UNIVERSITY OF ZAGREB

FACULTY OF CHEMICAL ENGINEERING AND TECHNOLOGY

Polymers science and technology

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Polymer blends

- Polymer blends are **mixtures** of two or more polymers with/without any chemical bonding between them

- The objective of polymer blending is achieving commercially viable products through either **unique properties or lower cost** (engineering resins diluted it with a low-cost polymer)

- **Less expensive than the development of new products** by synthesis, rapid development of modified polymeric materials to meet needs by by-passing the polymerization step

- A balanced set of desired properties (Extended service temperature range, enhanced ozone resistance, improved modulus and hardness, improved barrier property and flame-retardant property, improved impact and environmental stress cracking resistance, etc.)

Polymer blends

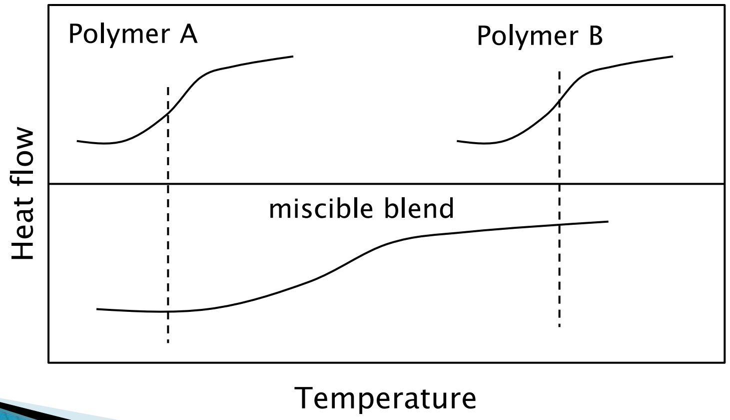
Type	Description
Mechanical blends	Polymers are mixed at temperatures above T_g for amorphous and above T_m for semicrystalline polymers. Component polymers are pre-mixed and fed into an extruder which heats the polymers to temperatures above T_g or T_m and introduces a high degree of mechanical work into the blend to ensure intensive mixing
Mechanochemical blends	Polymers are mixed at shear rates high enough to cause degradation. Resultant free radicals combine to form complex mixtures
Solution-cast blends	Polymers are dissolved in common solvent and solvent is removed
Chemical blends Interpenetrating polymer networks (IPN)	Crosslinked polymer is swollen with different monomer, then monomer is polymerized and crosslinked

Polymer blends

1) **Completely miscible blends**
2) **Partially miscible blends**
3) **Fully immiscible blends**

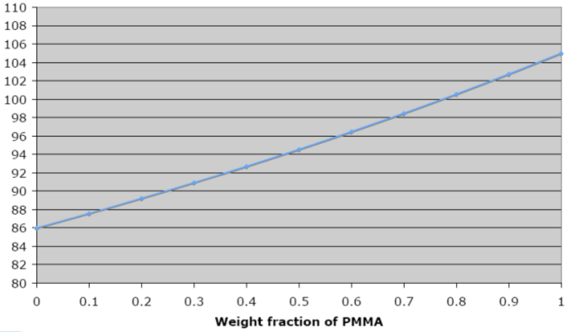
1) Completely miscible blends

- **Homogeneous** one phase blends
- This type of blends exhibits **only one glass transition temperature** (T_g), which is in between the glass transition temperatures of the blend components in a close relation to the blend composition



Fox equation for a binary system

$$\frac{1}{T_g} = \frac{x_1}{T_{g,1}} + \frac{x_2}{T_{g,2}}$$

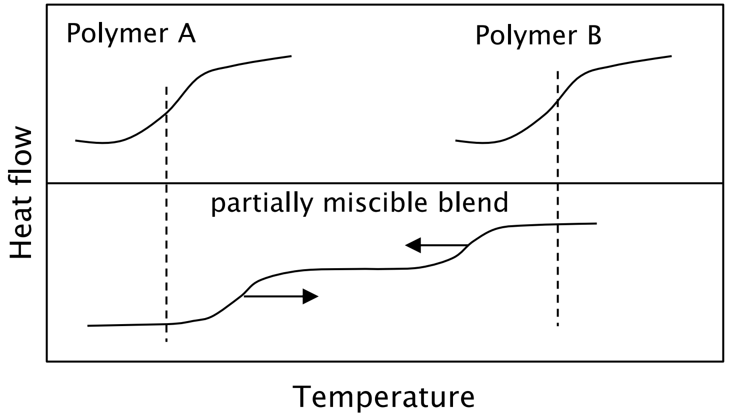


PMMA/PVC example

Polymer blends

2) Partially miscible blends

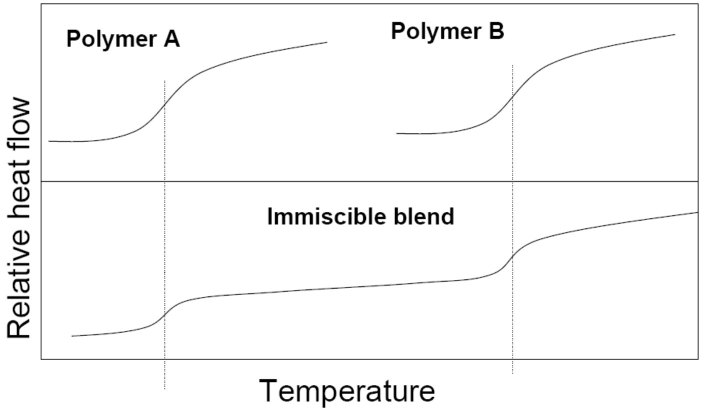
- This type of blend, which exhibits a **fine phase morphology** and **satisfactory properties**, is referred to as **compatible**
- Both blend phases are homogeneous, and **have their own T_g**
- Both T_g are shifted from the values for the pure blend components towards the T_g of the blend component



Polymer blends

3) Fully immiscible blends

- Have a **coarse morphology**, sharp interface and poor adhesion between the blend phases
- These blends will exhibit T_g corresponding to the T_g of the component polymers

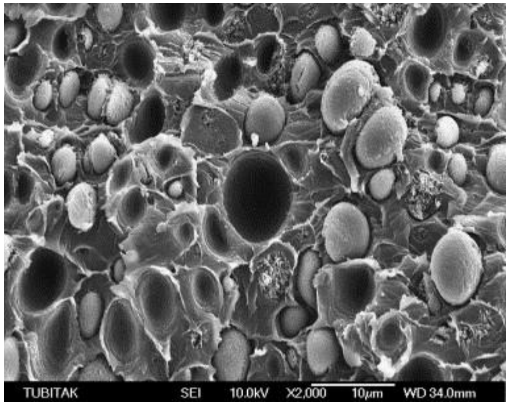


- But the phase-separated materials often turn out to be useful

Polymer blends

Example is high-impact polystyrene (HIPS)

- Partly grafted polystyrene (PS) on polybutadiene (PBD), partly blend of PS and PBD
- When PS is mixed with a small amount of PBD, the two polymers won't blend – they are immiscible
- The polybutadiene will separate from the polystyrene into little spherical particles
- Polystyrene is a rather stiff but brittle material
- Little polybutadiene spheres are rubbery, and they can absorb energy under stress
- This keeps the polystyrene from breaking
- This immiscible blend has more ability to bend instead of breaking than regular polystyrene, it's tougher and more ductile



