Department of Water and Sewage Management and Waste Technology

**Recycling**

# LABORATORY 1

## Topic: IDENTIFICATION OF POLYMERS

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### 1. Structure of Polymers

The essential characteristics that differentiate a polymer from other compounds stem from its structure. It is composed of distinguishable and repeating units – mers (Figure 1). Furthermore, polymers possess different properties compared to monomers. A monomer is any chemical compound capable of undergoing polymerization. The term "polymer" translates to a compound consisting of "many mers." This definition suggests a way to describe this compound: it is a chain-like structure similar to a string of pearls. By analogy, one could say that the properties of the polymer chain should be derived from the characteristics of the individual pearls (monomers), their arrangement in the chain, and its total length. It is also evident that "tangling" can occur in such a string, along with the presence of multiple strings, which affects the material's properties. Therefore, understanding the elements of the chain structure is crucial for assessing the polymer's characteristics more accurately [1]. Polymers are large organic molecules (macromolecules) with a high molecular mass ($10^4$ – $10^7$ atomic mass units) made up of many repeating structural units called mers. A polymer can be schematically represented as a chain of repeating constitutive units (mers).

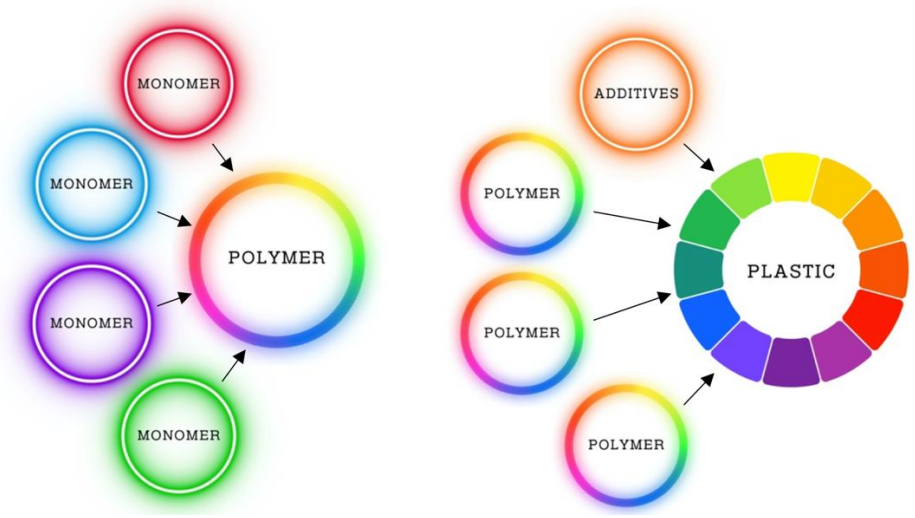


Figure 1. Schematic of polymer and plastic structure.

Plastics are utility materials derived from polymers combined with various additives. The purpose of these additives is to modify the polymer's properties to create new utility materials. Common polymer additives include:

- **Fillers –** improve mechanical properties, stiffness, thermal resistance, electroinsulating or conductive properties, and reduce the cost of the final product.

- **Stabilizers** – enhance thermal stability and prevent polymer degradation due to oxygen and ultraviolet radiation.
- **Plasticizers** – facilitate processing and modify mechanical and thermal properties.
- **Dyes and pigments** – impart color to the product.
- **Antistatic agents** – eliminate static electricity by modifying the surface properties (increase surface or bulk conductivity of the polymer).
- **Flame retardants** – delay combustion and reduce flammability and smoke formation.

Polymer identification is an important aspect of recycling plastics. Most polymer-based materials are labeled with symbols for easy identification, but many plastic items do not have such labels. The goal of polymer identification is to determine the polymer, which is typically the main component of the analyzed material.

**Procedure for Plastic Identification:**

**A. Visual appearance assessment:**
- color,
- transparency,
- surface type (smooth/rough).

**B. Evaluation of basic mechanical properties:**
- deformability,
- scratch resistance.

**C. Density measurement**

**D. Chemical resistance assessment**

**E. Flammability test / flame test:**

**Flammability** refers to the ability of a material to burn under specific conditions, according to PN-EN ISO 9773:2003 (Flammability – UL94) [2].

