Technical Sciences, 2026, 29, 203–253

UNIWERSYTET WARMIŃSKO-MAZURSKI W OLSZTYNIE

Yearbook peer-reviewed scientific journal
ISSN 1505-4675
e-ISSN 2083-4527
TECHNICAL SCIENCES
Homepage: https://czasopisma.uwm.edu.pl/index.php/ts/




DOI: https://doi.org/10.31648/ts.13177

# POLYMER MATERIALS TECHNOLOGY

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Received 22 September 2026, accepted 7 October 2026, available online 27 October 2026.

K e y w o r d s: polymers, plastics, polymerization, processing, recycling, circular economy.

A b s t r a c t

Polymer materials are among the most widely used engineering materials, but their mass production generates growing volumes of waste that hinder the transition to a circular economy. The aim of this narrative review is to provide an integrated overview of polymer materials technology that links the structure of polymers with their synthesis, processing, applications and end-of-life management. The review is based on peer-reviewed literature indexed mainly in the Scopus, Web of Science and ScienceDirect databases, supplemented by IUPAC recommendations, monographs, standards and EU legal acts; of the 136 sources cited, 82% were published in 2022–2026. The covered areas include: polymer structure, morphology and thermomechanical properties; chain-growth and step-growth polymerization, their kinetics, catalysts and industrial polymerization techniques; methods of polymer characterization; cross-linking and vulcanization; the classification of plastics and antimicrobial additives; processing methods; the main groups of polymers and their applications; and mechanical recycling, feedstock (chemical) recycling and energy recovery. Comparative tables summarize the main technological options together with their advantages and limitations. The review shows that the properties and recyclability of plastic products are largely predetermined at the stages of molecular design, formulation and processing. Mechanical recycling remains the preferred route for clean, homogeneous thermoplastic streams, depolymerization is most effective for polymers with cleavable main chains (e.g., PET, polyamides), thermochemical processes are suited to mixed

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polyolefin waste, and energy recovery should be limited to residual fractions. The main research gaps concern the quality of recyclates, the recycling of thermosets and multilayer materials, the influence of additives on recyclability and safety, and the lack of comparable life cycle and techno-economic data.

## Introduction

Polymers are macromolecular compounds composed of repeating structural units whose properties depend on their chemical structure, chain length and architecture, degree of order, and interchain interactions. Due to their varying chain lengths, polymeric materials generally do not have a single, defined molar mass. Therefore, average molar masses and molar mass distributions are used to characterize them. Branching, cross-linking, tacticity, and degree of crystallinity are also important structural parameters (SCHMID 2023). Monomers, on the other hand, are compounds capable of polymerization and incorporation into a nascent macromolecule. The constitutional unit derived from a monomer and present in a polymer chain is the mer, and the degree of polymerization determines the number of monomeric units constituting a given macromolecule. The number of covalent bonds that a monomer can form during macromolecule formation describes the monomer's functionality (HODGE et al. 2025). Difunctional monomers, such as ethylene glycol, can lead to the formation of linear structures, while multifunctional monomers, such as glycerol, promote the formation of branching and spatial networks, influencing, among other things, stiffness, solubility, swelling, and thermal behavior of the material. Synthetic polymers are particularly important, forming the basis for the production of plastics - materials that, in addition to the polymer, may also contain plasticizers, stabilizers, dyes, fillers, and reinforcing agents. The most commonly used plastics include polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC), polystyrene (PS), and polyethylene terephthalate (PET), used in applications such as packaging, construction, automotive, medicine, and electronics. Their widespread use stems from their advantageous combination of low density, durability, chemical resistance, and the ability to shape their properties and process them. However, increasing production and consumption lead to an increase in the amount of polymer waste, the management of which poses a significant environmental and technological challenge. One of the primary ways to mitigate this problem is recycling, which aims to reuse waste materials or recover the raw materials contained within them. Mechanical and chemical recycling, including depolymerization and pyrolysis, are particularly prominent, as their development is crucial for reducing the consumption of primary raw materials and fostering a circular economy.

Although numerous reviews address individual aspects of polymer science – e.g., the terminology of polymerization mechanisms (EPPS et al. 2022), polymer processing (CUNHA et al. 2022), cross-linked networks (RAJAWASAM et al. 2024) or chemical recycling (LUO et al. 2024, SCHADE et al. 2024) – these topics are usually discussed separately. This makes it difficult to trace how decisions taken at the stage of molecular design, synthesis and processing determine the performance of a product and the options available for its end-of-life management. The principal objective of this paper is therefore to provide a concise, integrated review of polymer materials technology that follows the life cycle of polymer materials from macromolecular structure to waste management. The scope of the review covers: (i) the structure, morphology and mechanical and thermal properties of polymers; (ii) polymerization mechanisms, catalysts, and

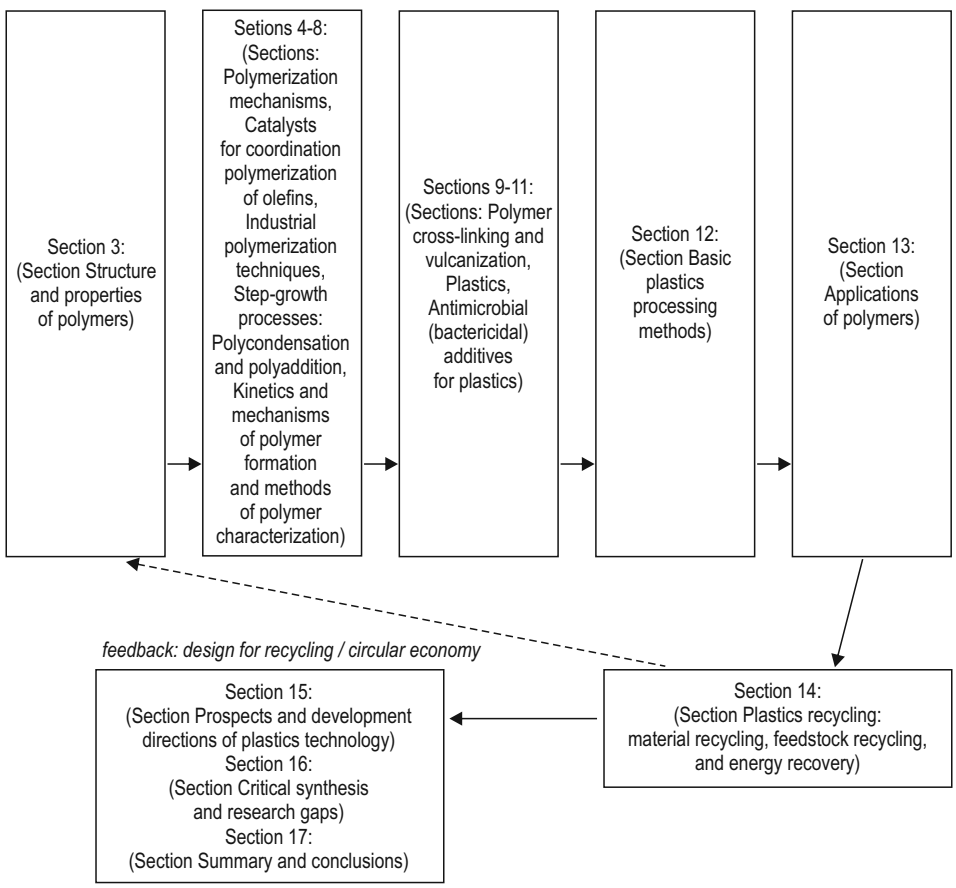



Fig. 1. Conceptual framework and structure of the review: relationships between polymer structure, synthesis, processing, applications and end-of-life management.
Source: own elaboration

industrial polymerization and polycondensation techniques; (iii) the kinetics of polymer formation and the methods of polymer identification and characterization; (iv) cross-linking and vulcanization; (v) the classification of plastics and functional (antimicrobial) additives; (vi) the main processing methods; (vii) the principal groups of polymers and their applications; (viii) mechanical recycling, feedstock (chemical) recycling and energy recovery; and (ix) prospective development directions. Compared with existing, more specialized reviews, the intended contribution of this paper consists in linking these areas within a single structure–synthesis–processing–application–end-of-life framework (Fig. 1), in a critical comparison of alternative technological routes presented in comparative tables (Tables 1–6), and in the identification of the main technological limitations, unresolved problems and research gaps (Section Critical synthesis and research gaps).