Polymer blends

- **Improving immiscible blends properties**

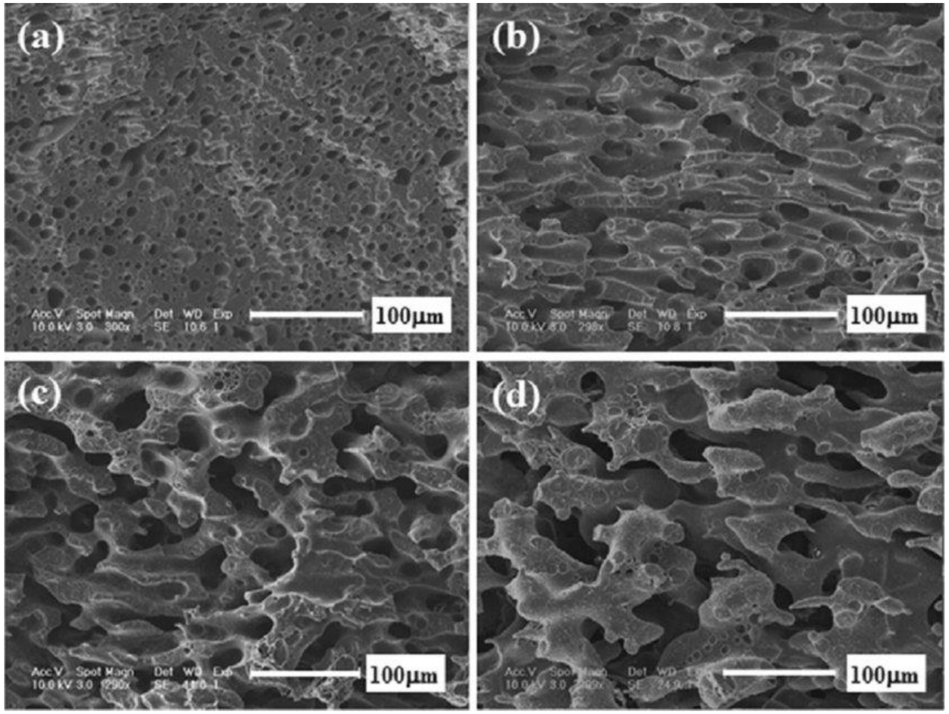
1) Co-continuous morphology

- To make a strong immiscible blend – use of **more equal amounts of the two polymers.** When the relative amounts of the two polymers are equal, we get a different morphology than when one is in large excess
- When polymer A and polymer B are present in roughly equal amounts, they form two **co-continuous phases**
- This means both phases will be bearing the load of any stress on the material, so it will be stronger

Polymer blends

- Co-continuous morphology SEM images

PS/PP blend



95/5

90/10

70/30

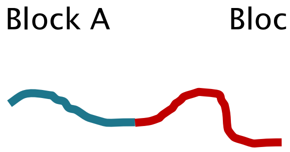
50/50

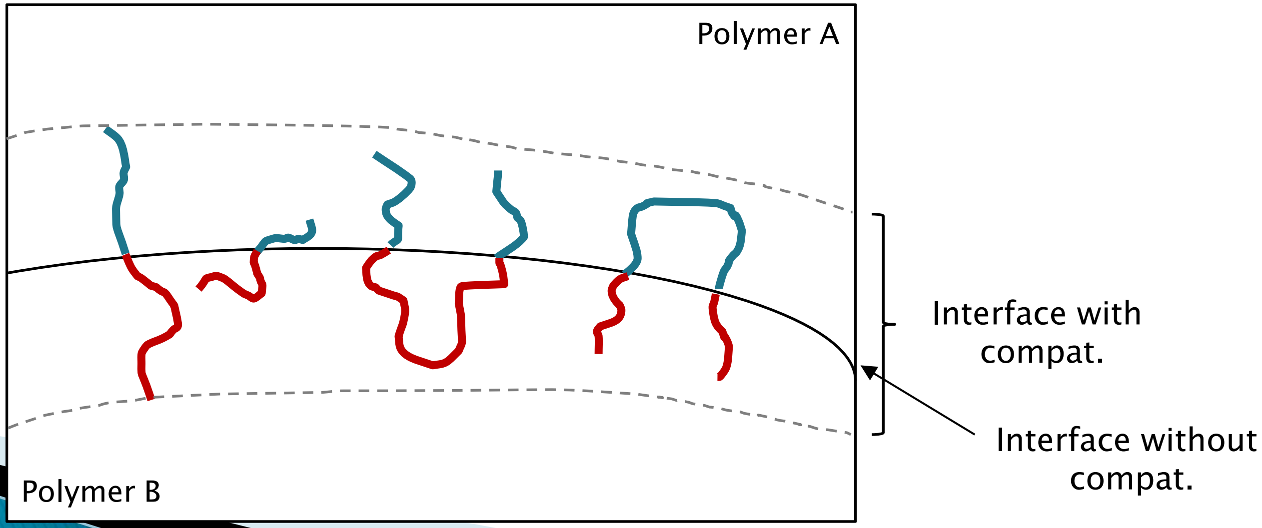
Polymer blends

➢ Improving immiscible blends properties

2) Compatibilization

- A compatibilizer is anything that helps **bond the two phases** to each other more tightly
- In an immiscible blend, the two phases are not bonded very strongly to each other
- Compatibilizer reduces interfacial tension, **enhances adhesion between phases** and improves the overall mechanical properties of the products
- Many times, a compatibilizer is a **block copolymer** of the two components of the immiscible blend