## 2. Flame Test Procedure:

The sample should be placed on a spatula and introduced to the non-luminous part of the gas burner flame. Observations should be made during direct contact with the flame and after removing the sample. If the sample burns, the flame should be blown out. During the analysis, record the following:

- flammability degree,
- whether the sample self-extinguishes after removal from the flame,
- flame type (luminous or sooty),
- flame color and any color borders (e.g., colored edge),
- changes in the appearance of the material when exposed to the flame (melting, charring, blistering, etc.),
- odor of the gases released during combustion.

**Note:**

Heat the sample slowly. If the flame is too large, decomposition will occur too quickly to observe the phenomena.

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**Observations:**

**Non-burning polymers:**

a) glowing in the flame – silicone rubber or polyamides,
b) glowing with residue from filler (e.g., fibers) – asbestos-filled laminates or other inorganic-filled polymers,
c) glowing with a blue-green flame tip, no charring – polytetrafluoroethylene or chlorine-containing polymers,
d) the sample retains its shape, in all cases the smell of formaldehyde is felt:
    - no other smell – urea-formaldehyde resin,
    - strong fishy smell – melamine-formaldehyde resin,
    - smell of formaldehyde and phenol – phenol-formaldehyde resin.

**Burns in flame but self-extinguishes after removal:**

a) Bright yellowish or smokeless flame, forms bubbles – polycarbonate or uncured phenolic or formaldehyde resins
b) The flame has a yellow-green color:
    - smell of burning rubber,
        - green border – chlorinated rubber,
        - green border surrounded by yellow – neoprene,
    - does not ignite, the polymer changes color to yellow, then to brownish red and finally black, sharp smell (HCl) – polyvinyl chloride and its derivatives,
    - sweet smell, black ash – polyvinylidene chloride,
    - smell of burnt milk – casein.

**The polymer burns when removed from the flame. The flame is observed during the first seconds of burning.**

a) Very violent burning with an intense flame:
    - camphor smell – plasticized (softened) cellulose nitrate,
    - no camphor smell – cellulose nitrate,
    - vinegar and burnt paper smell, yellowish, dripping – cellulose acetate.
b) Bright flame, mainly blue with a small white tip:
    - very sweet fruity smell, crackling, dripping drops – methacrylates,
    - difficult to light, smell reminiscent of burning hair or horn, white flame, later bluish-yellow, crackling, trailing (sometimes foaming) drops – polyamide,
    - weak, sweet smell – polyvinyl formal,
    - smell of rancid butter
        - sparkling flame – cellulose acetate butyrate,
        - no sparks – polyvinyl butyral,
c) Flame surrounded by a red border, sparks, smell of acetic acid – polyvinyl acetal
d) Yellow flame:
    - butyric acid odor – cellulose acetate butyrate,
    - sweet, floral odor (hyacinths), flame, sometimes yellow-orange, strongly smoky, flashing – polystyrene,
    - weak, sweet odor – polyvinyl formal,
    - burning paper odor – cellulose,
    - bright flame, difficult to ignite, unpleasant odor (isocyanates), foams, drops – polyurethanes,
    - blue flame center, paraffin odor – polyethylene, polypropylene.

e) Flame with yellow-green border:
- burns very hard and sparkles, smell of acetic acid. Molten burning material dropped into water forms heavy brown-black foaming granules or flakes – cellulose acetate,
- starts burning immediately, faint sweet smell, melted polymer dropped into water forms flat disks that are light nutty when the polymer is uncoloured – ethyl cellulose [3].