## Review methodology

This paper was prepared as a narrative (state-of-the-art) review. The literature search was carried out mainly in the Scopus, Web of Science Core Collection and ScienceDirect databases, supplemented by Google Scholar. Combinations of the following keywords were used: "polymer structure", "crystallinity", "molar mass distribution", "chain-growth polymerization", "step-growth polymerization", "Ziegler–Natta catalysts", "suspension polymerization", "emulsion polymerization", "polycondensation", "cross-linking", "vulcanization", "thermoplastics", "thermosets", "extrusion", "injection molding", "antimicrobial additives", "mechanical recycling", "chemical recycling", "depolymerization", "pyrolysis" and "energy recovery".

Peer-reviewed review papers and original research articles published in English were included if they (i) concerned synthetic or bio-based polymers and plastics, (ii) addressed at least one of the thematic areas defined in the Introduction, and (iii) provided technological, mechanistic or comparative information. Priority was given to publications from 2022–2026 in order to reflect the current state of knowledge. Older sources were included only when they constitute basic references for terminology and fundamentals, i.e., IUPAC recommendations (Jones et al. 2009, Hess et al. 2013), classic papers that introduced fundamental concepts of polymerization kinetics and mechanisms (Carothers 1936, Mayo, Lewis 1944, Szwarc 1956, Cossee 1964) and monographs (Flory 1953, Koenig 1999, Ehrenstein et al. 2004, Odian 2004, Osswald, Hernández-Ortiz 2006, Tadmor, Gogos 2006, Menczel, Prime 2009), or when they report results directly relevant to the discussed topics. The terminology of waste management and the regulatory context were based

on the relevant ISO standard and European Union legal acts. After screening of titles, abstracts and full texts, 136 sources were cited, of which 112 (82%) were published in 2022–2026.

The selected literature was analysed qualitatively and grouped according to the thematic areas listed above. For each area, the information was synthesized with respect to the governing structure – property relationships, the available technological options, their advantages and limitations, and the related research needs. The results of this synthesis are summarized in comparative tables (Tables 1–6) and figures, and the cross-cutting conclusions are discussed in Section Critical synthesis and research gaps. Since the review is narrative rather than systematic, no quantitative meta-analysis was performed, and the conclusions should be interpreted with this limitation in mind.

## Structure and properties of polymers

a) *polymer nomenclature*

Polymer nomenclature is more complex than that of small molecules. This is due to the heterogeneity of macromolecules in terms of chain length, architecture, and composition (MATSON et al. 2024). A distinction is made between nomenclature based on the source compound and structural nomenclature. In source nomenclature, the polymer name refers to the monomer or starting compound, e.g., polyethene, polypropene and polystyrene. In practice, traditional names such as polyethylene (PE), polypropylene (PP), or polystyrene (PS) are also often used (WEERASINGHE et al. 2023). Structural nomenclature, on the other hand, is based on the actual chemical structure of the chain and the constitutional repeating unit (e.g., poly(methylene) for polyethylene), thus enabling a more precise description of polymers with complex structures. In the case of copolymers, the arrangement of individual units must also be taken into account, distinguishing, among others, statistical, alternating, block, and graft copolymers (RAJAWASAM et al. 2024). Historically, according to Carothers' concept, polymers were classified as addition and condensation polymers, based on the change in chemical composition between the monomer and the repeating unit and the possible release of a small-molecule by-product. Modern classification focuses primarily on the mechanism of macromolecule growth and distinguishes chain-growth and step-growth polymerization. In chain polymerization, chain growth occurs through an active center, to which monomer molecules are successively attached. In step-growth polymerization, reactions occur between monomers, oligomers, and the resulting macromolecules containing appropriate functional groups (WEERASINGHE et al. 2023).

b) *structure of polymers*

Polymer structure encompasses both the chemical structure of repeating units and the architecture of entire macromolecules. Topology includes:

• linear polymers – the chains are not connected by chemical cross-links, but they can create mutual physical entanglements, significantly affecting the mechanical and rheological properties;

• branched polymers – branching modifies the way macromolecules are packed, their hydrodynamic volume, viscosity, density, and ability to crystallize. Special architectures include star, graft, and hyperbranched polymers;

• cross-linked polymers – contain cross-links between chains, leading to the formation of a three-dimensional network. An increase in the degree of cross-linking limits the mobility of macromolecules, increases resistance to deformation, and may lead to the formation of insoluble materials that swell in appropriate solvents (RAJAWASAM et al. 2024).

c) *tacticity and stereoregularity*

Tacticity, which determines the spatial arrangement of substituents along the chain, is an important structural parameter for polymers containing stereogenic repeating units. Polymers are classified as isotactic, syndiotactic, and atactic. High stereoregularity can promote orderly chain packing and crystallization, while stereochemical irregularity typically hinders the formation of crystalline structures. Tacticity therefore influences the degree of crystallinity and thermomechanical properties, such as glass transition temperature, melting point, stiffness, and strength (TU et al. 2023).

d) *morphology and degree of crystallinity*

Polymer morphology is related to the degree of macromolecular ordering. Amorphous materials do not exhibit long-range crystalline order and exhibit only a glass transition, whereas semi-crystalline polymers contain both crystalline and amorphous phases and therefore exhibit both a glass transition (of the amorphous phase) and melting (of the crystalline phase). Typical amorphous polymers include polystyrene and poly(methyl methacrylate) (PMMA). In contrast, polyethylene, polypropylene, polyethylene terephthalate (PET), and polyamides can form semi-crystalline structures. The degree of crystallinity depends not only on chemical structure but also on molar mass, tacticity, processing conditions, cooling rate, and chain mobility (SAALWÄCHTER et al. 2023). Furthermore, the quantity of the crystalline phase must be distinguished from the quality and perfection of the resulting crystalline structures (VENKATRAM et al. 2023).

e) *molar mass and molar mass distribution*

Molar mass is one of the fundamental parameters characterizing polymers. Unlike low-molecular-weight chemical compounds, a polymer sample contains macromolecules of varying lengths; consequently, average molar masses are used, and their distribution is described. An increase in molar mass typically leads to a greater number of chain entanglements, which can result in higher viscosity and improved mechanical properties but simultaneously makes processing more difficult. Methods used to determine average molar masses include light scattering, osmometry, and size-exclusion chromatography (SEC/GPC); the latter yields absolute molar masses only when coupled with a molar-mass-sensitive detector, such as multi-angle light scattering (SEC-MALS). Another important parameter is dispersity (Đ), defined as the ratio of the weight-average molar mass to the number-average molar mass. While this parameter characterizes the breadth of the molar mass distribution, it does not describe the distribution's full shape (MATSON et al. 2024).

