Aalto University
School of Chemical
Technology

Polymer blends and composites
- compatibilization

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Useful books:

- Polymer Blends and Composites Chemistry and Technology

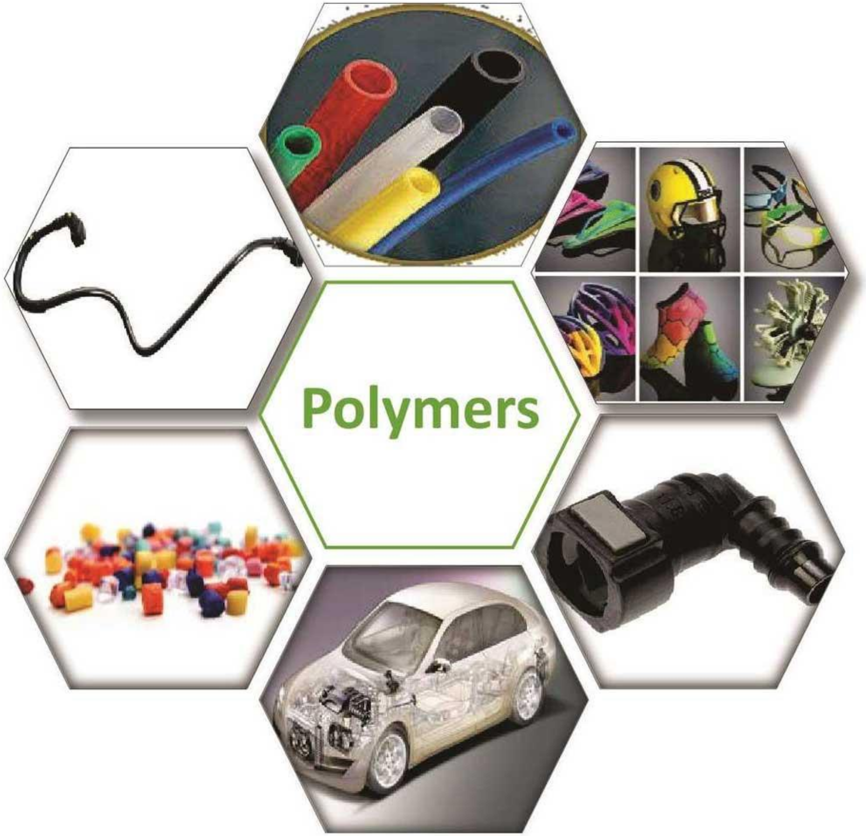
Muralisrinivasan Natamai Subramanian, 2017, John Wiley & Sons

- Handbook of Polymer Blends and Composites

A.K. Kulshreshtha, C. Vasile, 2002, Rapra Technology Limited

- An Introduction to Composite Materials

D. Hull, T. W. Clyne, 1996, Cambridge Solid State Science Series


Polymers

Outline

1. **Fundamental of Polymers**
2. **Polymer blends and plasticisers**
3. **Compatibilization of polymer blends**
4. **Composites**
5. **Wetting and compatibilization of composites**
6. **Nanocomposites**
7. **Compatibilization of nanocomposites**

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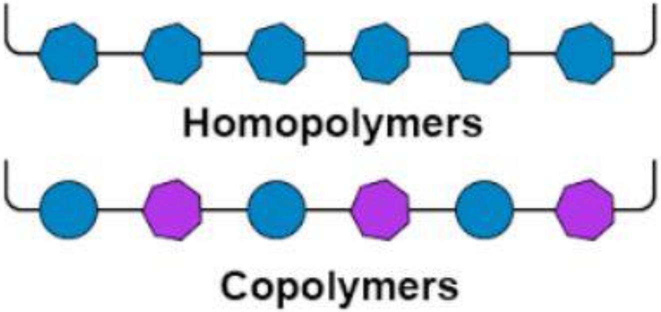
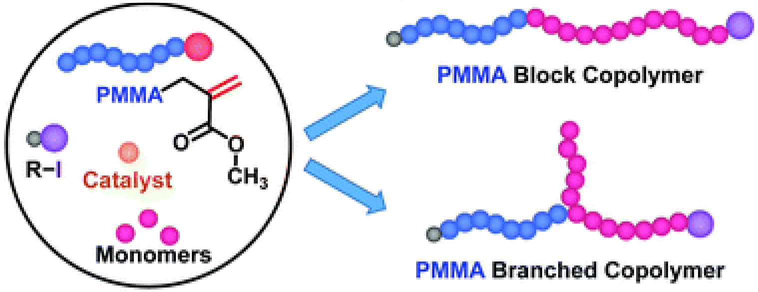
FUNDAMENTALS

OF POLYMERS

Classification of polymers

1. **Bio-based/synthetic**
2. **Homopolymers/copolymers**
3. **Thermoplastics, thermosets, elastomers**
4. **Semicrystalline –amorphous**
5. **Biodegradable/Not biodegradable**
6. **Commodity/Engineering/High performance**





Plastic → formulation of a polymer

Same polymer type (e.g. Polyurethanes) can be thermoset and thermoplastic

Polymers vs metals

- When compared to metals;
  the modulus are ~ 100 times lower
  and strengths ~5 times lower
  thermal resistance much lower
  Much lighter
  Proccesability/price

	Y. Modulus (GPA)	Stress at break (MPa)	Density (Kg/dm3)	Specific Modulus
Polymer	0.3-20	12-140	0.9	11
Steel	200	200	8	25
Aluminum	70	200	2.7	26

Polymers/Plastics

Wishlist of polymers:

- **High Temperature resistance, (thermomechanical, Tg and degradation)**
- **High impact strength/mechanical properties**
- **Chemical resistance and**
- **Low price (commodity, engineering speciality/high performance)**
- **other special properties**
  - Bio-based, recyclability, biodegradable, barrier properties,

Methods to increase the stiffness and strength of polymers

1) Crystallization (thermal treatments)

- Semicrystalline polymers, increased crystallinity generally better properties (mech/barrier)
- Except transparency/clarity, and strain at break
- Degree of crystallinity (but also crystalline morphology and other parameters)
- Application of thermal treatments (e.g. 10 mins at 120C)

2) Polymer blends, composites, reinforcements, plasticisers

3) Modification of physical/chemical structure

- Modify the monomers to get different polymers
- Modify chain lenght/polydispersity

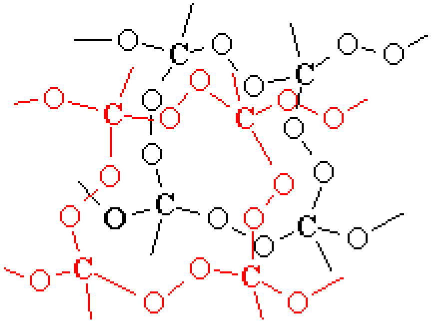
Methods to increase the stiffness and strength of polymers

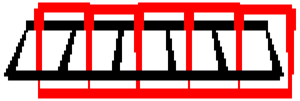
4) Copolymerization

- Desing a polymer using different monomers
- Lot of options

5) IPN (Interpenetrating networks) structures

- Two thermosets
- Each polymer its own chain





6) Radiation

- Usually for polymer degradation

Methods to increase the stiffness and strength of polymers

7) Multilayer

NOT a polymer blend

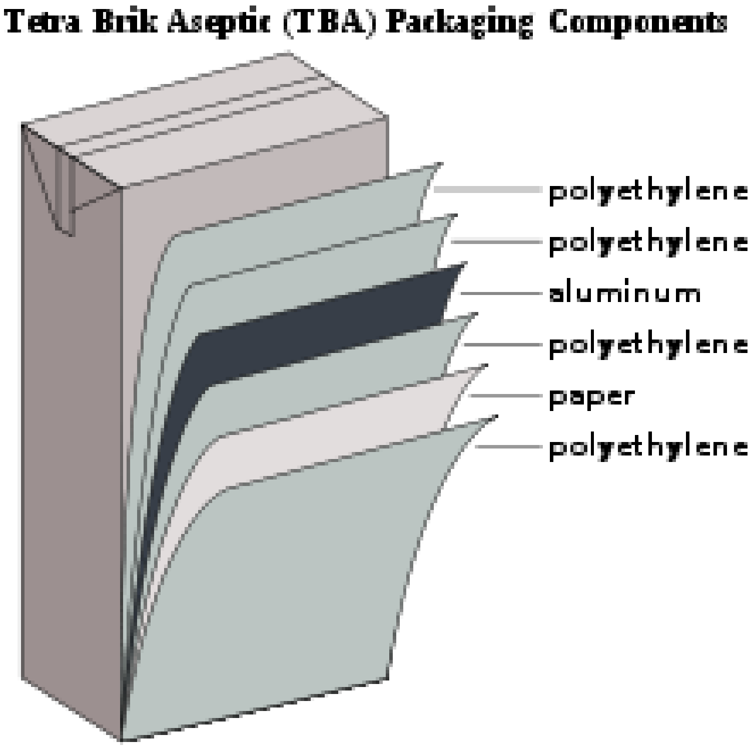
Tetrabrick

PE water barrier + adhesion

Not neccesarily same PE

Paper/cardboard mechanical prop

Aluminum oxygen barrier



Formation of polymer blends and composites

Polymer

+

Blends: Other polymer - Composites: Reinforcing agent/filler/fibre

+

Compatibilizing agent/plasticizer/additives

+

Melt Mixing/processing

Definitions

- “Composite is a multicomponent material comprising multiple different (nongaseous) phase domains in which at least one type of phase domain is a continuous phase”
- “Polymer composite refers to the composite in which at least one component is a polymer” (W.J.Work et al., Pure Appl. Chem. 76(2004)1985-2007)
- “A polymer blend is a member of a class of materials analogous to metal alloys, in which at least two polymers are blended together to create a new material with different physical properties.” [Gert R. Strobl (1996). The Physics of Polymers Concepts for Understanding Their Structures and Behavior]