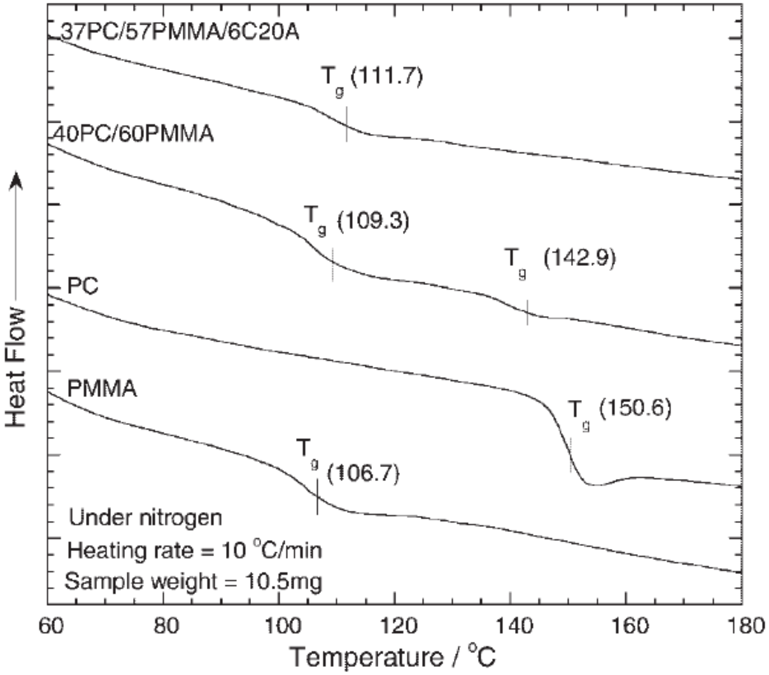


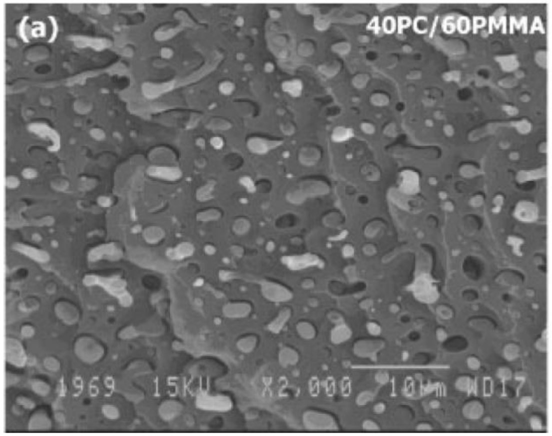


Polymer blends

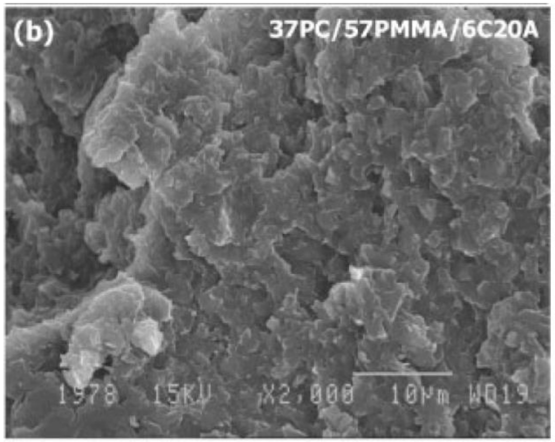
Compatibilizer effect

Polycarbonate/Poly(methyl methacrylate) blend





two-phase structure, indicating the expected immiscibility of the components



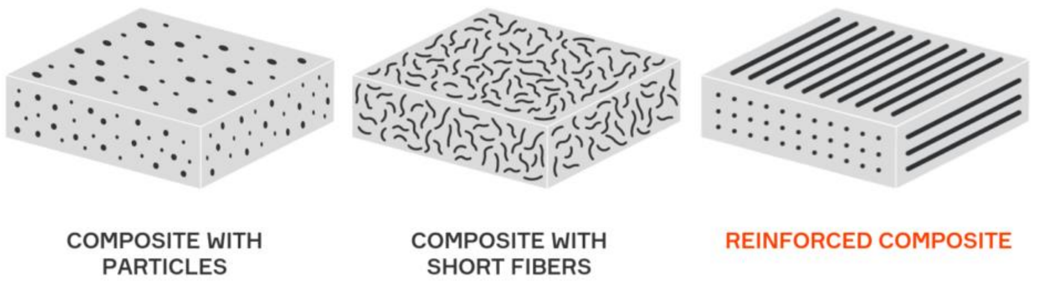
the size of the dispersed PC particles was reduced significantly upon the addition of C20A

Polymer composites

- Composites can be defined as **materials that consist of two or more chemically and physically different phases** separated by a distinct interface
- The basic difference between blends and composites is that **the two main constituents in the composites remain recognizabl**e while these may not be recognizable in blends
- Most primitive man-made composite materials were straw, and mud combined to form bricks form building construction

Polymer composites

- Composite material is a material composed of two or more distinct phases (**matrix phase and dispersed phase**) and having bulk properties significantly different from those of any of the constituents
- **Matrix phase** is the primary phase having a continuous character
- **Matrix** is usually more ductile and less hard phase – **polymer**
- It holds the dispersed phase and shares a load with it
- **Dispersed (reinforcing) phase** is embedded in the matrix in a discontinuous form
- **Dispersed phase** is usually stronger than the matrix – **inorganic/organic filler**

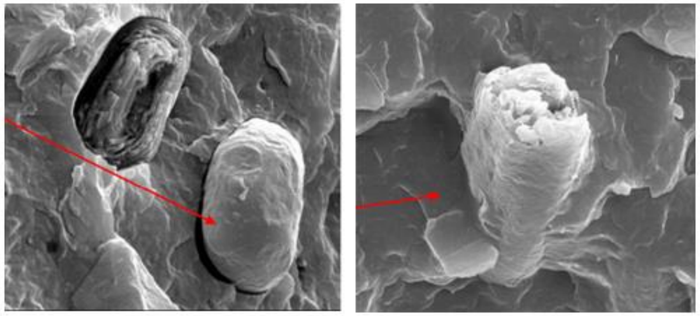


Polymer composites

- **Factors affecting properties of polymer composites**
- ❑ Interfacial adhesion
- ❑ Shape and orientation of dispersed phase
- ❑ Matrix properties
- ❑ Concentration of dispersed phase
- ❑ Size of dispersed phase

Interfacial adhesion

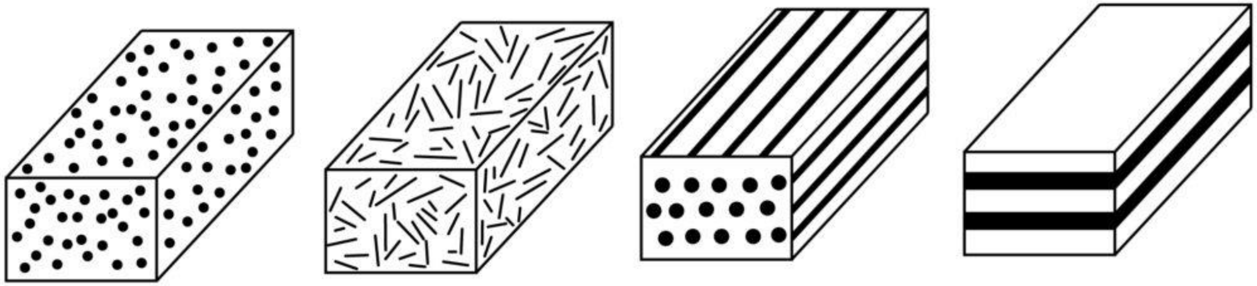
- For good mechanical properties the interfacial adhesion should be strong
- Matrix molecules can be anchored to the fiber surface by chemical reaction or modification of filler surface to enhance adhesion (similarly to blends)