f) *correlation between structure and performance properties*

The performance properties of polymers result from the interplay of their chemical structure, macromolecular architecture, molar mass and its distribution, tacticity, degree of crystallinity, intermolecular interactions, and degree of cross-linking. Longer chains and a higher number of entanglements can increase strength and viscosity; branching affects packing and crystallinity; while cross-linking restricts chain mobility, thereby increasing stiffness and resistance to permanent deformation. Increasing the crystalline phase content generally improves stiffness, strength, chemical resistance, and barrier properties, though it may reduce ductility. Consequently, the final properties depend not only on the amount of the crystalline phase but also on its morphology (RAJAWASAM et al. 2024, SAALWÄCHTER et al. 2023, VENKATRAM et al. 2023).

g) *degradation, depolymerization, and waste management*

Polymer structures can undergo changes during processing, use, and storage as a result of degradation processes. These processes can be triggered by factors such as temperature, oxygen, UV radiation, moisture, and mechanical or chemical agents (DINTCHEVA 2024, LIU et al. 2024). Degradation can lead to chain scission and a reduction in molar mass - for instance, through thermal degradation, oxidation, hydrolysis, or photodegradation. In some cases, however, the formation of additional inter-chain linkages and an increase in the degree of cross-linking may also occur (OH, STACHE 2024). Depolymerization is a specific type of polymer breakdown involving chain scission that yields monomers, oligomers, or other low-molar-mass products. It plays a crucial role in the chemical recycling of polymers, particularly for materials such as PET, polyamides, polycarbonates, and certain

polyesters (CLARK, SHAVER 2024, LOHMANN et al. 2024). Polymer destruction, on the other hand, is a broader term referring to the extensive breakdown of the material – resulting in the loss of its original structure and properties – without necessarily leading to monomer recovery (DINTCHEVA 2024). The relationship between chemical structure, macromolecular architecture, morphology, and properties forms the basis for the design and selection of polymer materials. These factors determine not only performance properties but also the behavior of polymers during processing, aging, and end-of-life management, including their recyclability and the potential for raw material recovery (AARSEN et al. 2024).

h) *influence of structure and thermal history on material properties*

Mechanical and thermal properties are among the most important characteristics determining the application of polymeric materials. They are determined by the chemical structure of the macromolecules, their molar mass and molar mass distribution, chain architecture, degree of branching and cross-linking, tacticity, degree of crystallinity, and the strength of intermolecular interactions. Polymer behavior is also influenced by temperature, the rate and duration of loading, and the material's thermal history. Consequently, the properties of the same polymer can vary significantly depending on usage conditions (DE BEUKELAER et al. 2022).

i) *characterization of basic mechanical properties*

Key mechanical properties include stiffness, tensile strength, yield strength, elongation at break, hardness, impact strength, fracture toughness, creep, and fatigue. Material stiffness is characterized by, among other factors, Young's modulus; a higher value indicates lower susceptibility to deformation under stress. Rigid and highly cross-linked polymers typically exhibit a higher modulus than elastomers. Tensile strength depends on factors such as molar mass, the number of chain entanglements, the degree of cross-linking, macromolecular orientation, crystallinity, temperature, and the rate of deformation. Elongation at break describes a material's capacity to deform prior to failure and is particularly high for elastomers and certain thermoplastics. Excessive cross-linking can increase stiffness and strength but simultaneously limit deformability and promote brittle fracture (PENG et al. 2023). Impact strength defines the ability to absorb energy during rapid loading, whereas fracture toughness refers to a material's resistance to crack initiation and propagation.

j) *phenomenon of viscoelasticity, creep, and stress relaxation*

A characteristic feature of polymers is viscoelasticity, the simultaneous exhibition of elastic and viscous properties. Consequently, a material's response

depends on the duration of the applied load, temperature, deformation rate, and macromolecular structure. One manifestation of viscoelasticity is creep, which involves an increase in deformation over time under a constant load. A related phenomenon is stress relaxation, the reduction of stress while maintaining constant deformation. Viscoelasticity is of particular importance during the long-term service and processing of polymers, and in the molten state, it is a subject of rheological study (BANERJEE 2023).

k) *thermal parameters and characteristic transformation temperatures*

Mechanical properties are closely linked to the behavior of polymers during temperature changes. Key thermal parameters include the glass transition temperature ($T_g$), melting temperature ($T_m$), crystallization temperature ($T_c$), and decomposition temperature ($T_d$), as well as thermal stability, thermal expansion, and thermal conductivity.

• The glass transition temperature refers to transformations occurring in the amorphous phase and denotes the temperature range in which chain segment mobility increases and a transition takes place from the glassy state to a state more susceptible to deformation. It is not synonymous with the melting temperature. The $T_g$ value depends on factors such as chain stiffness, molar mass, substituents, intermolecular interactions, the degree of cross-linking, and the presence of plasticizers (DE BEUKELAER et al. 2022).

• Melting temperature refers to the loss of order in the crystalline phase and is primarily relevant to crystalline and semi-crystalline polymers. Completely amorphous polymers do not exhibit a classic crystalline-phase melting temperature. The value of $T_m$ is influenced by factors such as chain regularity and symmetry, tacticity, molar mass, degree of crystallinity, the strength of inter-chain interactions, and the morphology of crystalline structures. Upon cooling a molten semi-crystalline polymer, crystallization may occur; the course of this process depends on factors including temperature, cooling rate, molar mass, tacticity, and the presence of nucleating agents. Cooling conditions thus influence the final degree of crystallinity and the material's morphology (ZHU et al. 2023).

l) *thermal stability, expansion, and thermal conductivity*

Thermal stability, defined as a polymer's ability to retain its structure and properties during heating, is a crucial parameter for processing. Exceeding the appropriate temperature range can lead to chain scission, oxidation, the elimination of small molecules, depolymerization, or cross-linking. Decomposition temperature depends on the testing method and the degradation criterion applied; therefore, it should not be treated as a universal material constant. In practice, the processing temperature must ensure adequate polymer fluidity while simultaneously limiting degradation. The width of the processing window is

particularly important for materials where the melting temperature and the onset of degradation occur within a relatively narrow range (BANERJEE 2023). Thermal expansion and thermal conductivity are also significant thermal properties. Changes in polymer dimensions with temperature are particularly relevant when the polymer is joined with materials having different expansion coefficients, such as metals, glass, or ceramics. Conversely, most polymers exhibit relatively low thermal conductivity; while this enables their use as insulating materials, it limits the ability to dissipate heat effectively. Appropriate fillers and composites are used, among other methods, to modify this property. The mechanical properties of polymers are strongly temperature-dependent. Below the glass transition temperature ($T_g$), many amorphous polymers exist in a glassy state characterized by restricted segmental mobility, high stiffness, and often reduced deformability. Near the $T_g$, segmental mobility increases, leading to distinct changes in mechanical properties. Above the glass transition temperature ($T_g$), the material can enter a rubbery state, characterized by increased deformability and the manifestation of viscoelastic behavior. In semi-crystalline polymers, the material's behavior is additionally influenced by the crystalline phase, which retains its ordered structure up to the melting temperature (ZHU et al. 2023).