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POLYMER BLENDS AND PLASTICISERS

Polymer blends

- **Blending:**
    - Mixing (at least) two polymers
    - Enhance properties of polymers
    - Reduce the cost of an expensive engineering thermoplastic
    - Improve the processability of a high-T or heat sensitive thermoplastic
    - Provide some bio-based nature

Polymer blends – an example

Polyamide 6 (PA6)

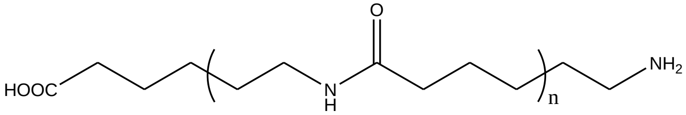
+ stiff, strong

+ good ’barrier’-properties (oxygen, solvents)

+ good thermal properties

- brittle

- sensitive to moisture



Polyethylene (PE)

+ tough

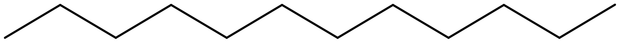
+ no water absorption or permeability

+ processability

+ affordable

- swelling by solvents

- high oxygen permeability



- Recently, there has been interest in blends containing three-component polymers. (TERNARY BLENDS)

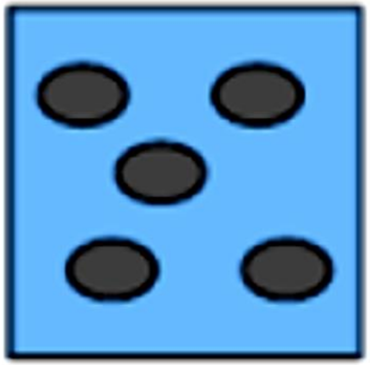
PMMA-PEMA-Poly (styrene-co-acrylonitrile) (SAN)

- SAN is compatible (miscible) with PMMA and PEMA.

- But, PMMA and PEMA are immiscible.

Miscibility

Miscible PB



Immiscible PB

Type of polymer blend (homogenous or phase separated) will depend upon many factors such as;

- kinetics of the mixing process
- processing temperature
- presence of solvent or other additives

Types of polymer blends:

1- Miscible polymer blend: A homogenous polymer blend associated with the negative value of the free energy of mixing:

$\Delta G_m = \Delta H_m \leq 0$,

and a positive value of the second derivative:

$\partial^2 \Delta G_m / \partial \varphi^2 > 0$.

It has a single –phase structure, has properties of average values between the values of properties of its components, **isotropic**, and **has one glass transition temperature** (T_g) *(if mixed correctly)*.

2-Immiscible polymer blend: A blend exhibits more than two phases. It is a blend whose free energy of mixing; $\Delta Gm = \Delta Hm > 0$

Usually, has two T_g's , since the two components are phase separated.

$$\Delta G_m = \Delta H_m - T\Delta S_m$$

If ΔG_m is positive at a given temperature, polymers in the blend will separate into phases.

For complete miscibility, two considerations are necessary:

- ΔG_m must be negative
- 2nd derivative of ΔG_m with respect to volume fraction of component 2 (ϕ_2) must be greater than zero

$$\left(\frac{\partial^2 \Delta G_m}{\partial \phi_2^2}\right)_{T,P} > 0$$

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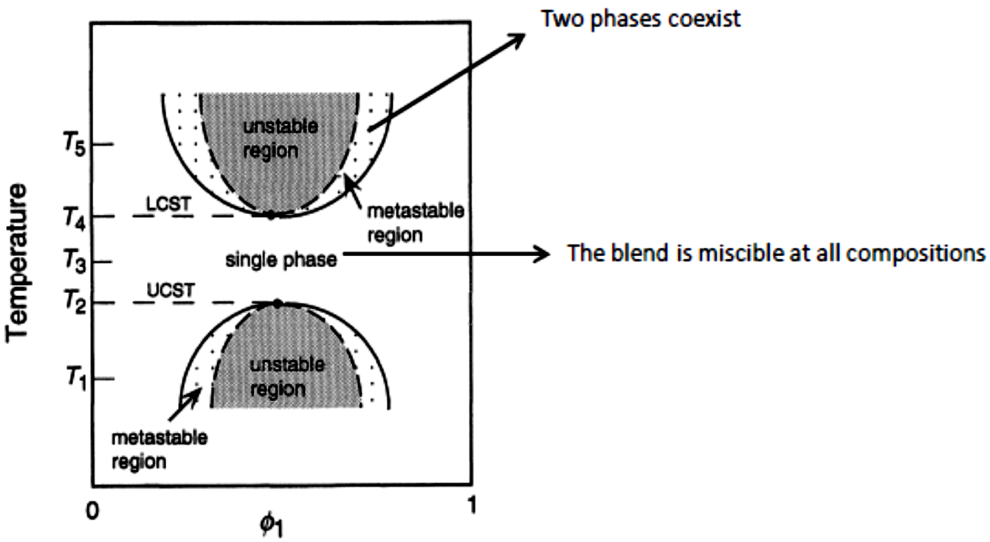
In general, polymer blends, which will separate at equilibrium into two mixed-composition, can exhibit a wide range of phase behaviour, including upper and lower critical solution temperatures **(UCST/LCST)**.



Idealized phase diagram for a polymer blend

- Miscible polymers tend to phase separate at elevated temperature.
- Critical temperature with LCST increases with pressure.
- Polymer mixtures would be immiscible or would exhibit phase separation only upon lowering of temperature yielding a UCST.

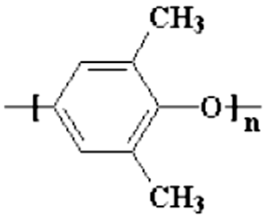
- LCST behavior is quite common for polymer blends compared to UCST behavior.

- LCST=240^{o}C. This means, if the blend is melt processed above 240^{o}C, phase separation occurs.

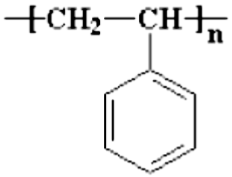
- UCST behavior may be observed only in a solution which is a low M_W solvent used.

Examples of some miscible and immiscible blends

- **Miscible blends**
  - PS/PPO,
  - PVC/NBR,
  - PVC/polyesters, PET/PBT,
  - PVDF/PMMA



poly(phenylene oxide)



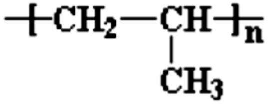
polystyrene

- **Immiscible blends**
  - High impact polystyrene (HIPS) (PS+ polybutadiene),
  - PE/PP

polyethylene

$$-\!\!\left[CH_2-CH_2 \right]\!\!-_n$$

polypropylene

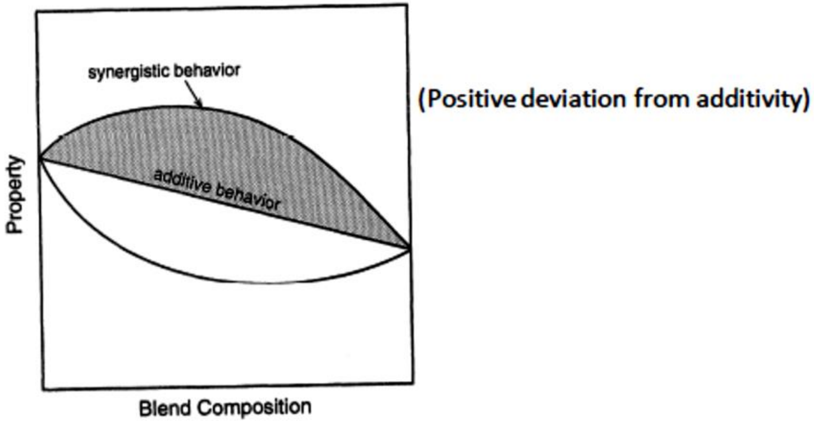


$$-\!\!\left[CH_2-\underset{CH_3}{\underset{|}{CH}} \right]\!\!-_n$$

Properties of Blends

- Properties of miscible polymer blends may be intermediate between those of the individual components (i.e. additive behavior)

- In other cases blend properties may exhibit either positive or negative deviation from additivity.