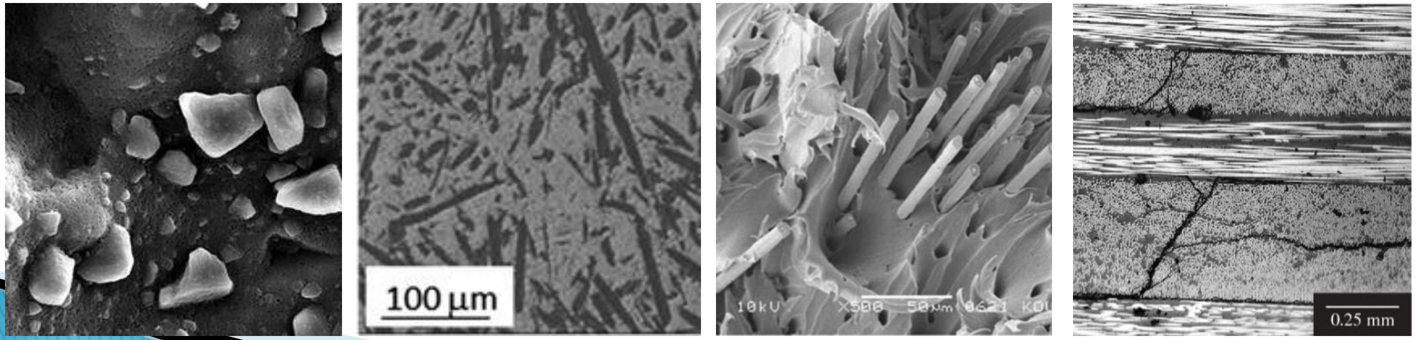
Polymer composites

Shape and orientation of fillers

- The type of the fillers can be:
- **Particles** (spherical, cubic, flakes)
- **Fibers** (short-whiskers or continues)
- **Laminates**



Particles Short fibers or whiskers Continues fibers Sheet laminates

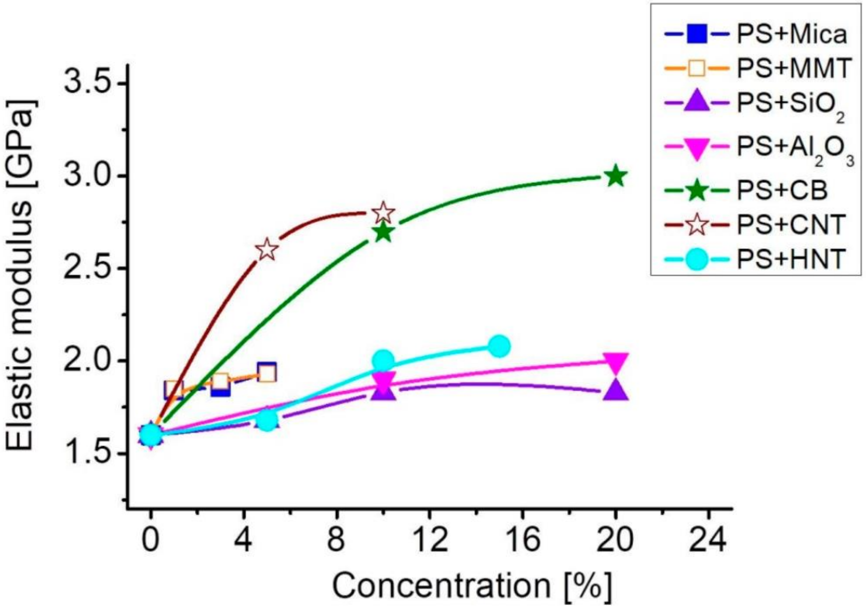


Polymer composites

Matrix properties

- Thermoplastic
- Thermoset
- Elastomer
- Polymer blend

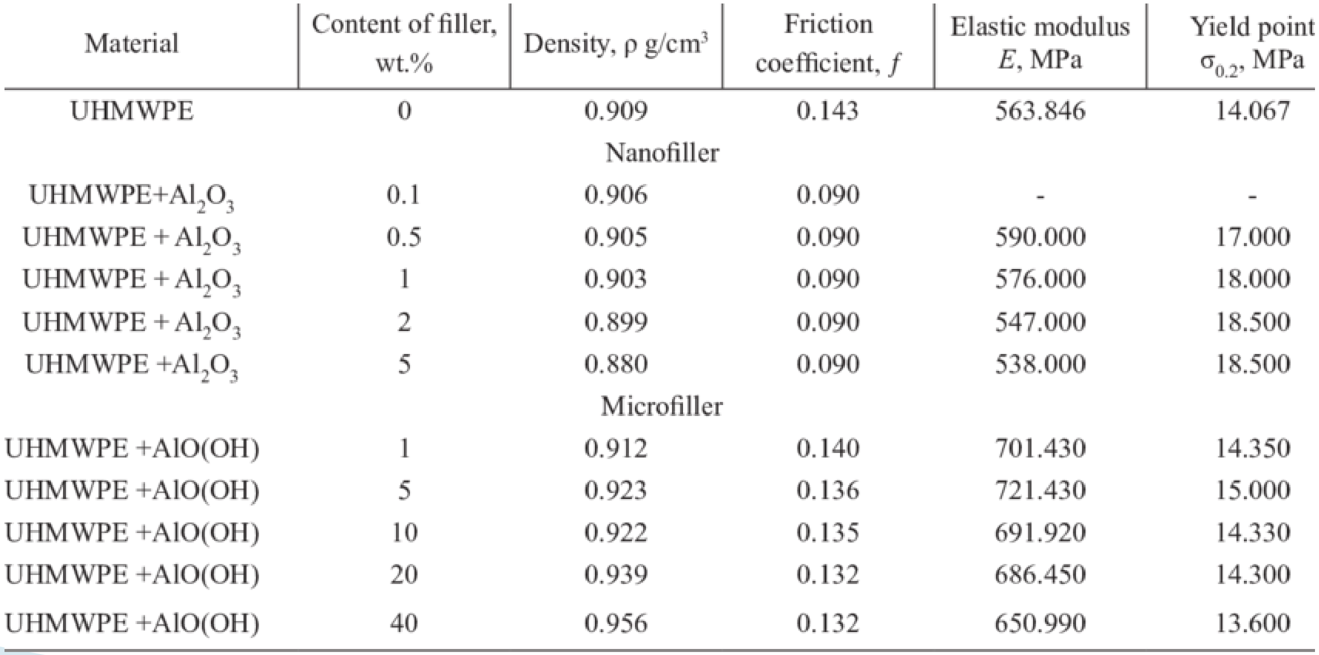
Concentration of dispersed phase



Polymer composites

Size of dispersed phase

- Micro- and nanofillers
- Nanofillers – at least one dimension below 100 nm
- ❑ Large surface area
- ❑ Added in smaller quantities



Material	Content of filler, wt.%	Density, ρ g/cm^3	Friction coefficient, *f*	Elastic modulus *E*, MPa	Yield point $\sigma_{0.2}$, MPa
UHMWPE	0	0.909	0.143	563.846	14.067
		Nanofiller			
UHMWPE+Al_2O_3	0.1	0.906	0.090	-	-
UHMWPE + Al_2O_3	0.5	0.905	0.090	590.000	17.000
UHMWPE + Al_2O_3	1	0.903	0.090	576.000	18.000
UHMWPE + Al_2O_3	2	0.899	0.090	547.000	18.500
UHMWPE +Al_2O_3	5	0.880	0.090	538.000	18.500
		Microfiller			
UHMWPE +AlO(OH)	1	0.912	0.140	701.430	14.350
UHMWPE +AlO(OH)	5	0.923	0.136	721.430	15.000
UHMWPE +AlO(OH)	10	0.922	0.135	691.920	14.330
UHMWPE +AlO(OH)	20	0.939	0.132	686.450	14.300
UHMWPE +AlO(OH)	40	0.956	0.132	650.990	13.600