## Polymerization mechanisms

Polymerization is a chemical reaction in which low-molecular-weight molecules (monomers) are joined to form macromolecules (polymers). According to the current classification recommended by IUPAC, polymerization processes are distinguished primarily by the mechanism of chain growth (EPPS et al. 2022, HODGE et al. 2025):

• step-growth polymerization – macromolecules grow through reactions between functional groups of monomers, oligomers and polymer chains of any length; high molar masses are obtained only at very high conversion of functional groups, as described by the Carothers equation (ODIAN 2004). Depending on whether a low-molecular-weight by-product is released, step-growth processes are divided into polycondensation and polyaddition (Section Step-growth processes: Polycondensation and polyaddition). Therefore, the modern classification into step-growth and chain-growth polymerization should be distinguished from the historical classification into addition and condensation polymers (EPPS et al. 2022);

• chain-growth polymerization (chain polymerization) involves the successive addition of monomers to an active center located at the end of a growing chain. Unlike step-growth polymerization, high molar masses can be achieved even at relatively low monomer conversion. The active center may be radical, cationic, or anionic in nature, or associated with the organometallic center of a catalyst. The typical process comprises initiation, propagation, and chain termination,

with its specific characteristics depending on the mechanism employed (RAUSCHENBACH et al. 2024). Depending on the nature of the active center, the following types of chain-growth polymerization are distinguished:

• radical polymerization – one of the most industrially important methods. It is used to produce, among others, low-density polyethylene (LDPE, in the high-pressure process), polystyrene, poly(methyl methacrylate), polyacrylates, polymethacrylates, polyvinyl chloride, and numerous copolymers. Initiation occurs through the formation of radicals, most commonly via the decomposition of an initiator, followed by their addition to the multiple bond of the monomer. Chain growth proceeds through successive propagation reactions, while termination can occur via the recombination or disproportionation of macroradicals. Chain transfer reactions also influence the molar mass and structure of the product (RIGO et al. 2023, AUTZEN et al. 2024). A significant phenomenon in radical chain polymerization is the Trommsdorff-Norrish effect, also known as the gel effect. At high conversion levels, the increase in mixture viscosity restricts macroradical diffusion and reduces the rate of termination, leading to auto-acceleration of the process.

This phenomenon can cause a rapid rise in both the polymerization rate and temperature; therefore, it is a crucial factor in the design and safe operation of technological processes (SUZUKI et al. 2024). Key methods of controlled radical polymerization include Atom Transfer Radical Polymerization (ATRP), Reversible Addition-Fragmentation Chain Transfer (RAFT), and Nitroxide-Mediated Polymerization (NMP). These methods enable the synthesis of polymers with more predictable chain lengths and complex architectures, such as block, graft, and star copolymers (LEE 2024):

• ionic polymerization – in cationic polymerization, the active center is a carbocation, and the process is primarily applied to monomers with electron-donating substituents capable of stabilizing a positive charge (e.g., isobutylene, vinyl ethers); conversely, anionic polymerization utilizes anionic centers and, as a living process, enables the synthesis of, among others, styrenic and diene polymers and block copolymers (e.g., styrene–butadiene–styrene thermoplastic elastomers) with controlled microstructure (UCHIYAMA et al. 2024).

However, ionic processes are particularly sensitive to the presence of impurities, moisture, and substances capable of deactivating the active center (ZHU et al. 2024):

• coordination polymerization – a specific type of chain polymerization in which chain growth proceeds via a transition metal complex that coordinates the monomer and enables its controlled incorporation into the macromolecule. The polymerization of olefins, primarily ethylene, propylene, and higher α-olefins, is of the greatest industrial importance. A significant advantage of this process is the ability to control the polymer's microstructure, including its molar mass, linearity, degree of branching, and stereoregularity (SHAMS et al. 2024).

Coordination polymerization is particularly significant due to the ability to produce stereoregular polypropylene. The specific geometry of the catalytic center influences monomer orientation during coordination and insertion, enabling the preferential formation of isotactic polypropylene or other stereoregular structures (WANG et al. 2024). Tacticity determines the chains' ability to order and crystallize, thereby influencing the material's stiffness, mechanical strength, dimensional stability, and thermal properties (ANTINUCCI et al. 2026). Coordination polymerization is also crucial for the production of polyethylene. The choice of catalyst and process conditions allows for control over chain linearity as well as the number and distribution of branches. The copolymerization of ethylene with α-olefins, such as 1-butene, 1-hexene, or 1-octene, is particularly important, as it enables the tuning of polyethylene's density, crystallinity,

Table 1

Comparison of chain-growth and step-growth polymerization

| Feature | Chain-growth polymerization | Step-growth polymerization |
|---|---|---|
| Growth mechanism | Successive addition of monomer to a small number of active centers (radical, ion, metal–carbon bond) at the chain end | Reaction between any two molecules bearing complementary functional groups (monomers, oligomers, polymer chains) |
| Monomer during the process | Present until the end of the reaction; its concentration decreases steadily | Consumed at an early stage, mainly to dimers and oligomers |
| Molar mass vs. conversion | High-molar-mass chains are formed from the very beginning | Molar mass increases slowly and becomes high only at conversions above about 99% (Carothers equation) |
| Composition of the reaction mixture | Monomer, high polymer and a very low concentration of growing chains | Molecules of all sizes, from oligomers to macromolecules |
| Effect of reaction time | Mainly increases polymer yield (except in living polymerization) | Increases molar mass |
| Initiation | Requires an initiator or catalyst forming active centers | No initiator; catalysts may accelerate the reaction |
| By-products | Usually none | Released in polycondensation (e.g., water, alcohol, HCl); none in polyaddition |
| Stoichiometry | Not critical | Precise balance of functional groups required for high molar mass |
| Typical polymers | PE, PP, PVC, PS, PMMA, synthetic rubbers (e.g., SBR, BR) | PET, PBT, PA 6,6, polycarbonates, polyurethanes, epoxy networks |
| Key technological issues | Heat removal, gel (Trommsdorff–Norrish) effect, control of molar mass and microstructure | Removal of by-products, high temperature or reduced pressure, risk of thermal degradation |

Source: own elaboration based on CAROTHERS (1936), FLORY (1953), ODIAN (2004), EPPS et al. (2022) and HODGE et al. (2025); the kinetic background is discussed in Section Kinetics and mechanisms of polymer formation and methods of polymer characterization.

flexibility, and mechanical properties. This process yields, among other things, materials with a structure characteristic of linear low-density polyethylene (SHAMS et al. 2024).

Copolymerization, involving at least two different monomers, is a key tool for tailoring polymer properties. Depending on the arrangement of the monomers, copolymers are classified as statistical, alternating, block, or graft copolymers. Altering the composition, segment length, and architecture allows for the modification of properties such as stiffness, flexibility, impact strength, thermal and chemical resistance, and surface characteristics (AUTZEN et al. 2024, TANG et al. 2024). Block copolymers can undergo microphase separation and self-assembly to form ordered nanostructures, whereas graft copolymers are frequently used as compatibilizers in polymer blends. Copolymers find applications in areas such as structural materials, thermoplastic elastomers, nanotechnology, electronics, and biomedicine (YANG et al. 2024).

The main differences between chain-growth and step-growth polymerization, which determine the choice of process conditions and the attainable molar mass, are compared in Table 1. From a technological point of view, the key distinction is the relationship between conversion and molar mass: in chain-growth processes, the main challenges are heat removal and the control of microstructure, whereas in step-growth processes, high stoichiometric precision and efficient removal of by-products are decisive (EPPS et al. 2022, ODIAN 2004).