Dependence of miscible blend properties on composition

Determining miscibility

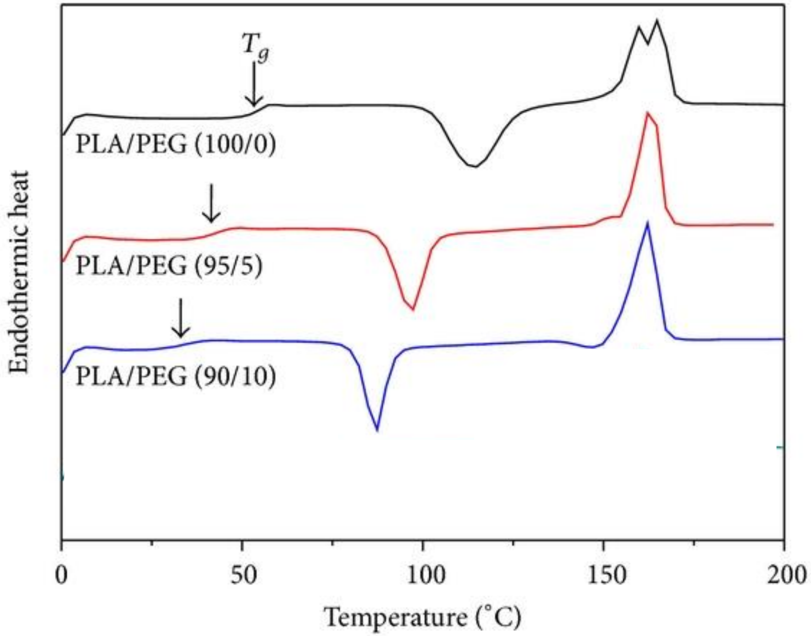
- **Dynamic Scanning Calorimetry (DSC)**
  - Standard instrument in polymer lab
  - Measures the energy needed to heat (increase temperature) a polymer
  - Measures thermal transition (extra heat needed)
  - Miscibility: measurement of Tg (glass transition)
  - Tg measures amorphous chains relaxation
    - 1 Tg → good mixing
    - 2 Tg → bad/partial mixing

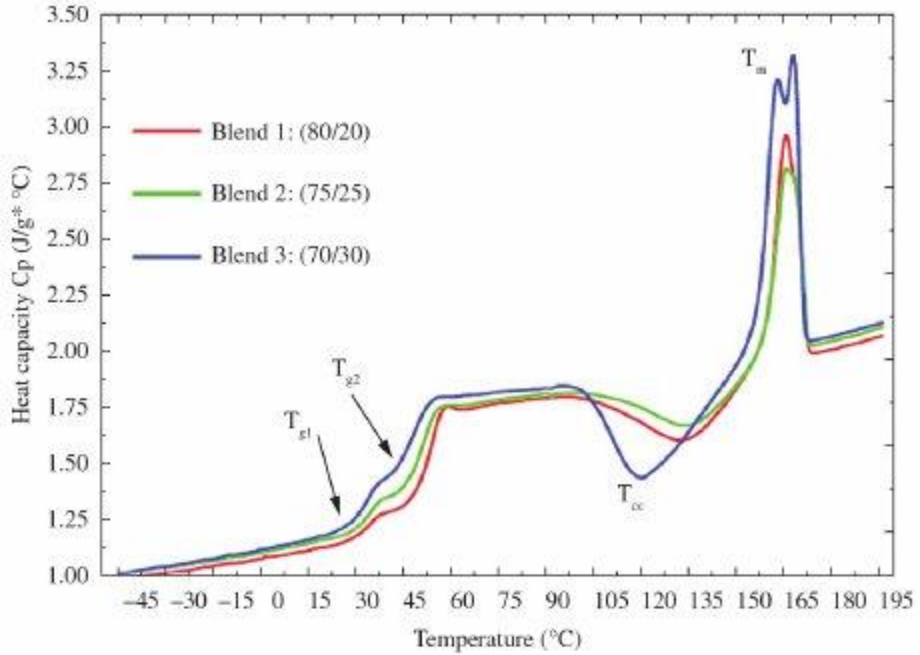
Miscible PB

Immiscible PB

DSC

Are well mixed?





Plasticiser

- Low molecular weight compounds (even humidity)

- Highly used additive for polymers

- Reduce the brittleness of the polymers

- Also reduces the thermomechanical stability (Tg)

- May affect crystallization process

Plasticiser

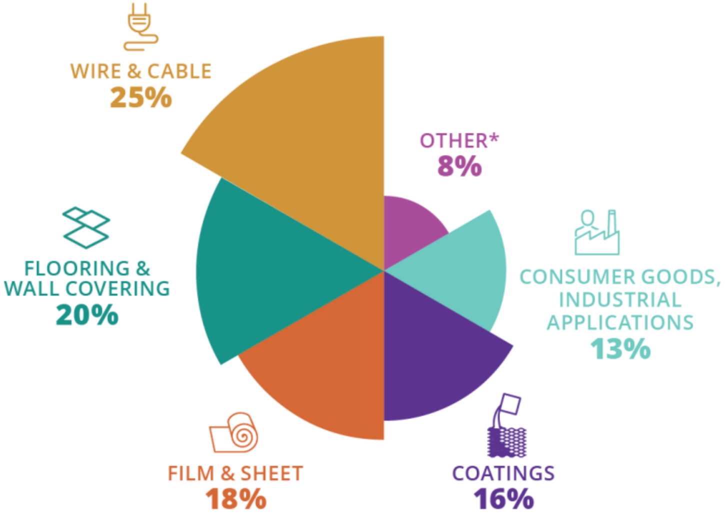
- Similar to adding oil to spaghetti

- The **most common plasticisers**

adipates, azelates, citrates, benzoates, ortho-phthalates, terephthalates, sebacates, trimellitates.

- Bisphenol A (BPA)
- Mostly banned in EU
  - especially for food contact.
- Issue: migration (to food or outside)

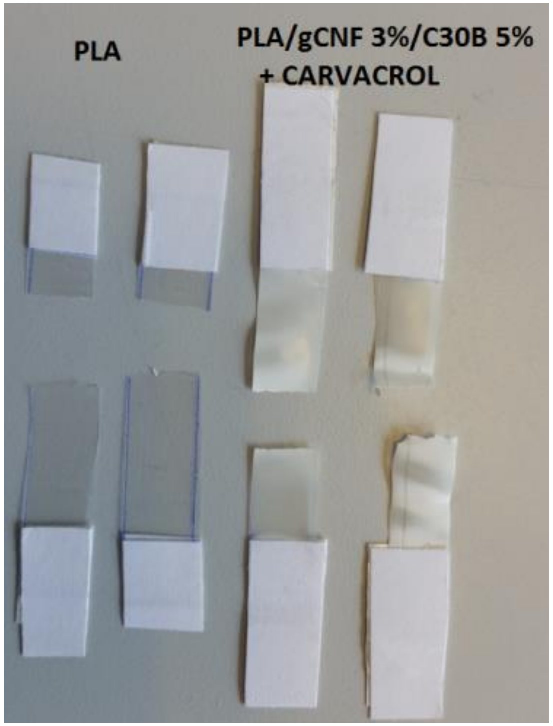
EUROPE'S PLASTICISERS USE (2017)

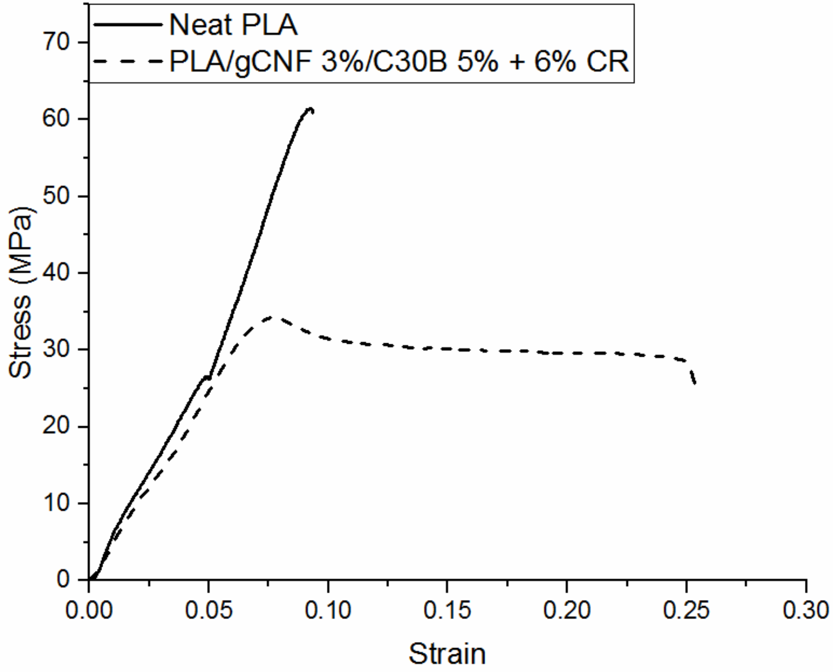


*Other: elastomers, surface coatings, rubber compounds and medical applications

Source: 2018 IHS and European Plasticisers estimates

Plasticiser: Carvacrol-PLA





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Compatibilization of blends

Compatibilizers

- Mechanical properties of immiscible blends are often poor due to the inadequate interfacial strength between the dispersed phase and matrix.
- “Compatibilization” is an interfacial phenomenon in the heterogeneous polymer blends.
- Compatibilization is a process by which the blend properties are enhanced while increasing adhesion between the phases, reducing the interfacial tension and stabilizing morphology.
- The degree of compatibility between the components in the blends can be enhanced through the addition of compatibilizers.

Definition

Additives to promote miscibility by reducing interfacial tension are called «compatibilizers»

- This interfacial activity can be modified by **reactive and nonreactive** processing strategies.
- Polymers with polar groups can interact between the components in the blend through nonbonded interactions such as dipole–dipole interactions and hydrogen bonding.

