrotomed specimen

unmodified SiO₂: agglomerates > 100 nm

APTS/MPTS - SiO₂: agglomerates consisting of 2-3 primary particles < 30 nm

Structural model after SAXS – analysis

Investigation of the agglomerate formation mechanism of the SiO₂ –particles During composite preparation

minimisation of the interfacial free energy

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