## Catalysts for coordination polymerization of olefins

Ziegler–Natta catalysts constitute the most historically significant group; their development in the 1950s enabled the industrial production of linear polyethylene and stereoregular polypropylene. Modern Ziegler–Natta systems are typically heterogeneous catalysts based on titanium compounds supported on magnesium chloride and activated by organoaluminum compounds. Electron donors can also play a crucial role, particularly in the production of stereoregular polypropylene (CANNAVACCIUOLO et al. 2025). Karl Ziegler and Giulio Natta were awarded the Nobel Prize in Chemistry in 1963 for their work on the catalytic polymerization of olefins. In addition to Ziegler–Natta catalysts, metallocene, post-metallocene, and chromium-based catalysts are employed, enabling the production of polymers with increasingly precise control over their microstructure. Post-metallocene catalysts are of particular importance, as they allow for the synthesis of functionalized polyolefins with enhanced performance characteristics (SZOT et al. 2024). Catalyst properties are directly linked to the structure of the resulting polymer. The geometry and electronic environment of the active site influence monomer orientation, propagation rates, and chain-transfer reactions, thereby affecting the material's molar mass, stereoregularity, branching,

crystallinity, and performance properties. Consequently, the development of modern catalysts focuses on enhancing activity and stereoselectivity, improving microstructural control, and enabling the synthesis of functionalized polyolefins (ANTINUCCI et al. 2026).

## Industrial polymerization techniques

Industrial polymerization can be carried out under various physical conditions, depending on the monomer properties, reaction mechanism, required molar mass and polymer structure, and heat removal capabilities. For chain-growth (mainly radical) polymerization, the principal process techniques are:

• bulk polymerization is carried out without the addition of a solvent, directly in the monomer containing an initiator and any potential molecular weight regulators. Its main advantages are the simplicity of the process and the ability to obtain high-purity products. However, as conversion increases, the viscosity of the system rises, hindering mixing and heat removal. In the case of radical processes, this can lead to the Trommsdorff-Norrish effect, an auto-acceleration of the reaction caused by restricted radical termination. This phenomenon increases the risk of localized overheating; therefore, controlling temperature and rheological properties is crucial. The method is used, among other applications, in the production of polystyrene, poly(methyl methacrylate), and resins (SUZUKI, MATSUMOTO 2026);

• solution polymerization – proceeds in the presence of a solvent that reduces the system's viscosity and facilitates heat removal. This allows for better temperature control than in bulk polymerization and may enable the direct use of the resulting solution in the production of adhesives, coatings, binders, and thickeners. The choice of solvent is significant due to its influence on reaction kinetics, molar mass, and the potential for chain transfer (WANG et al. 2023). A disadvantage of the method is the need to recover or remove the solvent, which increases energy consumption and process complexity;

• suspension polymerization is a heterogeneous process in which the monomer is dispersed in an aqueous phase as relatively large droplets. The initiator is typically located within the monomer phase, while a stabilizer prevents droplet coalescence. Each droplet acts as a microreactor where polymerization proceeds similarly to bulk polymerization, yet the water ensures effective heat removal. The size of the resulting beads depends on factors such as agitation intensity, the type and concentration of the stabilizer, temperature, and the phase ratio. This method enables the production of easily separable granules and is significant in the manufacture of PVC, polystyrene, and poly(methyl methacrylate) (PINTO et al. 2024). Its limitations include the need to control suspension stability and the potential presence of residual auxiliary substances in the product;

• emulsion polymerization is typically conducted in an aqueous medium, in the presence of an emulsifier and a water-soluble initiator. Polymer growth occurs primarily within polymer particles that form a stable colloidal dispersion, namely, a latex. The distribution of growing chains across numerous particles enables high polymerization rates and high molar masses, while simultaneously allowing for effective heat removal (SCHORK 2024). The resulting latex can be used directly in the production of paints, coatings, adhesives, and elastomeric materials. If a dry polymer is required, additional steps such as coagulation, separation, and drying are necessary. Significant limitations also include the need to use emulsifiers and to control the colloidal stability of the system (XIANG et al. 2024).

The techniques discussed above are compared in Table 2. The comparison shows that the main technological trade-off in industrial polymerization is between product purity and process controllability. Bulk polymerization yields the purest product but offers the poorest heat removal, whereas heterogeneous processes (suspension and emulsion polymerization) provide excellent temperature

Table 2

Comparison of industrial polymerization techniques

| Technique | Reaction system | Advantages | Limitations | Typical products |
|---|---|---|---|---|
| Bulk | Monomer with initiator, no solvent | Simple process, high product purity | High viscosity, poor heat removal, gel effect and risk of local overheating | PS, PMMA, resins |
| Solution | Monomer and polymer dissolved in a solvent | Lower viscosity, good temperature control, solution can be used directly | Solvent recovery, chain transfer to solvent, higher energy consumption | Adhesives, coatings, binders, thickeners |
| Suspension | Monomer droplets dispersed in water; initiator in the monomer phase | Very good heat removal, easily separable beads | Control of suspension stability, residues of stabilizers | PVC, PS (including EPS beads), PMMA |
| Emulsion | Aqueous medium, emulsifier, water-soluble initiator; latex particles | High rate and high molar mass simultaneously, low viscosity, latex used directly | Emulsifier residues; coagulation and drying needed to obtain solid polymer | Paints, coatings, adhesives, synthetic rubbers |
| Interfacial | Two immiscible phases with dissolved reactive monomers (step-growth) | Fast reaction under mild conditions, very thin layers | Mass-transport limitations, reactive monomers and organic solvents | Polyamide RO/NF membranes, thin films, microcapsules |

Source: own elaboration based on WANG et al. (2023), LIU et al. (2024), PINTO et al. (2024), SCHORK (2024), XIANG et al. (2024) and SUZUKI, MATSUMOTO (2026).

control at the expense of residual auxiliary substances (stabilizers, emulsifiers), which may affect product properties and should also be taken into account in subsequent processing and recycling (PINTO et al. 2024, XIANG et al. 2024).

## Step-growth processed: Polycondensation and polyaddition

Polycondensation is a step-growth polymerization process in which monomers bearing two or more functional groups react with one another, simultaneously releasing low-molecular-weight by-products. On an industrial scale, the process method is selected primarily based on the physical states of the reactants and the product, the ability to effectively dissipate heat, the viscosity of the system, and the efficient removal of by-products. Key methods include melt, solution, interfacial, and solid-state polycondensation. These technologies differ in their operating conditions, and the choice of method influences the resulting molar mass, product properties, and production economics (LIU et al. 2024). Based on the nature of the chemical reaction, a distinction is made primarily between polycondensation and polyaddition. Polycondensation proceeds with the release of a low-molecular-weight by-product, such as water, an alcohol, or hydrogen chloride, whereas polyaddition occurs without the formation of such a by-product. Thus, the term "step-growth polymerization" refers to the mode of macromolecule growth, while "polycondensation" and "polyaddition" describe the nature of the reaction forming the polymer bonds (EPPS et al. 2022). Polycondensation is a significant method for producing polyesters, polyamides, polycarbonates, and resins. Examples include the synthesis of poly(ethylene terephthalate) (PET), used for bottles, fibers, films, and packaging, from a diol and a dicarboxylic acid, as well as the production of polyamides such as nylon-6,6. In the case of equilibrium polycondensation, the removal of by-products is a crucial condition for achieving high conversion and molar mass. In practice, methods such as elevated temperature, reduced pressure, inert gas purging, or distillation are employed (DIXON et al. 2025). In processes utilizing more reactive monomer derivatives, the reaction can proceed virtually irreversibly and very rapidly. Interfacial polycondensation is of particular importance; it is used, for instance, to produce thin polyamide layers for reverse osmosis and nanofiltration membranes. A classic example of the industrial application of melt polycondensation is the production of poly(ethylene terephthalate) (PET). It can proceed via the direct esterification of terephthalic acid with ethylene glycol or through the transesterification of a suitable terephthalic acid ester. In both cases, low-molecular-weight by-products are formed; their removal shifts the equilibrium toward polymer formation. The final stages of the process are often conducted under reduced pressure, facilitating by-product removal and an increase in molar mass. This method is of great

importance in the large-scale production of PET and other polyesters, such as poly(butylene terephthalate) (PBT). The main advantages of melt polycondensation include the absence of solvents, a relatively simple process setup, the feasibility of continuous operation, and favorable economics. However, a significant limitation is the high temperature, which can cause thermal degradation of the polymer, side reactions, discoloration, or chain scission. Consequently, for thermally sensitive materials, a balance must be struck between reaction rate, the ability to remove by-products, and the stability of the resulting polymer.