Compatibilizers

- **Two sides, one compatible with A, another compatible with B**
- **For both blends and composites**
- **Provide miscibility or compatibility**
  - Immiscible or partially immiscible materials
- **Helps of forming a “homogenous” product**
- **Reduce interfacial tension**
- **Concentrated at phase boundaries**
- **Reactive**
  - Chemically react with blend components.
- **Nonreactive**
  - Physical effects (Block or graft copolymers of the blend homopolymers).

Charraher

How to select the compatibilizer /coupling agent

- **Chemical structure and the interfaces of**
  - Polymer matrix
  - Reinforcement/filler
  - Application limits
    - *Food contact approved? Thermal stability? Color?*

How compatibilize?

1. **Addition of a small quantity of a third component that is miscible with both phases (covalent) (e.g. PLA, cellulose, maleic acid)**
2. **Addition of a copolymer whose one part is miscible with one phase and other with another phase (e.g. 0.5-2 wt%, usually blockcopolymer, seldom graft)**
3. **Addition of a large amount, usually 25-35 wt% copolymer having multipurpose nature (e.g. + impact modifier)**
4. **Using chemical reactants in compounding (*in situ* formation of compatibilizers)**

Utracki, 1998

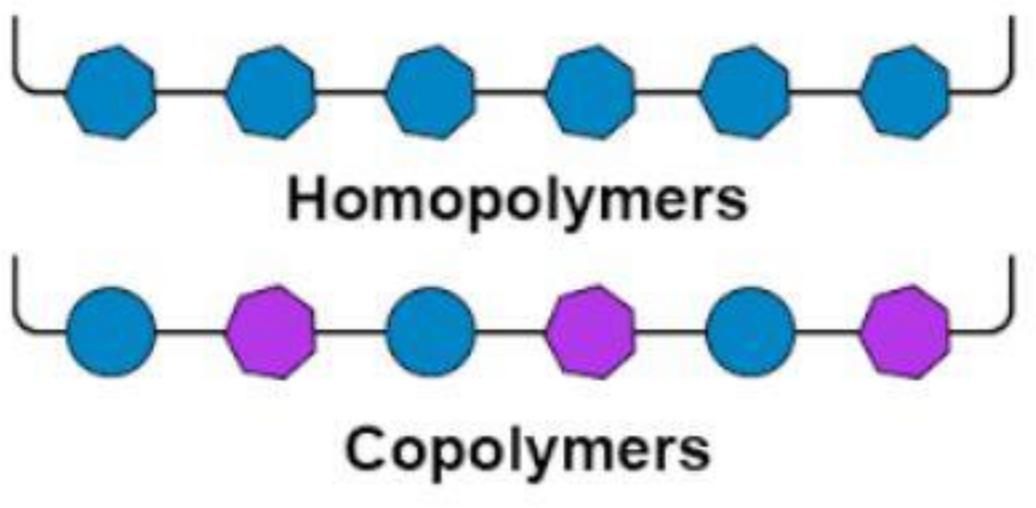
Methods for improving blend compatibility

1) Addition of a third polymer (partially) miscible with all blend phases
2) Addition of low molecular weight chemicals
3) Addition of reactive polymers
4) Addition of premade grafted and block copolymers
5) Addition of selective crosslinking agents
6) Interchange reactions
7) Mechanochemistry
8) Introduction of specific interactions
9) Addition of ionomers
10) Others
    1) Common solvent/reactive filler

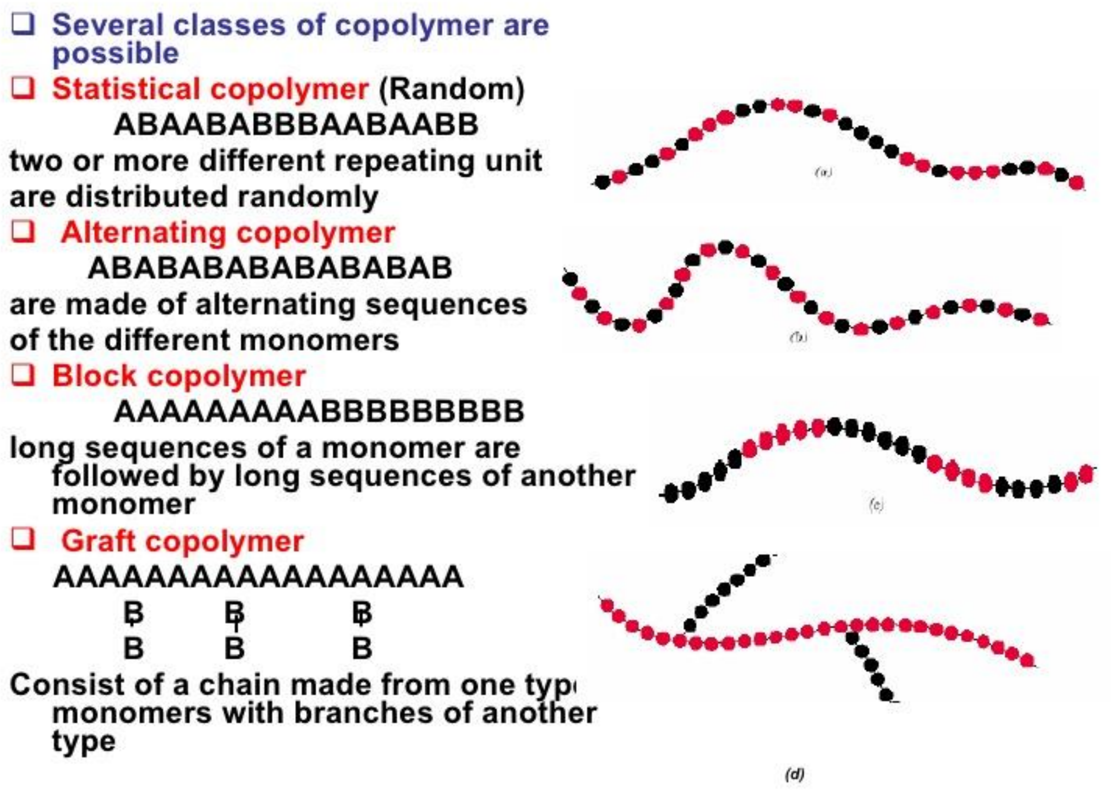
STRATEGIES FOR COMPATIBILIZATION OF POLYMER BLENDS Progress in polymer science (1998), vol. 23, iss. 4, pp. 707-757 https://orbi.uliege.be/bitstream/2268/4370/1/Koning_C_1998_Prog%20polym%20sc_%2023_4_707.pdf

1. Compatibilization of incompatible blends using block- and graft copolymers

Copolymers vs homopolymers



Copolymers



☐ Several classes of copolymer are possible

☐ **Statistical copolymer** (Random)