Polymer processing

- Different processing technologies for shaping polymeric materials have been developed
- Processes for processing polymeric materials can be divided into **two categories**
  - **Primary molding processes**
  - **Reshaping processes**

- **Primary molding processes** – formless raw material (powder or granulate) is turned into a cohesive material as a finished product or into semi-finished forms, such pipes and sheets which are raw materials to be processed further and reshaped
- **The reshaping processes** – processing techniques for semi-finished products, the shape of product is changed without any material being added to

Polymer processing

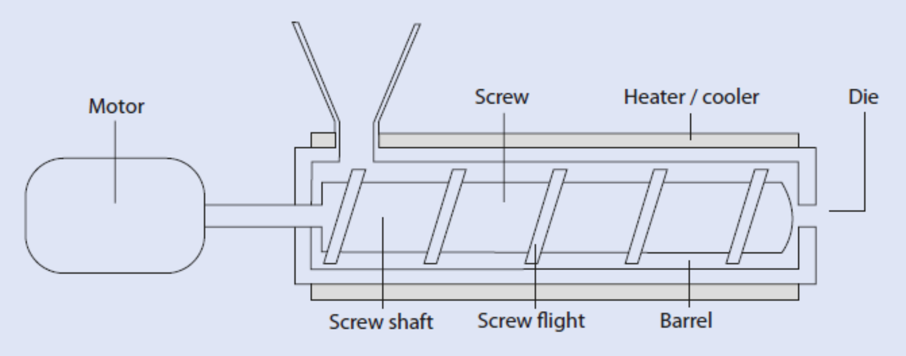
Primary Molding Processes

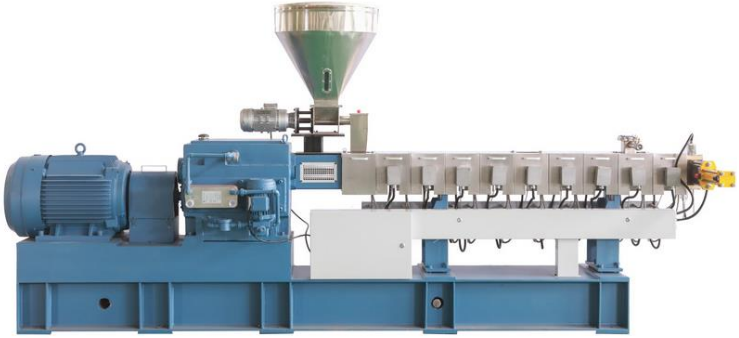
- **Shaping thermoplastics is a physical process**: the material is heated until its viscosity allows processing; it is then subjected to a shaping process and finally cooled down again. This process can be repeated multiple time
- **Cross-linked polymers as thermosets and elastomers can be shaped only once.** The cross-linking takes place during the shaping of these materials so that they are then transformed into insoluble and infusible material. No further reshaping can take place
- Some of the most important molding processes
  - **Extrusion**
  - **Injection molding**
  - **Blow molding**

Polymer processing

Extrusion

- Mixing of additives and polymers usually takes place in the melt. This cannot be done in a conventional stirred vessel because of the high viscosity of polymer melts → **extruder** is used. It is made up of a massive, cylindrical case with a screw rotating inside



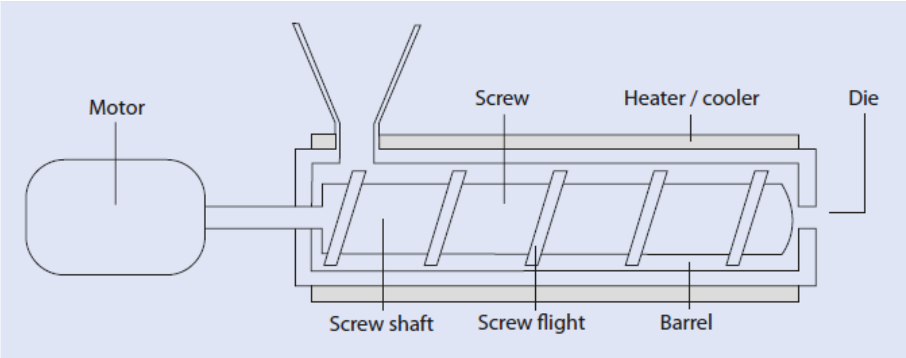


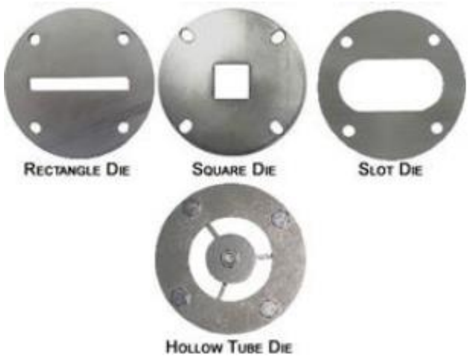
- Heating and cooling elements are integrated in the extruder housing. The **cold extruder needs to be heated to ensure that the polymer melts**. When the extruder is running the **friction between the screw and the viscous polymer** melt generates so much heat that **external heating can be reduced, or cooling** may even be necessary

Polymer processing

- **Extrusion**

- Once the polymer mass has reached the end of the extruder it **exits the system through a die (nozzle)**
- By using **different shaped dies** the cross-section of the extruded material can be varied
- If the extruder is being used to mix a compound for further processing, the polymer strand is after cooling (water or air) cut by knives to granules
- **Products made by extrusion: pipes, sheets, films, blown films**

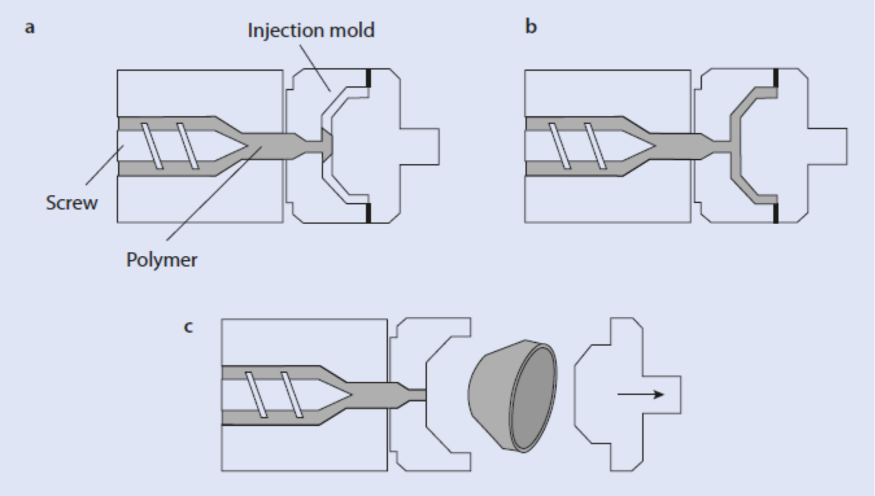




Polymer processing

Injection molding

- The most important shaping process for plastics. It can be used for thermoplastic materials and for thermosets and elastomers. In contrast to extrusion, **injection molding is a batch process**
- During this process **mold is filled with a precise amount of polymer melt** from a short extruder. The amount of material injected can weigh from a few milligrams to several kilograms. For thermoplastic polymers, the **injected form is cooled until it can no longer be plastically deformed** (**amorphous polymers** are cooled to **below T_g** and **crystalline polymers** to temperatures **below T_m**)