In addition to the melt process described above, the main industrial polycondensation techniques include:

• solution polycondensation – carried out in the presence of a suitably selected solvent containing the reactants and, depending on the system, the resulting polymer. The presence of a solvent reduces the mixture's viscosity, facilitates mixing and mass transport, and improves temperature control. This method is particularly useful for polymers with high melting points or materials susceptible to degradation during melt-phase processing. By-products can be removed via distillation or other separation operations, among other methods, and the resulting polymer may either remain in solution or be precipitated. The primary advantage of solution polycondensation is easier control of temperature and viscosity compared to the melt process. However, a limitation is the necessity of using a solvent, which must be recovered, removed, or retained in the product if it is intended for use in solution form. This increases energy consumption, processing costs, and safety and environmental requirements. The solvent can also influence the reaction rate and the mechanism of by-product removal; therefore, its selection is a crucial aspect of process design (McNeeley, Liu 2024);

• interfacial polycondensation occurs between reactants located in two immiscible phases, most commonly an aqueous phase and an organic phase. Monomers are distributed across the phases based on their solubility and subsequently migrate toward the interface, where a rapid reaction forming polymer bonds takes place. This process is particularly characteristic of reactions involving highly reactive monomer derivatives, allowing it to proceed under relatively mild conditions and at high rates. The process is governed not only by chemical reactions but also by mass transport and the diffusion of reactants to the interface (Liu et al. 2024). A particularly important application of interfacial polycondensation is the production of thin polyamide layers used in reverse osmosis and nanofiltration membranes. This technology enables the direct fabrication of very thin, cross-linked layers with selective properties, which is crucial for water treatment, desalination, and other separation processes. Limitations of the method include the requirement for two immiscible phases, the need to control reactant diffusion, and the reliance on reactive monomers and organic solvents. The properties of the resulting layer depend on reactant concentration and reactivity, diffusion, temperature and mixing conditions

(Di et al. 2024, Sarkar et al. 2024, Wu et al. 2024), and the technique is also used for the fabrication of thin films and microcapsules. Because the process is strongly governed by mass transport, an appropriate selection of the reaction phases is essential (Yokawa, Higashihara 2025; Dixon et al. 2025), and solutions are being developed to reduce the use of hazardous substances and enhance the sustainability of the process (Ben-Zvi et al. 2024);

• solid-state polycondensation (SSP) – is primarily used to increase the molar mass of a previously synthesized polymer. The process is conducted at a temperature above the glass transition temperature but below the melting point; this ensures the material remains in the solid state while its segments retain sufficient mobility for further end-group reactions. Low-molecular-weight by-products are generated and removed during the process, enabling continued chain growth. This method is particularly significant in PET technology, where it often serves as the final stage for increasing molar mass following initial melt polycondensation. A key advantage of solid-state polycondensation is the ability to increase molar mass without subjecting the material to a high-temperature melt for extended periods. This limits the risk of certain degradation processes and yields PET with the properties required for technical applications. However, the process is slower than melt polycondensation and requires careful control of temperature, time, crystallinity, and by-product removal. Ensuring the appropriate material structure prior to SSP is crucial, as insufficient crystallinity can lead to particle softening and agglomeration during the process (Odian 2004).

Polyaddition is a type of step-growth polymerization in which the formation of successive bonds occurs without the release of low-molecular-weight by-products. A prime example is the production of polyurethanes through the reaction of polyols with diisocyanates or polyisocyanates. Depending on the functionality of the reactants, either linear or cross-linked materials are formed, such as rigid and flexible foams, elastomers, adhesives, coatings, and sealants (Xu, Yang 2024). The widespread use of polyurethanes stems from the ability to tailor their properties by selecting specific reactants and controlling the degree of cross-linking. Non-isocyanate systems offer an alternative route for polyurethane synthesis; these include materials derived from plant-based feedstocks, which are being developed to reduce reliance on traditional petrochemical raw materials (Rayung et al. 2024). Epoxy networks, produced by reacting epoxy groups with multifunctional amines, alcohols, phenols, acids, or anhydrides, also constitute an important class of polyaddition products. Epoxy ring-opening leads to the formation of a three-dimensional network characterized by high rigidity, chemical resistance, and thermal stability. Epoxy materials are used in adhesives, protective coatings, binders, structural components, and electronics applications. Of particular significance is the potential to design bio-based epoxy-alcohol networks synthesized via step-growth polyaddition processes (Fantoni et al. 2024).

## Kinetics and mechanisms of polymer formation and methods of polymer characterization

The structure and properties of polymers discussed in the previous sections are determined already at the synthesis stage by the mechanism and kinetics of chain growth, while their identification and verification require instrumental characterization methods. This section summarizes the kinetic relationships that govern molar mass in chain-growth and step-growth processes, the influence of monomer structure on the polymerization mechanism, the mechanism of Ziegler–Natta catalysis, and the main methods used to identify polymers and characterize their properties (ODIAN 2004).

a) *classification of polymerization processes according to Carothers and Flory*

Carothers divided polymers into condensation and addition polymers, depending on whether the composition of the repeating unit differs from that of the monomer because a low-molecular-weight by-product is eliminated (CAROTHERS 1936). Flory proposed a classification based on the mechanism of chain growth, distinguishing chain-growth and step-growth polymerization (FLORY 1953). The two classifications do not overlap completely: polyurethanes are formed by step-growth polyaddition without the release of any by-product, whereas polyamide 6, obtained by ring-opening polymerization of ε-caprolactam, has the structure of a condensation polymer although no by-product is formed. The kinetic consequences of both mechanisms are compared in Table 1.

b) *kinetics of free-radical polymerization*

In free-radical polymerization, the rates of initiation ($R_i$), propagation ($R_p$) and termination ($R_t$) are expressed as:

$$R_i = 2fk_d[I], \quad R_p = k_p[M][M^\bullet], \quad R_t = 2k_t[M^\bullet]^2$$

where $f$ is the initiator efficiency, $k_d$, $k_p$ and $k_t$ are the rate constants of initiator decomposition, propagation and termination, [I] and [M] are the initiator and monomer concentrations, and [M•] is the concentration of propagating radicals. Under the steady-state assumption ($R_i = R_t$), the rate of polymerization is:

$$R_p = k_p(fk_d/k_t)^{1/2}[M][I]^{1/2}$$

and the kinetic chain length, i.e., the average number of monomer molecules consumed per initiating radical, is:

$$\nu = R_p/R_i = k_p[M] / [2(fk_dk_t[I])^{1/2}]$$

These relationships have direct technological consequences. Increasing the initiator concentration or the temperature accelerates polymerization but reduces the molar mass, because more chains grow simultaneously and terminate earlier. The number-average degree of polymerization equals 2ν when termination occurs by combination and ν when it occurs by disproportionation, and it is further reduced by chain transfer to monomer, solvent, initiator or deliberately added chain-transfer agents. At high conversion, the steady-state assumption no longer holds because of the gel effect described in Section Polymerization mechanisms (ODIAN 2004, WANG et al. 2023).