Table 1. Behavior of materials in the burner flame [7,8]

| **Behavior in flame** (type of flame) | **Behavior in a flame before combustion** | **Additional characteristic features** | **Type of material** |
|---|---|---|---|
| the sample burns with a non-smoky flame | darkens and drips | noticeable smell of burning protein (hair), threads can be pulled out of the alloy | PA |
| | dripping | after extinguishing the flame, the smell of paraffin is clearly noticeable | PE |
| | | a sharp smell reminiscent of burning candles, threads can be pulled out of the alloy | PP |
| | does not drip, burns with a crackling flame | the sample bubbles on the surface, there is a noticeable smell reminiscent of nail polish remover | PMMA |
| | it ignites with difficulty and goes out when removed from the flame | noticeable smell of formalin | PF |
| | | noticeable smell of burnt fish | MF |
| the sample burns with a smoky flame | dripping | a sharp scent, reminiscent of hyacinths in large dilutions | PS |
| | no dripping | aromatic scent | PET |
| | | goes out when removed from the flame, darkens where burned | PC |
| | | characteristic suffocating smell, insoluble | PUR |
| | | very pungent odor, sample burns or goes out after removal from flame, darkens, gives green flame in presence of copper wire, moistened indicator paper exposed to vapors becomes colored from released HCl | PVC |

## 3. Classification of polymers based on density

Table 2. List of polymers and their densities [4].

| **Density [g/cm$^3$]** | **Polymer name** | **Density [g/cm$^3$]** | **Polymer name** |
|---|---|---|---|
| <1 | Expanded polystyrene | 1.17 – 1.20 | Polyvinyl acetate |
| 0.80 | Silicone rubber (depending on filling, e.g. silica up to 1.25) | 1.18 – 1.24 | Cellulose propionate |
| 0.83 | Polymethylpentene | 1.19 – 1.35 | Plasticized PVC (approx. 40% plasticizer) |
| 0.85 – 0.92 | Polypropylene | 1.20 – 1.22 | Polycarbonate (from bisphenol A) |
| 0.89 – 0.93 | High-pressure polyethylene (LD) | 1.20 – 1.26 | Cross-linked polyurethanes |
| 0.91 – 0.92 | Polybutene-1 | 1.26 – 1.28 | Phenol-formaldehyde resins (unfilled) |
| 0.91 – 0.93 | Polyisobutylene | 1.21 – 1.31 | Polyvinyl alcohol |
| 0.92 – 1.0 | Natural rubber | 1.25 – 1.35 | Cellulose acetate |
| 0.94 – 0.98 | Low pressure polyethylene (HD) | 1.30 – 1.41 | Phenol-formaldehyde resins (filled with organic fillers) |
| 1.01 – 1.04 | Nylon 12 (polyamide 12) | 1.3 – 1.4 | Polyvinyl fluoride |
| 1.03 – 1.05 | Nylon 11 (polyamide 11) | 1.34 – 1.40 | Celluloid |

| | | | |
|---|---|---|---|
| 1.04 – 1.06 | Acrylonitrile-butadiene-styrene copolymer (ABS) | 1.38 – 1.41 | Polyethylene terephthalate |
| 1.04 – 1.08 | Polystyrene | 1.38 – 1.41 | Hard PVC |
| 1.05 – 1.07 | Polyphenylene oxide | 1.41 – 1.43 | Polyoxymethylene (polyformaldehyde) |
| 1.06 – 1.10 | Styrene-acrylonitrile copolymer | 1.47 – 1.52 | Urea resins with melamine-formaldehyde fillers (filled with organic fillers) |
| 1.07 – 1.09 | Nylon 6,10 (polyamide 6,10) | 1.47 – 1.55 | Chlorinated PVC |
| 1.12 – 1.15 | Nylon 6 (polycaprolactam) | 1.5 – 2.0 | Phenoplasts and aminoplasts filled with organic fillers |
| 1.13 – 1.16 | Nylon 6,6 (polyamide 6,6) | 1.7 – 1.8 | Polyvinyl fluoride |
| 1.1 – 1.4 | Epoxy resins, unsaturated polyester resins | 1.5 – 2.9 | Glass fiber filled polyester and epoxy resins |
| 1.14 – 1.17 | Polyacrylonitrile | 1.86 – 1.88 | Polyvinylidene chloride |
| 1.15 – 1.25 | Cellulose acetobutyrate | 2.1 – 2.2 | Polytrifluoromonochloroethylene |
| 1.16 – 1.20 | Polymethyl methacrylate | 2.1 – 2.3 | Polytetrafluoroethylene |