(a) Start of the polymer melt injection. (b) End of the injection. (c) Demolding and ejection

Polymer processing

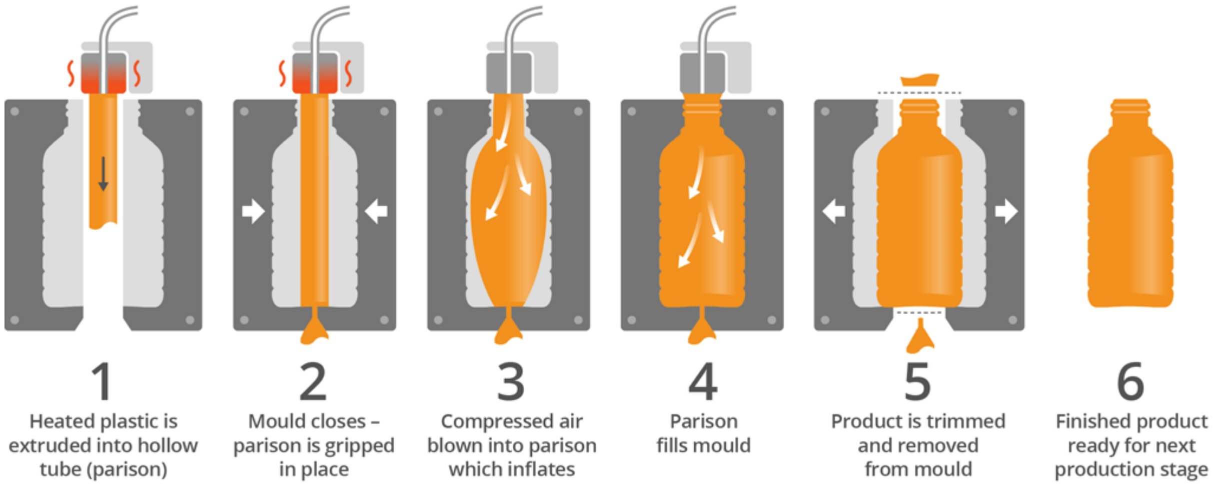
Injection molding

- **Thermoset** and **elastomer** molded parts, which at the time of injection are not cross-linked, are heated after injection and the chemical cross-linking reaction is initiated. **This process is referred to as reactive injection molding.** The molded part can then be taken out of the mold (demolded) after complete cross-linking
- The hardening process, i.e., the period between the injection of the polymer melt and the demolding of the finished part, is dependent on the form used and the geometry of the part and (for semi-crystalline thermoplastics) the rate of crystallization
- This process can take from **under 1 s to several minutes.** If high quality products are required, it is important not to demold too early
- Very fast cooling leads to the best surface appearance and can reduce cycle times and thus cost
- **Very precise geometry** (such as molded parts for precision engineering) can be produced. However, the **injection tools are very expensive**, so this technique is only economically viable for larger scale production processes
- Lately forms can be made using **3D printing techniques.** These forms are **much cheaper** and can be used for prototype production but are generally **not suitable for large series products** (longer time and lower precision)

Polymer processing

Blow molding (extrusion blowing)

- Two-step method used to produce hollow parts from thermoplastic polymers
- In the first step a **tube-like preform**, the so-called **parison**, is produced using a conventional extrusion process with a ring die (1)
- In the second step mold is closed and parison is gripped in place, end is **welded together and sealed** (2)
- Hot and malleable **parison is blown by compressed air**, inner contours of mold correspond to the outer contours of the molded part being produced (3-4)
- Mold is cooled and **product is trimmed and removed from mold** (5-6)



POLYMER MATERIALS AND ENVIRONMENT

- **Polymer Waste Management**
  - Mechanical Recycling
  - Chemical Recycling
  - Energetic Recovery

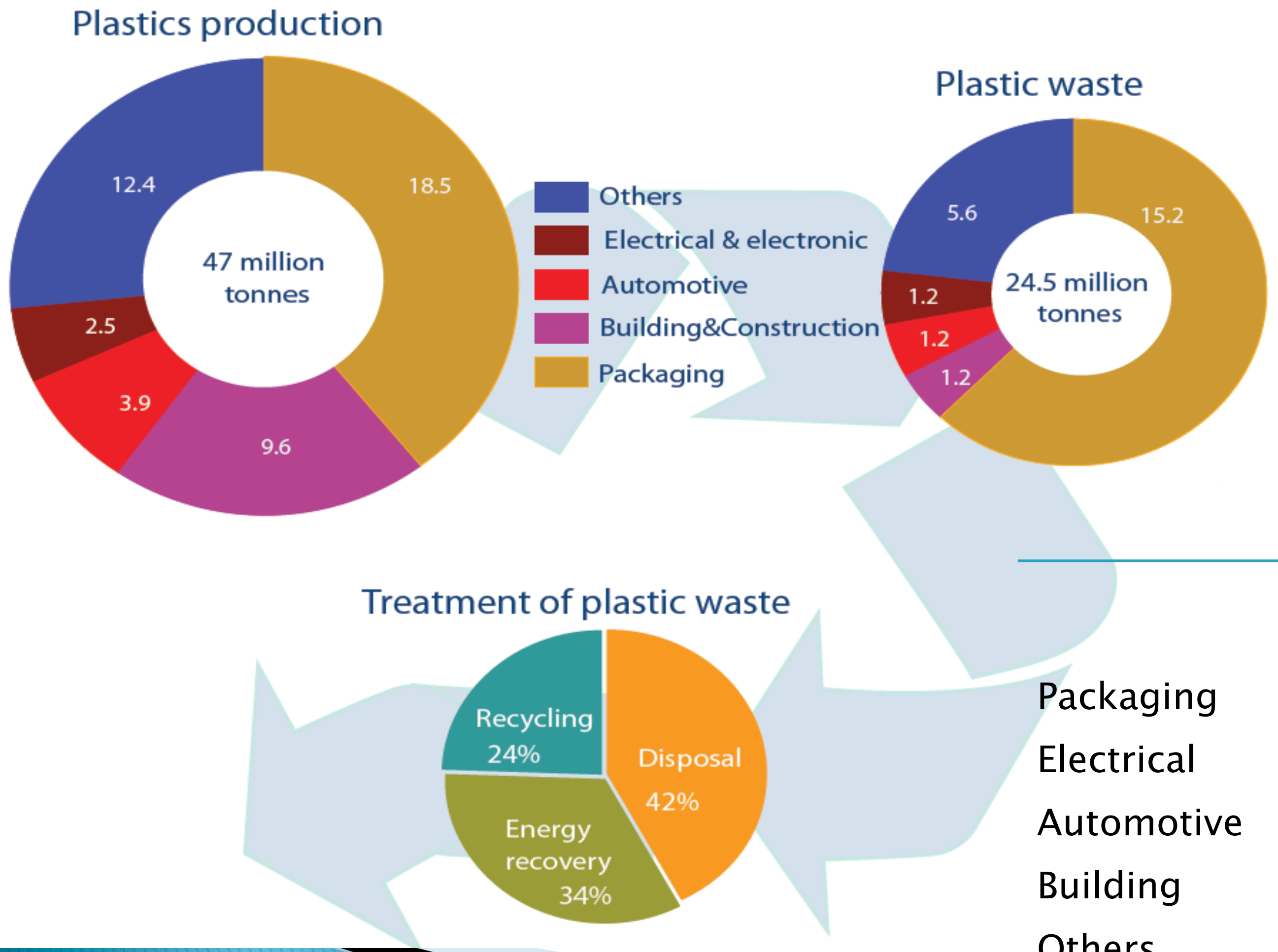
Polymer Waste Management

- There are **three main problems of the plastic waste**:
- ☐ Raw material for plastic production is crude oil (**non-renewable**)
- ☐ Most plastics **do not biodegrade** at the landfill, plastic waste will not degrade for many years, **turns to microplastics** with years
- ☐ Voluminous, takes a **huge volume & low weight** during disposal/collection