In copolymerization, the composition of the copolymer formed at a given moment is described by the Mayo–Lewis equation (MAYO, LEWIS 1944):

$$d[M_1]/d[M_2] = ([M_1]/[M_2]) \cdot (r_1[M_1] + [M_2]) / ([M_1] + r_2[M_2])$$

where $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$ are the reactivity ratios. When $r_1 r_2 \approx 1$, the comonomer units are distributed randomly (ideal copolymerization); when $r_1 r_2 \approx 0$, an alternating copolymer is formed, as in the copolymerization of styrene with maleic anhydride; when both ratios are greater than 1, long sequences of the same monomer are favored. Because the more reactive monomer is consumed faster, the copolymer composition drifts with conversion, which in industrial practice is compensated by continuous dosing of the more reactive comonomer (ODIAN 2004).

c) *influence of monomer structure on the polymerization mechanism*

The type of active center that can propagate depends on the substituents attached to the carbon–carbon double bond. Electron-donating substituents (alkyl, alkoxy) stabilize carbocations; therefore, isobutylene and vinyl ethers polymerize cationically. Electron-withdrawing substituents (nitrile, ester, carbonyl) stabilize carbanions, which enables the anionic polymerization of acrylonitrile, methacrylates and cyanoacrylates; the latter polymerize even in the presence of traces of moisture, which is the basis of their use as instant adhesives. Free-radical polymerization is the least selective and is possible for most monomers whose radicals are stabilized by resonance, such as styrene, methyl methacrylate, vinyl chloride and vinyl acetate. Styrene and 1,3-dienes can polymerize by all three mechanisms, because the phenyl or vinyl group delocalizes a radical as well as a positive or negative charge. Propylene and higher α-olefins do not yield high polymers by radical or cationic routes because of degradative chain transfer via abstraction of allylic hydrogen atoms; for this reason, they are polymerized with coordination catalysts (ODIAN 2004).

d) *living polymerization*

Living polymerization is a chain-growth process in which termination and chain transfer are absent. It was first demonstrated by Szwarc, who polymerized styrene anionically with sodium naphthalene in tetrahydrofuran; the chain ends remained active after the monomer had been consumed and resumed growth when fresh monomer was added (SZWARC 1956). If initiation is fast compared with propagation, all chains grow simultaneously. For a monofunctional initiator, such as n-butyllithium, the number-average degree of polymerization is then determined by the ratio of the consumed monomer to the initiator:

$$X_n = p[M]_0/[I]_0$$

where $p$ is the monomer conversion, and the molar mass distribution is very narrow, with a dispersity Đ close to 1. Sequential addition of different monomers yields block copolymers, such as styrene–butadiene–styrene (SBS) thermoplastic elastomers. Because living ionic systems are deactivated by water, oxygen and other protic impurities, they require high monomer and solvent purity. Living cationic polymerization of vinyl ethers and isobutylene, as well as the reversible-deactivation radical methods (ATRP, RAFT, NMP) described in Section Polymerization mechanisms, extend the living character to other groups of monomers (ODIAN 2004).

e) *mechanism of Ziegler–Natta polymerization*

Ziegler–Natta catalysts consist of a transition-metal compound, most often titanium chloride supported on magnesium chloride, and an organoaluminum cocatalyst, such as triethylaluminum, which alkylates the titanium atom and creates a Ti–C bond adjacent to a vacant coordination site (SHAMS et al. 2024). According to the Cossee–Arlman mechanism, the olefin first coordinates through its π electrons to the vacant site and then inserts into the Ti–C bond via a four-center transition state; the growing chain is thereby extended by one monomer unit, and the vacant site is regenerated for the next coordination (ARLMAN, COSSEE 1964, COSSEE 1964). The chiral environment of the active site forces successive propylene molecules to coordinate with the same orientation, which leads to isotactic polypropylene. Chain growth is terminated mainly by chain transfer to hydrogen, which is used industrially to control molar mass, as well as by ß-hydride elimination and chain transfer to the organoaluminum compound. Heterogeneous Ziegler–Natta catalysts contain several types of active sites and therefore yield polymers with a broad molar mass distribution, whereas single-site metallocene catalysts activated with methylaluminoxane (MAO) produce polymers with a narrow distribution (Đ ≈ 2) and uniform comonomer incorporation (ODIAN 2004).

f) *kinetics of step-growth polymerization and the Carothers equation*

In the step-growth polymerization of bifunctional monomers, the extent of reaction $p$ is the fraction of functional groups that have reacted. Each reaction reduces the number of molecules by one, which leads to the Carothers equation (CAROTHERS 1936):

$$X_n = 1/(1 - p)$$

For $p = 0.95$, $X_n = 20$; for $p = 0.99$, $X_n = 100$; and for $p = 0.995$, $X_n = 200$. Engineering polyesters and polyamides therefore require conversions above 99%, which explains the strict requirements for monomer purity, equimolar stoichiometry and efficient by-product removal discussed in Section Step-growth processes: Polycondensation and polyaddition. When one monomer is used in excess, the stoichiometric ratio $r = N_A/N_B$ ($r \leq 1$) limits the degree of polymerization:

$$X_n = (1 + r)/(1 + r - 2rp)$$

At complete conversion, this reduces to $X_n = (1 + r)/(1 - r)$; even a 1 mol% excess of one monomer ($r = 0.99$) limits $X_n$ to 199. This effect is used intentionally: small amounts of monofunctional reagents, such as acetic acid in the production of polyamide 6,6, stabilize the molar mass and prevent its further increase during processing (ODIAN 2004, YOKAWA, HIGASHIHARA 2025).

In equilibrium polycondensation, such as polyesterification, the degree of polymerization attainable in a closed system is limited by the equilibrium constant K: $X_n = 1 + K^{1/2}$. For the low equilibrium constants typical of esterification, high molar masses can be achieved only when the by-product is continuously removed, e.g., by vacuum or inert-gas purging during the melt polycondensation of PET. In non-equilibrium polycondensation, which uses highly reactive monomers such as acid chlorides, the reaction is practically irreversible. A typical example is the interfacial polycondensation of hexamethylenediamine with sebacoyl chloride to polyamide 6, 10, in which the process is controlled by the diffusion of reactants to the interface rather than by the overall stoichiometry of the system (ODIAN 2004).