ABAABABBBAABAABB

two or more different repeating unit are distributed randomly

☐ **Alternating copolymer**

ABABABABABABABAB

are made of alternating sequences of the different monomers

☐ **Block copolymer**

AAAAAAAAABBBBBBBBB

long sequences of a monomer are followed by long sequences of another monomer

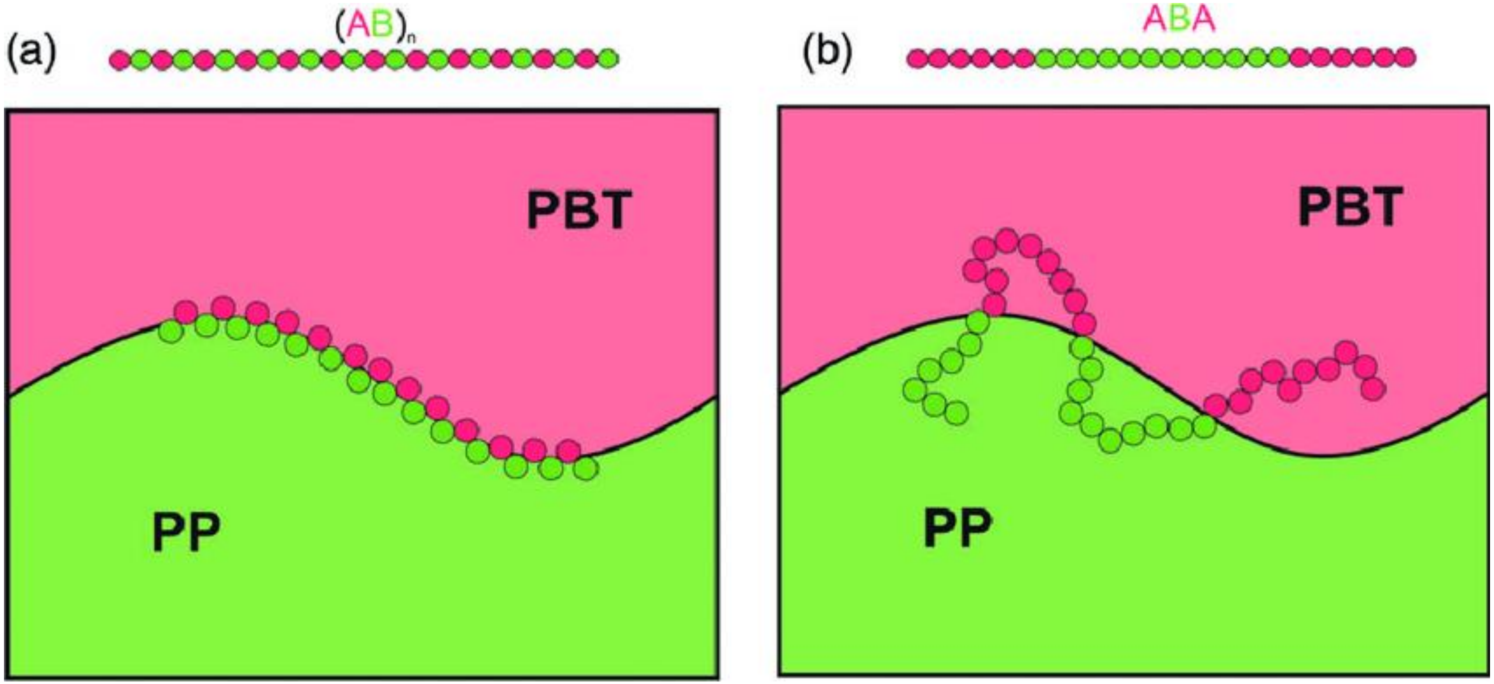
☐ **Graft copolymer**

AAAAAAAAAAAAAAAAA
B B B
B B B

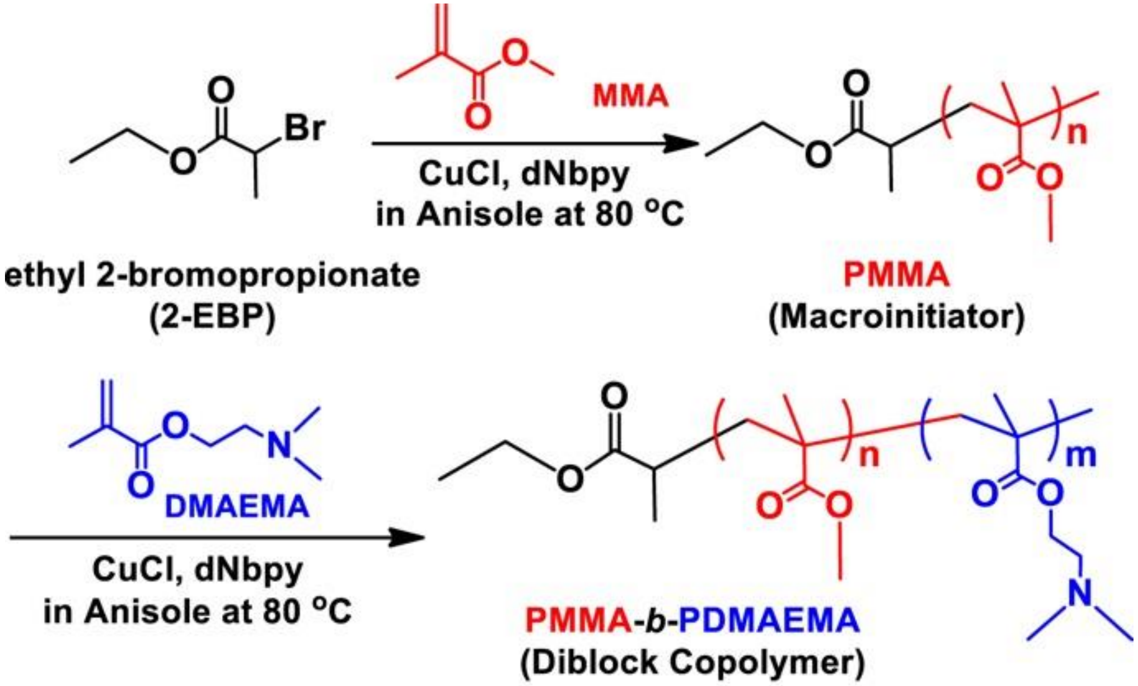
Consist of a chain made from one typ monomers with branches of another type

Copolymers

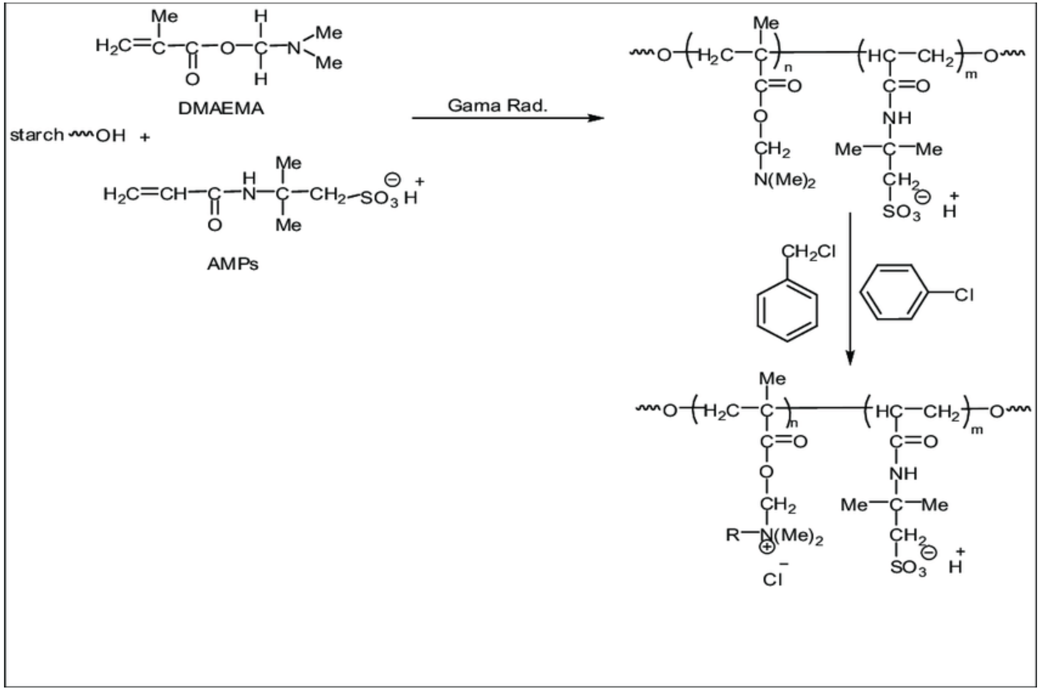
- Two polymers, one chain



Example


MMA
CuCl, dNbpy
in Anisole at 80 °C
ethyl 2-bromopropionate
(2-EBP)
PMMA
(Macroinitiator)
DMAEMA
CuCl, dNbpy
in Anisole at 80 °C
PMMA-*b*-PDMAEMA
(Diblock Copolymer)
n
m

Grafting copolymerization of 2-acrylamido-2-methylpropane-1-sulphonic acid (AMPS) and dimethylaminoethyl methacrylate (DMAEMA) onto starch

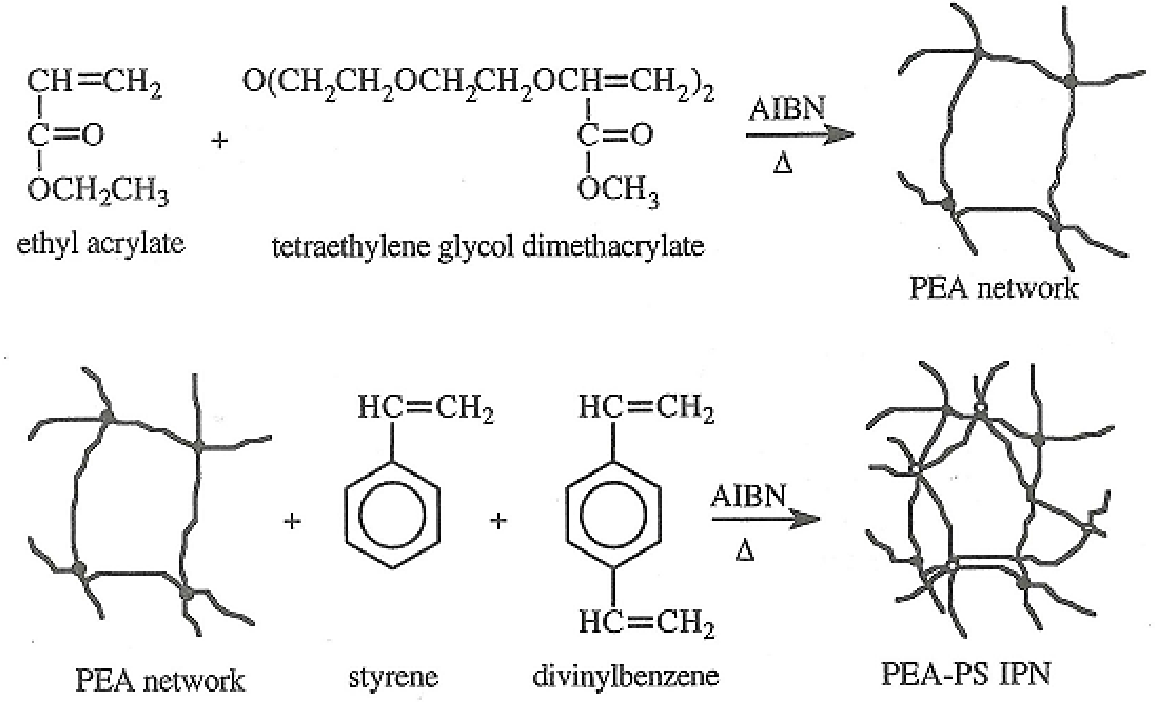


Copolymers

- At the end of the day the strategy of copolymers is similar to the use of low molecular weight compounds, surfactants, third polymer, ..