- The motivations for plastics recycling:
- ☐ Plastics **store the energy,** which may be recovered
- ☐ New products can be made from waste plastic
- ☐ Legislation and government regulations of the waste recycling policy

Polymer Waste Management

- **Production** of polymers, **generation** of polymer **waste** by **sector** in the **first year** of application and recycling of plastic waste



	% in use	% in waste in 1st year
Packaging	**40**	**82**
Electrical	5,3	48
Automotive	8,3	31
Building	20,4	12,5
Others	26,4	45,1

Microplastics

- Microplastics (MPs) are very small, solid particles made of synthetic polymers
- Generally, the term “**microplastics**” was related to **particles with less than 5 mm**, accepted due to the bordering size which can readily be ingested by organisms
- Recently that is **redefined to the items <1 mm**
  - classification recognizes mesoplastics 1-5 mm
  - microplastics 0.1-1 mm
  - nanoplastics <0.1 µm

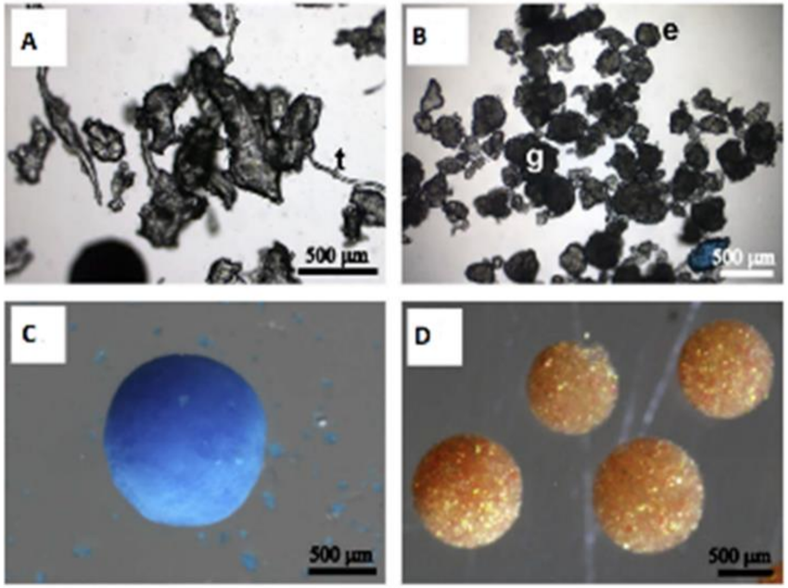
- **Primary MPs** are **manufactured as small particles** and used in products for specific purposes, “rinse-off” **cosmetic and personal care products**, as well as industrial scrubbers used in abrasive cleaning agents
- may reach the aquatic environment through the municipal wastewater treatment plants

- **Secondary MPs** are produced by the **fragmentation during the use of polymer** materials, **abrasion of tires, washing of synthetic textiles**, and **breakdown of larger plastic products** and wastes

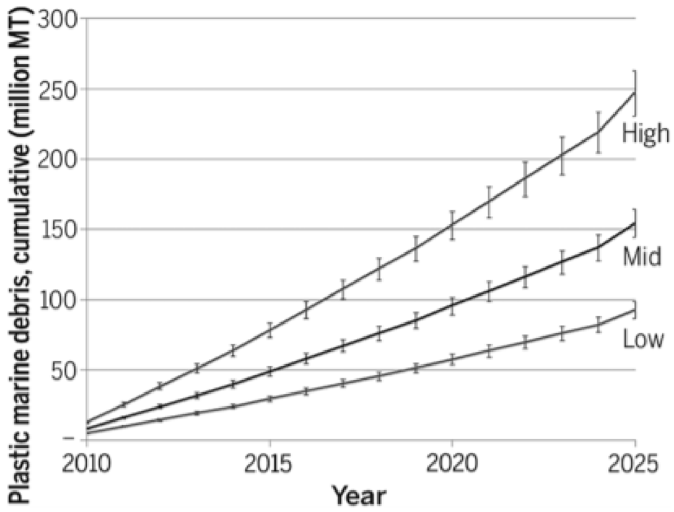
Microplastics

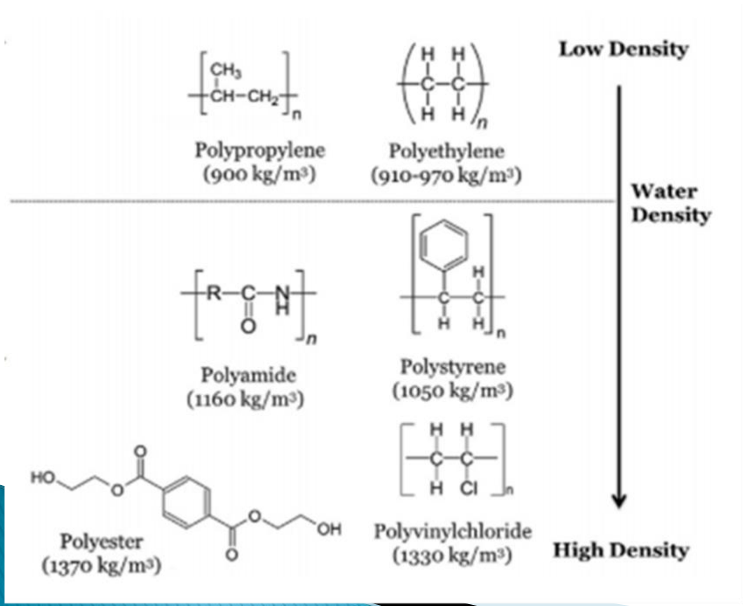
- **Causes of degradation**
  - Temperature
  - Oxygen
  - Ozone
  - Radioactive/electromagnetic radiation
  - Mechanical stress
  - Chemicals

- **Particle shapes**
  - Filament
  - Beads
  - Fragment
  - Pellet
  - Film
  - Granule
  - Foam



Microplastics





- MP particles **create biofilm** in seas and oceans – reduction of light penetration important for aquatic organisms
- MP particles contain solvents and surfactants as well as **polymer additives** (plasticizers, flame-retardants, pigments and UV-stabilizers) for properties enhancement, which are **released into environment** or in **digestive systems of living organisms**
- Different prevalence of MP at different depths