## 4. Classification of polymers based on their appearance

Table 3. Summary of classification based on appearance and flexibility [4].

| **Polymer** | **Most common appearance** | | | | **Polymer flexibility** | | |
|---|---|---|---|---|---|---|---|
| | Transparent thin foil | Transparent, bright | Opaque | It usually contains fillers | Soft, rubbery, leather-like | Flexible, springy | Rigid |
| Cellulose nitrate | + | + | | | | + | + |
| Cellophane (regenerated cellulose) | + | | | | | + | |
| Methylcellulose | | | | | | | |
| Cellulose acetate | + | + | | | | + | + |
| Polyvinyl alcohol | + | | | | + | + | |
| Crystalline polyamide | + | | + | | | + | + |
| Amorphous polyamide | | + | | | | | + |
| Polyvinylidene chloride | | | + | | | | + |
| Polyvinyl chloride (plasticized) | + | + | + | | + | | |
| Polyvinyl chloride (pure) | | + | | | + | + | |
| Polyethylene | + | | + | | | + | + |
| Polyisobutylene | | | | + | + | | |
| Polymethyl methacrylate | | + | | | | | + |
| Polyacrylates in copolymer | suspensions | | | | + | + | |
| Polyvinyl acetate | suspensions | | | | + | + | |
| Polypropylene | + | | + | | | | + |
| Polystyrene (pure) | + | + | | | | | + |
| High impact polystyrene (with butadiene) | + | + | | | | | + |
| Polytetrafluoroethylene | | | + | | | + | |
| Polyethylene terephthalate (PET) | | + | | | | | + |
| Cross-linked polyurethanes | | | + | | + | + | + |
| Rope polyurethanes, rubber-like | + | | + | | + | | |
| Polycarbonate | + | + | | | | | + |
| Polyvinyl butyral | safety glass | | | | + | | |
| Polyvinyl formal | | | + | | | | + |
| Epoxy resins | | + | | | | | + |
| Unsaturated polyester resins (unfilled) | | + | | | | | + |
| Unsaturated polyester resins (filled) | | | + | + | | | + |

Table 4. Characteristics of typical plastics [5,6]

| Marking | Name of the material | Appearance and characteristics | Application |
|---|---|---|---|
| PE | polyethylene | soft shapes or foil with a touch of hard paraffin | packaging bags, medicine and cosmetic bottles, coasters, food containers, electrical insulation |
| PE-LD | low density polyethylene | | |
| PE-HD | high density polyethylene | | |
| PP | polypropylene | harder than polyethylene | rigid foils, candy, wafer and pasta packaging, caps, rigid bottles, containers for various purposes, disposable plates, yoghurt packaging, syringes |
| PS | polystyrene | rigid, transparent or pigmented plastic with a metallic sound or rigid foam | cutlery, cups for drinks, various packaging, foil for lining chocolate boxes, toys, packaging and polystyrene insulation |
| PVC | polyvinylchloride | in the hard variety - winidur - similar in appearance to PP, in the soft variety - winiplast - softer than PE | pipes, plates, tablet and dragee packaging, toys, fuel hoses, foils, notebook and document covers |
| PMMA | poly(methyl methacrylate) | colorless and colored organic glass | reflective signs, car signal lamp covers, windows |
| PC | polycarbonate | organic glass similar to PS and PMMA but more mechanically durable | baby bottles, windows, car signal light covers |
| PA | polyamide | material resembling a horn | fibres or strands, electrical insulation, utility shapes, combs |
| PET | poly(ethylene terephthalate) | transparent material | beverage packaging |
| PBT | poly(butylene terephthalate) | more flexible material than PET | insulation, foils |
| PF | phenol-formaldehyde plastic (bakelite) | infusible, opaque material | caps, electrical insulators, everyday items, housings |
| MF | melamine-formaldehyde plastic | hard, opaque, white or colored, infusible material | plates, rigid packaging, insulators |
| PUR | polyurethane | flexible and rigid foams, flexible materials | sponges, seat fillings, shoe soles |

## 5. References:

[1] Kozłowski M., et al.: Basics of plastics recycling, OWPWr, Wrocław, 1998
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