2. Interpenetrating Networks (IPNs)

Sequential IPN



swollen with styrene+DVB

IPNs are combinations of two or more polymers in network form.

IPNs include PUs, PS, PEA, PMMA.

Earliest commercialized IPNs used in many automotive applications, consists of PP and EPDM (ethylene-propylene-diene terpolymer)

IPN structures are used for:

- Soft contact lenses
- Ion exchange resins
- Pressure sensitive adhesives
- Controlled release of drugs
- Preparation of novel membranes

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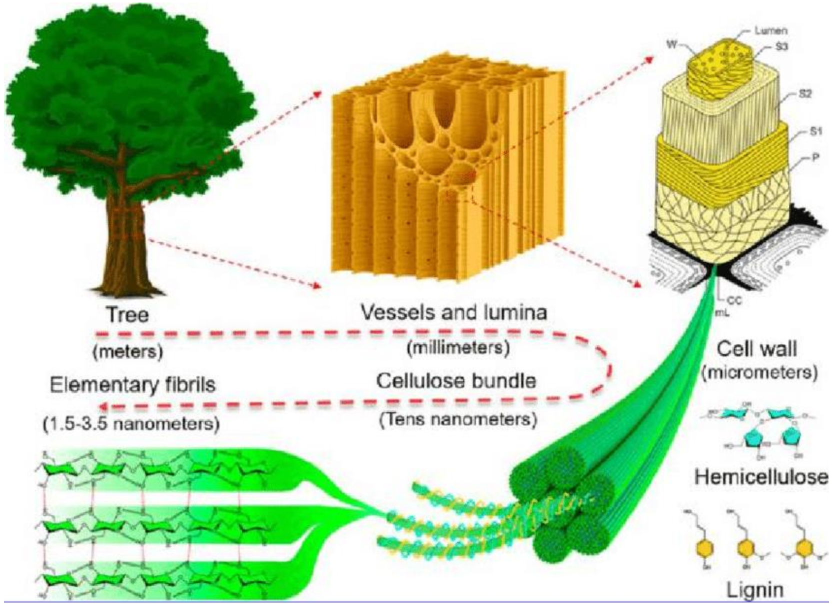
Composites

Composite

Most composites have two constituent materials:

- *Matrix and Reinforcement*



Composites: Matrix

The role of the matrix is to bind the reinforcement together so that the applied stress is distributed among the reinforcement and to protect the surface of the reinforcement from being damaged.

Composites are classified according to their matrix phase:

- **Polymer matrix composites (PMC's)**
- Ceramic matrix composites (CMC's)
- Metal matrix composites (MMC's)

Composites: Isotropy vs Anisotropy

¤ Isotrophy: The properties of a material are (macroscopically) constant in x,y,z

*** Powders, chopped fibers, sawdust, good blends**

¤ Anisotrophy: The properties of a material differs

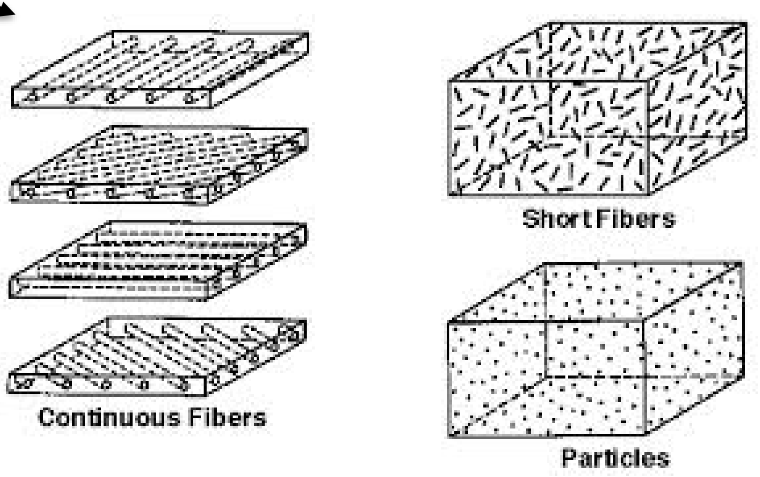
*** Long/continous fibers**

Reinforcements

The role of reinforcement in composite materials is primarily to add mechanical properties to the material such as **strength** and **stiffness**

Reinforcements basically come in three forms

- *particulate*
- *discontinuous fiber*
- *continuous fiber*



Reasons to consider polymer blends and composites

- They offer the simplest route for combining outstanding properties of different existing polymers;
- The synthesis of new polymer is very costly;
- They offer interesting engineering applications;
- **Lightweight**
- They improve processing ability (sometimes);
- They are used as an alternative for tailoring degradability
- They are a simple solution to the complex problem of disposal of polymer (or other waste, fillers - sawdust).

Reasons to consider polymer blends and composites

- The source of raw materials for the manufacture of synthetic polymers appears to be limited;
- They are a cost-effective way for new materials and products to fill the economic and performance gap;
- They provide properties of importance which can be maximized;
- They produce materials and products with tailor-made properties;
- They are a convenient way of developing materials with novel or selectively enhanced properties which are possibly superior to those of the components

Advantages of Polymer Matrix Composites

Polymer composites are ***lightweight materials*** providing an advantage for;
- aircraft body, bicycle bodywork,
- military and heavy goods vehicles use composites in both bodywork and engine and transmission systems.
- mass transit systems in trains, subways and buses use composites for ceilings, walls, floors and seating.
- small issue: ”sudden break”, microcracks, hinders aeronautical application

Polymer composites have a ***high resistance to chemical corrosion*** and ***scratching***. Their **resilience to seawater and rust** is an advantage when used in boats or other marine craft manufacture.

http://news.tvb.com/gallery/o_gallery154.htm

Easy to fabricate of very complex parts with low tooling cost.

Reinforcing agents have following abilities/functions

- Must be stiffer and stronger than the polymer matrix
- It has good particle size, shape and surface for effective mechanical coupling to the matrix
- It preserves the desirable qualities of the polymer matrix

STRESS TRANSFER

The strength of the composite depends on the strength of the bond between particle and matrix.

The more interface → effective reinforcement

Effectiveness of a reinforcement → A/V ratio

A: surface area of a particle → **Nanoparticles**

V: its volume

A/V to be as high as possible

Quantity and **quality** of surface.

Asumming that the role of the filler is to increase properties.

Classes of reinforcing agents/fillers

- Fibres (glass fibres, carbon fibers, Kevlar fibres, natural fibres)

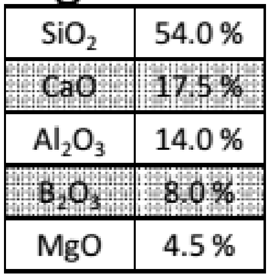
- Platelets (mica/talk/organoclays)

- Sawdust

Aalto University
School of Chemical
Technology

Glass fiber is widely used one

E-glass



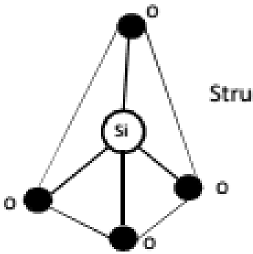
SiO_2	54.0 %
CaO	17.5 %
Al_2O_3	14.0 %
B_2O_3	8.0 %
MgO	4.5 %

S-glass: higher modulus and strength

C-glass: improved resistance to water and acids

Glass fibers are manufactured by extruding molten glass at high linear velocity through a large number (100-1000) of holes in a platinium plate known as a «bushing».
Then they cooled and solidify.

HYDROPHILIC



Structure of silica glass

tetrahedrom

Advantages of glass fibers:

- Resistance to high temperatures – softening point is 850^{o}C.
- Transparency to visible light – takes the color of matrix
- Isotropy – such as thermal expansion is identical in axial and radial directions.

Disadvantages:

- Susceptible to surface damage

- Carbon and Kevlar fibers are less widely used than glass fibers due to their relatively high cost.
- Best carbon fibers are produced from PAN (polyacrylonitrile)
- PAN is converted to graphite by controlled heating process.

Advantages of C fibers:

- Chemical inertness: resistance to moisture and common chemicals

- High electrical and thermal conductivity along the fiber axis (disadvantage)
- Dimensional stability: thermal expansion low and negative

Disadvantage:

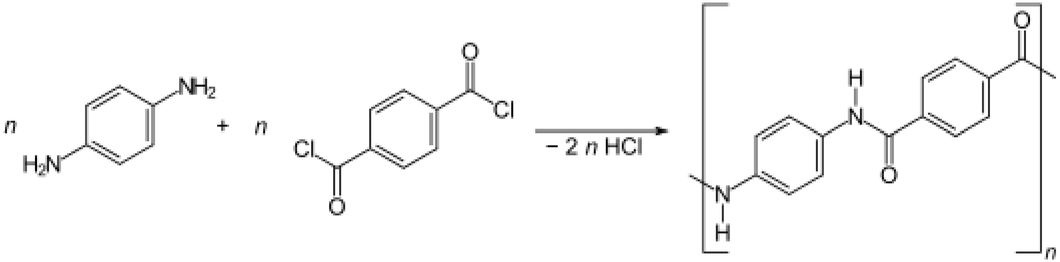
- Colour (difficult to change)

Mechanical properties of composites are strongly influenced by:

- Orientation (mostly long fibers)
- size
- type
- concentration
- dispersion of reinforcing agent (filler)
- interfacial tension between the matrix and filler (surface quality)

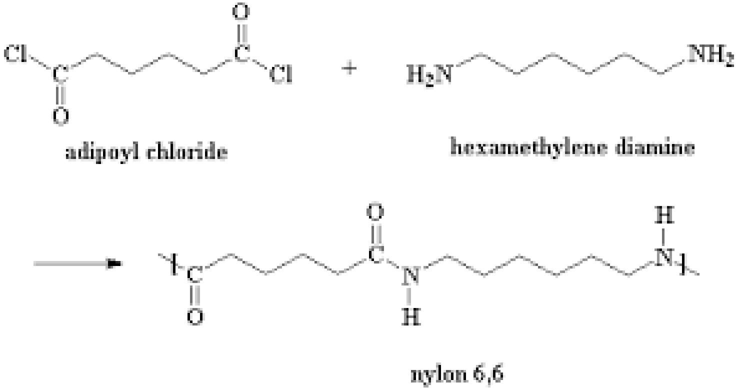
Kevlar (Matrix and reinforcement)

- Kevlar is a heat-resistant and strong synthetic fiber.
- Kevlar is synthesized in solution through condensation of 1,4-phenylene-diamine (para-phenylenediamine) and terephthaloyl chlorid.