Microplastics

- Due to MPs physicochemical properties and high surface/volume ratio, **different water pollutants can be adsorbed on a MPs surface**, so they can act as **vectors transporting them over larger distances**

- Since there is a high possibility for marine and freshwater organisms to ingest MP particles, the **contaminated MPs** which act as vectors for pollutants may cause **health issues or bioaccumulation**

- MPs are marked as emerging contaminants of potential concern (CPC) and there is need for development of monitoring approaches

- European Commission proposed set of measures to reduce or alter the consumption of the most commonly used plastic items for cosmetic and medical purpose, intentionally added or generated through wear and tear of products such as tires and clothes

Recycling of polymer waste

- Mechanical Recycling → **Material recovery**
- Chemical Recycling → **Material recovery**
- Incineration → **Energy recovery**
- Composting → **Material/Energy recovery**

Types of plastic waste and technology for recycling

Thermoplastics → Mechanical recycling
Thermosets → Chemical recycling/Incineration
Elastomers → Chemical recycling/Incineration

Recycling of polymer waste

- Sources of plastic waste for recycling
- Industrial waste
- Agricultural waste (containers, pipes, sheets)
- Municipal waste collected from households, hospitals, student dormitory, hotels, restaurants, shops, streets, parks, beaches

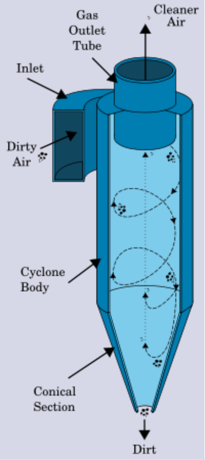
- Prior to recycling the plastic waste is sorted according to the coding system

Mechanical recycling of polymer waste

- **Mechanical recycling** of plastic waste means the **reprocessing of waste material by extrusion process** where polymers are melted at elevated temperature in order to obtain raw material or new products
- It is the simplest and relatively the cheapest recycling method

- **The steps of mechanical recycling are**

1) **Separation at source of the waste**
2) **Collecting** – It can be expensive, high volume, low mass of waste, needs to be compressed
3) **Sorting**
    - ❑ By hand
    - ○ 60-80 kg/h
    - ❑ Automated
    - ○ 4000 kg/h
    - ○ Sensors technics
    - ○ Cyclone, ….



Mechanical recycling of polymer waste

4) Cutting & shredding

- Large plastic parts are cut by saw or shears chopped into small flakes

5) Contaminants separation/Washing

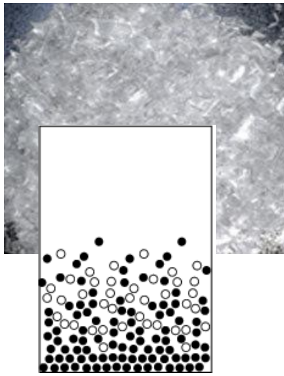
- **Contaminants** (e.g. paper, metal) **are separated** from plastic
- Cyclone separators or flotation
- Separation based on different density, flakes are **washed** and **dried**

6) Extrusion

- Flakes are fed into **extruder**, heated to melt

7) Pelletizing

- Polymer strands are cooled by water or air and cut into pellets, used for manufacturing new polymer products



Chemical recycling of polymer waste

- **Chemical recycling** of plastic waste is a catalytic process where polymer chain is **broken down into its constituents** – monomers or oligomers, by depolymerization
- The obtained monomers/oligomers are used as **raw material** for **manufacturing a new plastic products**, or some other compounds
- More expensive than mechanical recycling (catalytic process)
- Less in use
- Still researching to find the economical solution

Chemical recycling of polymer waste

1) Gasification

- Process of heating the waste plastic **with steam in presence of air** (500–1300 °C), to produce a valuable industrial gas mixtures called "**synthesis gas**", or **syngas**
- Syngas can be further **used as fuel** or **intermediate for production of hydrogen, ammonia, methanol,** and synthetic hydrocarbon fuels

Partial oxidation during incomplete combustion:

$$\text{Polymer} + H_2O \rightarrow CO + H_2$$

Syngas

Hydrocondensation of carbon monoxide – Fischer-Tropsch process

$$n\,CO + (2n + 1)\,H_2 \rightarrow C_nH_{2n+2} + n\,H_2O$$

Gas alkanes (propane, butane,...)
Complex hydrocarbons,
n can be from 1 to 40

- Hydrocarbons fractions contain various number of C-atom in molecules, classified as:
  - C_5–C_{12} for various type of **gasolines**
  - C_{12}–C_{22} for **diesel fuel**
  - Hydrocarbons with **C_{22} and higher** for **lubricants and paraffins**

Chemical recycling of polymer waste

2) Pyrolysis

- Chemical decomposition of polymers induced by heat **in the absence of oxygen**
- Main phases of the pyrolysis process:
  - 100 to 150 °C – drying
  - 200 to 550 °C – distillation and cracking
  - 600 to 700 °C – gasification

- The main product is **mixture of oil similar to crude oil.** This can be further refined into transportation fuels

- **Gas** from the pyrolysis process comprises:
- hydrogen (**H_2**), methane (**CH_4**)
- carbon monoxide (**CO**)
- carbon dioxide (**CO_2**)

Energetic Recovery of polymer waste

- Energetic recovery of plastic waste is a process during which incinerated plastic waste releases the heat
- **Incineration** take place at very high temperature (>**850 °C**), the obtained **steam** is **used** as a hot **steam** for heating or for **electricity** production
- **Controlled combustion decreases the amount of toxic** side products, like toxic gases (Cl_2, H_2S, NO, NO_2, …), lower temperatures produce additional toxic gases like **furans and dioxins**
- **The control of process & products**:
  - ☐ **temperature** (must be higher than 850 °C)
  - ☐ sufficient **oxygen**
  - ☐ **toxic gases** must be collected
  - ☐ **release** of the gases in environment **(HCl, NOx…)** monitored
  - ☐ **char residue** (heavy metals and other hazard compound) monitored

Energetic Recovery of polymer waste

- Incineration is good technology to recycle plastic waste:
- Decrease in the formation of greenhouse gases

Recycling of PET-a	decrease the emission
Mechanical	1000 -1700 eCO_2
Incineration	600 – 800 eCO_2

- Plastic waste has high caloric value – average is estimated at 35 MJ/kg

Caloric Value of Polymers

Polymer	ΔH (MJ/kg)	Polymer	ΔH (MJ/kg)
Polyethylene	46.5	Poly(vinyl chloride)	20.0
Polypropylene	46.0	Natural rubber	45.0
Polystyrene	42.0	Polyisobutylene	47.0
ABS	36.0	Polyester resins	18.0
Polyamide (6/66)	32.0	Cotton	17.0
Poly(methyl methacrylate)	26.0	Cellulose	17.5

Energetic Recovery of polymer waste

- Caloric Value of Polymeric Materials Compared to conventional fuels

Fuel	**ΔH (MJ/kg)**
Methane	53
Petrol	46
Oil	43
Coal	30
PE	46
Mixed plastic	30–40
Mixed municipal waste	10