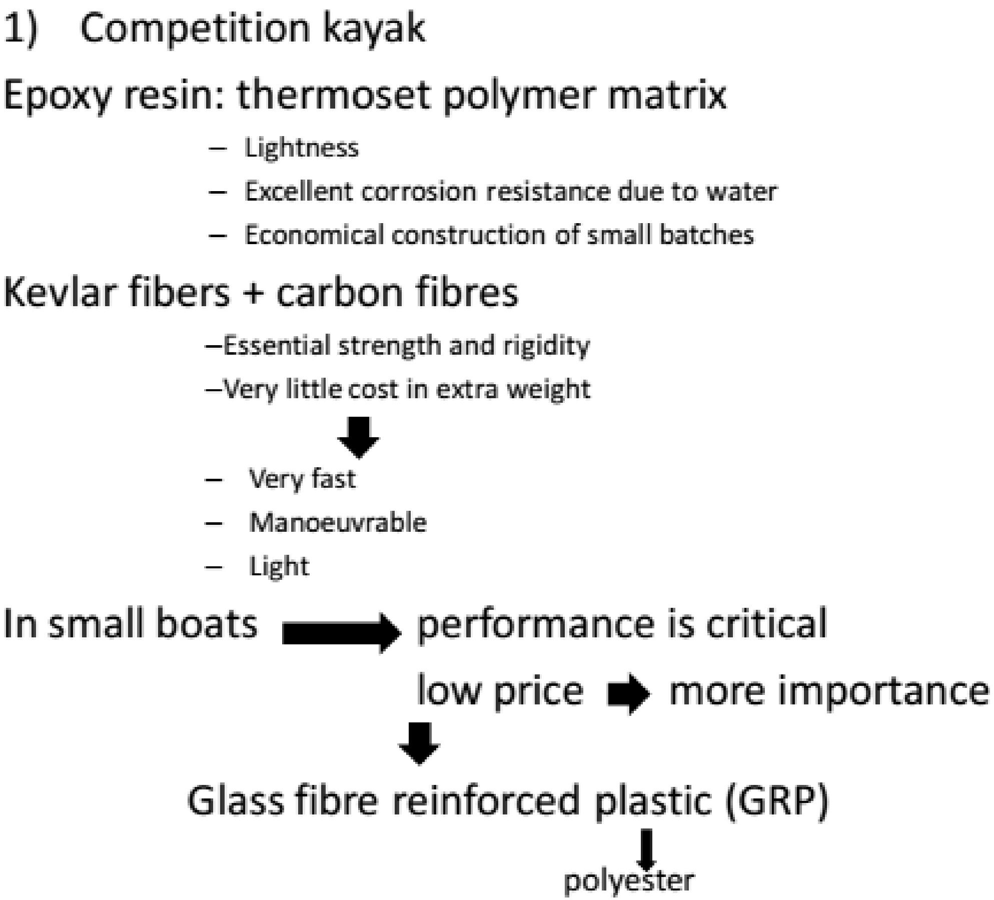


Nylon 66 (Fibre and Matrix)

Nylon 66 is a type of polyamide or nylon. It, and nylon 6, are the two most common for textile and plastics industries. Nylon 66 is made of two monomers each containing 6 carbon atoms, hexamethylenediamine and adipic acid, which give nylon 66 its name



Examples:



1) Competition kayak

Epoxy resin: thermoset polymer matrix

- Lightness
- Excellent corrosion resistance due to water
- Economical construction of small batches

Kevlar fibers + carbon fibres

- Essential strength and rigidity
- Very little cost in extra weight

↓

- Very fast
- Manoeuvrable
- Light

In small boats → performance is critical

low price → more importance

↓

Glass fibre reinforced plastic (GRP)

↓

polyester

2) Tennis racquet (Nylon matrix+carbon fiber)

Nylon^{66} matrix →

→ Low density

→ Economical construction by injection molding in large batches

↓

Polymer is moulded around the low T_m metal alloy core

75 km/h

3) Rubber car tyre

Reinforced at several different levels.

- at microscobic level

  - carbon black mixed with polymer increased stiffness, strength and wear resistance

- at macroscobic level

  - rigid cords (polyester fibres and/or steel wires)

  -to provide strength and stiffness in radial and circumferential direction

STRESS TRANSFER

The strength of the composite depends on the strength of the bond between particle and matrix.

The more interface → effective reinforcement

Effectiveness of a reinforcement → A/V ratio

A: surface area of a particle → **Nanoparticles**

V: its volume

A/V to be as high as possible

Quantity and **quality** of surface.

Asumming that the role of the filler is to increase properties.

Outline

1. Fundamental of Polymers
2. Polymer blends and plasticisers
3. Compatibilization of polymer blends
4. Composites
5. **Wetting and compatibilization of composites**
6. Nanocomposites
7. Compatibilization of nanocomposites

A surface issue

- Specially in long fiber composites we need to have a good adhesion between fibers and polymer.
- This means that
  - a) The polymer has to physically reach all the fibers.
  - b) The polymer has to “wet” the fibers
    - It has to create a lot of surface
  - c) It has to be a good contact
- This is a matter of **viscosity** and **surface tension of the resin.**

Viscosity and surface tension

- **The viscosity of a fluid is a measure of its resistance to deformation at a given rate (flow). For liquids, it corresponds to the informal concept of "thickness": for example, syrup has a higher viscosity than water**

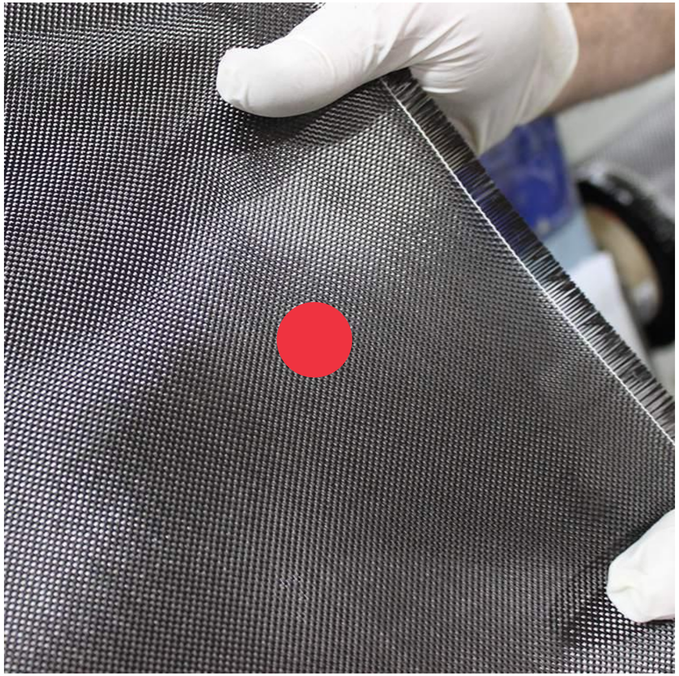
- **Surface tension is the tendency of liquid surfaces to shrink into the minimum surface area possible. The lower ST, the more surface you can create. Surface tension allows insects (e.g. water striders), usually denser than water, to float and slide on a water surface.**

  Surfactants, water, soap.

- **Usually are related, high viscosity – high surface tension. Water is an exception – that's why we use soap.**

A surface issue

If we drop resin in the red point we need to spread it to fill all of the fabric.
This depends mostly in viscosity



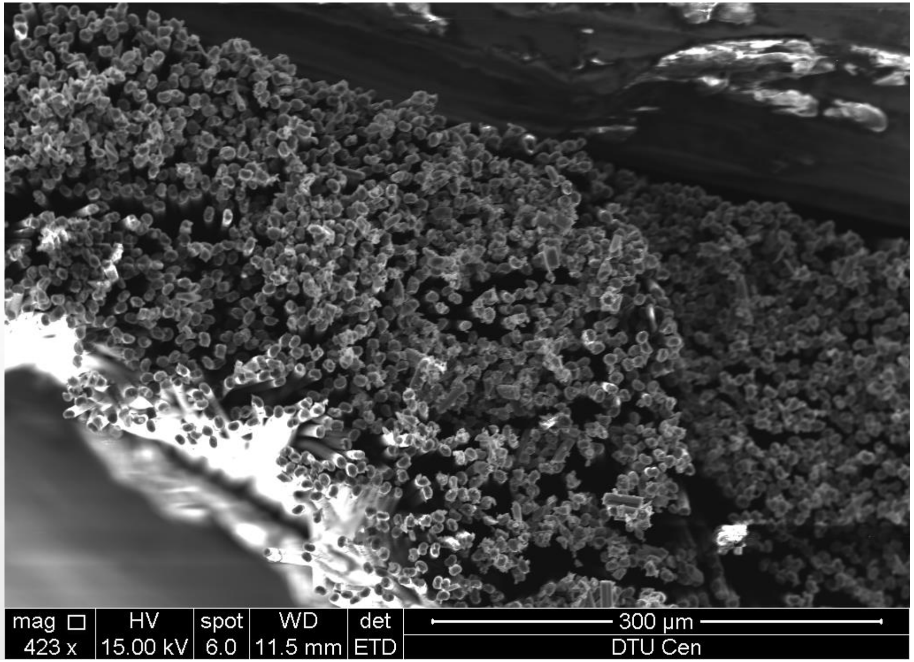
Infiltration

Then the resin has to wet the CF tow. (surface tension/viscosity).

- (app) **1 m2/g**

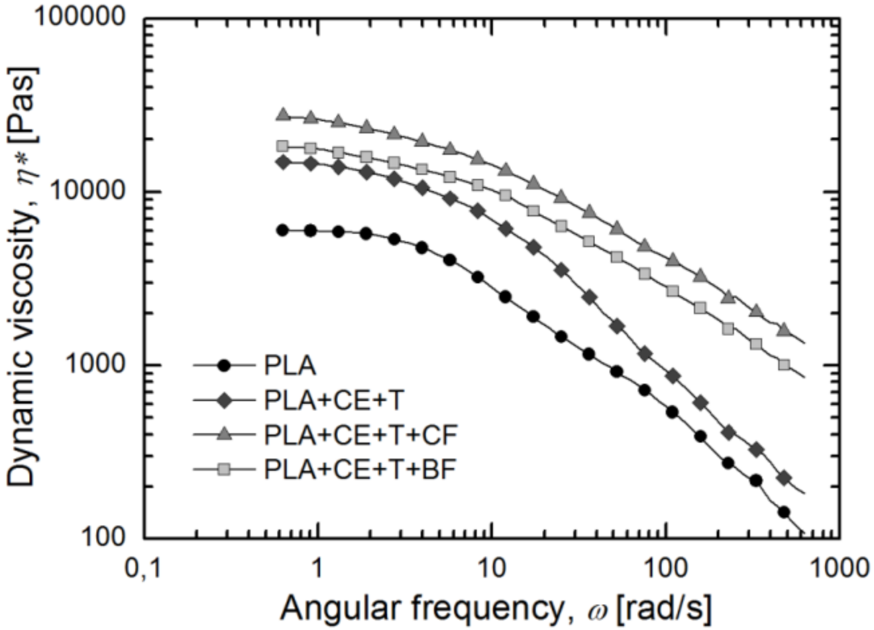
1 mL of resin should cover 0,5-1 m^2.

<u>VACUUM</u>

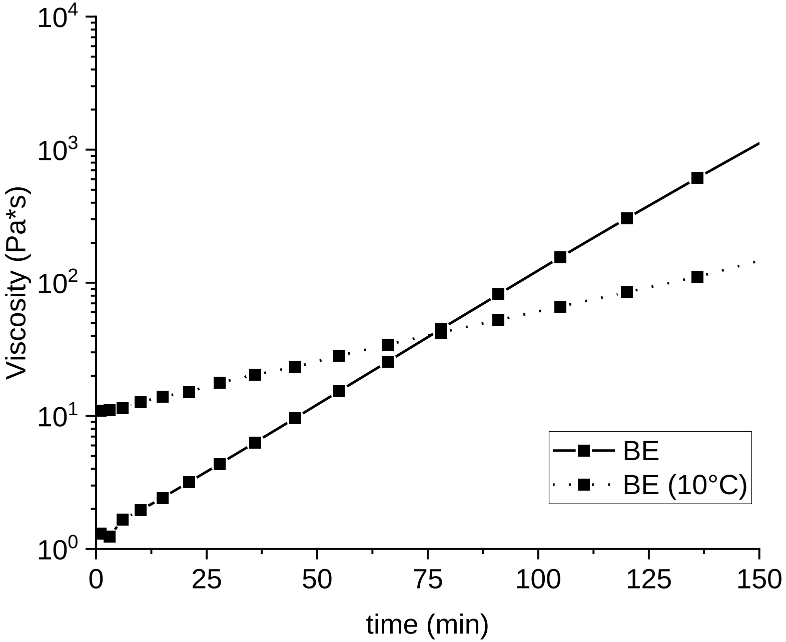


Thermosets vs molten thermoplastic

Molten PLA (>160C)



Thermoset bioepoxy resin (25C) (1 rad/s)



Conclusions

- Generally CF composites use thermosets are they are less viscous, have less surface tension so it is easier to make composites.

- Many thermosets have a “designed for composites” version of resins.

- We can use thermoplastics also, but its less common and more complex

- Sometimes thermoplastic monomers are used to wet fibers. And then polymerize. But curing it´s generally easier and less demanding (water, oxygen free environment, less heat needed) than polymerization.

Sizing of fibers

- Put a thin high-performance polymer coating at the surface of the fibers
- Common practice in the industry, you can buy sized fibers
- Increase compability between matrix/fibers
- Also protects the fiber (specially for glass)
- Thermal stability??

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Nanocomposites and compatibilization

Nanocomposites

- Nanoparticles much higher surface.
  - CF 1 m^2/g, CNF 1000 m^2/g

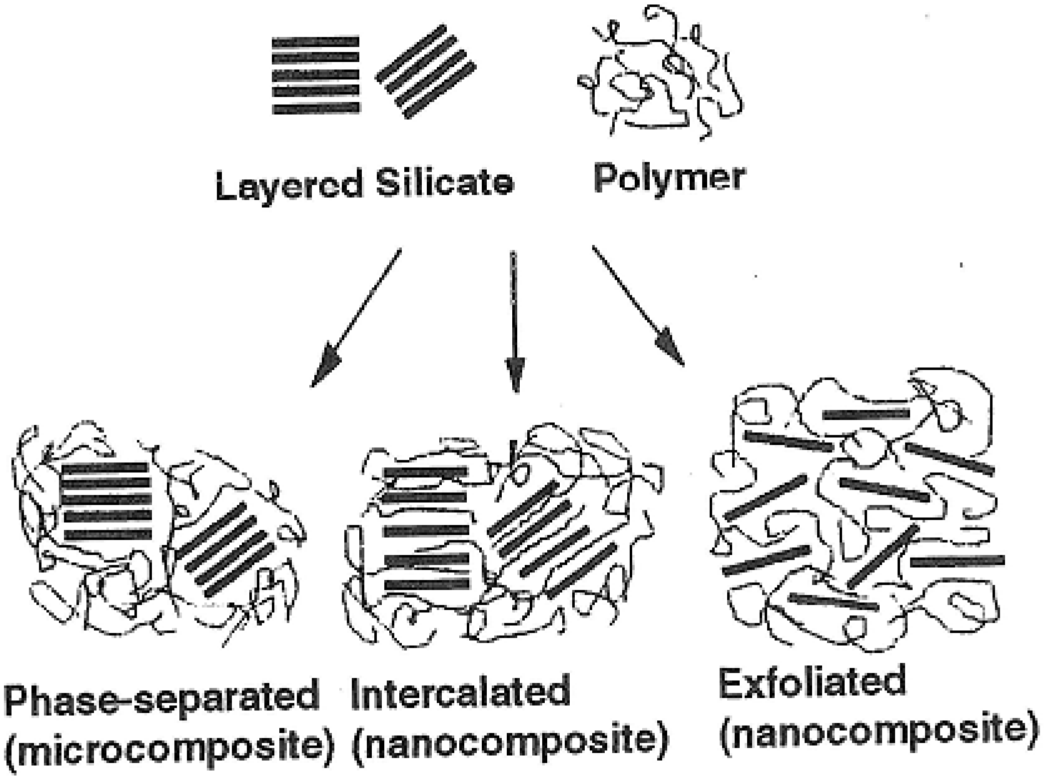
- Stress transfer depends on surface therefore they have more potential

- The surface has ultrahigh energy which hinders adhesion.
  This in fact makes NP to have different melting temperature

- Regulatory issue

- Graphene, nanocellulose, nanoclays, metallic nanoparticles, carbon nanotubes, carbon nanofibres, nanodiamonds

Platelet-based nanocomposites: Graphene/clay



Aalto University
School of Chemical Technology

Nanocomposites: Compatibilization

- Melt blending
- Solvent casting
  - Dissolve polymer and NP in common solvent. Cast and dry.
- In situ polymerization
  - Premix the NP with the monomer and react.
- **Grafting to/surface modification**
  - Put hydrophobic molecules in the surface of the NP.
  - Tetraalkylamonium in clay (C30B)
- **Grafting from**
  - Grafting to: put the monomer in the surface of the NP.
  - Starting polymerization in the surface of the NP.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P