In the polycondensation of monomers with a functionality greater than two, a cross-linked network is formed at the gel point. According to Carothers, the critical extent of reaction is $p_c = 2/f_{av}$, where $f_{av}$ is the average functionality of the monomer mixture. For the stoichiometric reaction of glycerol with phthalic anhydride (molar ratio 2:3, $f_{av} = 2.4$), this gives $p_c = 0.833$, whereas the statistical theory of Flory and Stockmayer predicts $p_c = 0.707$; gelation is observed experimentally at about $p = 0.77$. Control of the gel point is essential in the production of alkyd, phenol–formaldehyde and epoxy resins, which must remain fusible until they are shaped (FLORY 1953, ODIAN 2004).

g) *methods of identification and characterization of polymeric materials*

No single technique describes a polymeric material completely; therefore, identification and characterization combine complementary methods (KOENIG 1999, MENCZEL, PRIME 2009):

• chemical structure – Fourier-transform infrared spectroscopy (FTIR), usually in the attenuated total reflectance (ATR) mode, identifies functional groups, e.g., the carbonyl band at about 1720 $cm^{-1}$ in polyesters and PMMA and the amide I and amide II bands at about 1640 and 1540 $cm^{-1}$ in polyamides; near-infrared (NIR) spectroscopy is used in automatic sorting lines for plastic waste. Nuclear magnetic resonance ($^{1}H$ and $^{13}C$ NMR) spectroscopy determines copolymer composition, branching and tacticity, the latter from the methyl region of the $^{13}C$ NMR spectrum of polypropylene. Pyrolysis–gas chromatography–mass spectrometry (Py-GC/MS) identifies insoluble and cross-linked polymers as well as additives;

• molar mass – in addition to SEC/GPC (Section Structure and properties of polymers: *Molar mass and molar mass distribution*), dilute-solution viscometry gives the viscosity-average molar mass from the Mark–Houwink equation $[\eta] = KM^{a}$; end-group titration gives the number-average molar mass of polyesters and polyamides, and MALDI-TOF mass spectrometry is used for oligomers and end-group analysis;

• thermal properties – differential scanning calorimetry (DSC) determines $T_g$, $T_m$, $T_c$, the enthalpy of melting and the course of curing of thermosets; the degree of crystallinity is calculated as $X_c = \Delta H_m/\Delta H_m^{0}$, where $\Delta H_m^{0}$ is the enthalpy of melting of a fully crystalline polymer (about 293 J/g for polyethylene), and the oxidation induction time (OIT) is used to assess stabilizer effectiveness. Thermogravimetric analysis (TGA) gives thermal stability, decomposition temperature, and moisture, filler or ash content. Dynamic mechanical analysis (DMA) measures the storage modulus E′, loss modulus E″ and loss factor tan δ as functions of temperature and frequency; it detects the glass transition more sensitively than DSC and quantifies the viscoelastic behavior described in Section Structure and properties of polymers: *Phenomenon of viscoelasticity, creep, and stress relaxation*.

• thermomechanical analysis (TMA) gives the coefficient of thermal expansion, while the heat deflection temperature (HDT) and Vicat softening temperature describe practical heat resistance (EHRENSTEIN et al. 2004);

• structure and morphology – wide-angle X-ray diffraction (WAXD) identifies crystalline forms and determines the degree of crystallinity, small-angle X-ray scattering (SAXS) gives the lamellar thickness, polarized-light microscopy reveals spherulitic structures, and scanning electron microscopy (SEM) shows fracture surfaces, filler dispersion and the phase morphology of blends;

• mechanical properties – standardized tests determine tensile properties (ISO 527: modulus, yield stress, tensile strength, elongation at break), flexural properties (ISO 178), Charpy and Izod impact strength (ISO 179 and ISO 180), hardness (Shore hardness for elastomers, ball indentation or Rockwell hardness for plastics), creep and fatigue. Because polymer properties depend on temperature and humidity, specimens must be conditioned before testing, which is particularly important for hygroscopic polyamides;

• rheological and processing properties – the melt flow rate (MFR/MVR, ISO 1133) is a simple measure of melt viscosity used to select grades for injection molding (high MFR) or extrusion and blow molding (low MFR), while capillary and rotational rheometry describe the shear-thinning behavior relevant to extrusion and injection molding (Section Basic plastics processing methods);

• durability – accelerated weathering (UV and xenon-arc exposure), immersion tests of chemical resistance (changes in mass, dimensions and hardness, and swelling) and environmental stress cracking tests predict service behavior, including contact with fuels, oils and solvents.

In practice, an unknown plastic is usually identified by FTIR, its thermal transitions are determined by DSC, and its filler content by TGA; the results are then related to mechanical tests and processing behavior. Combining these methods links the chemical structure and synthesis conditions discussed above with the performance properties required in applications (Menczel, Prime 2009).

## Polymer cross-linking and vulcanization

Polymer cross-linking is a process that links macromolecular chains via permanent chemical bonds or reversible physical interactions. This results in the formation of a three-dimensional network structure that restricts chain mobility and alters the material's properties. Increasing cross-link density typically enhances stiffness, the elastic modulus, dimensional stability, and resistance to creep, heat, and solvents, while simultaneously limiting material flow. However, excessive cross-linking can lead to reduced elongation and increased brittleness. Thus, the material's properties are primarily determined by the type and density of the inter-chain linkages (Cerdan et al. 2024).

Based on the nature of the connections, a distinction is made between:

• chemical cross-linking – leads to the formation of stable covalent bonds between macromolecules and can occur during polymer synthesis or through the subsequent modification of the finished material. Agents such as peroxides, sulfur, multifunctional compounds, silanes, and ionizing radiation are employed. An example is the cross-linking of polyethylene to produce Cross-Linked Polyethylene (XLPE), a material characterized by enhanced thermal stability and resistance to deformation, used, among other applications, as insulation for wires

and cables (SHAPIRO et al. 2024, SELVIN et al. 2024). Another significant example of chemical cross-linking is the curing of epoxy resins using multifunctional curing agents, resulting in the formation of rigid, chemically resistant networks used as adhesives, coatings, binders, and structural materials;

• physical cross-linking relies on non-covalent interactions, such as hydrogen bonding, ionic interactions, metal-ligand coordination, π-π stacking, or van der Waals forces. Unlike permanent covalent bonds, these interactions can reversibly dissociate and reform in response to temperature, solvent, or stress. This enables the design of dynamic and self-healing materials. Networks based on multiple hydrogen-bonding interactions are of particular importance, as their properties can be tailored by modifying the network architecture (REN, DONG 2024). Combining permanent covalent bonds with reversible interactions leads to the formation of hybrid networks with properties customized for specific applications (CERDAN et al. 2024).

Vulcanization is a specific instance of cross-linking, specifically, the chemical cross-linking of rubbers. Classic sulfur vulcanization results in the formation of sulfur bridges between elastomer chains, restricting their relative movement and enhancing elasticity, strength, abrasion resistance, and dimensional stability. The process is applied to natural rubber and various synthetic elastomers, including styrene-butadiene rubber (SBR), butadiene rubber (BR), and butadiene-acrylonitrile rubber (NBR). The properties of the vulcanizate depend on the density and type of cross-links; consequently, both insufficient and excessive cross-linking can impair performance characteristics. Vulcanized elastomers are widely used in the manufacture of tires, gaskets, hoses, conveyor belts, and shock-absorbing components. In addition to sulfur vulcanization, other methods include peroxide cross-linking, radiation cross-linking, and cross-linking using metal oxides (BLUME et al. 2024). The degree of cross-linking distinguishes the fundamental behavior of cross-linked materials. Elastomers possess a relatively low cross-link density, allowing them to undergo significant elastic deformation, whereas thermosets form highly cross-linked spatial structures that cannot be remelted or reshaped after curing. Thermosets include, for example, cured epoxy resins and phenol-formaldehyde resins. High cross-link density also limits material solubility; cross-linked polymers do not undergo conventional dissolution but may swell in suitable solvents, a phenomenon utilized to assess the degree of cross-linking by determining the swelling degree and gel fraction (SHAPIRO et al. 2024). The durability of covalent networks enhances the performance properties of materials but simultaneously hinders their reprocessing. Thermosets and permanently cross-linked elastomers cannot undergo conventional thermoplastic recycling, which involves melting and remolding. Consequently, methods such as chemical recycling, devulcanization, and the design of materials incorporating reversible linkages are being developed (SELVIN et al. 2024). Dynamic polymer networks in which specific bonds can undergo exchange or reversible dissociation

are of particular importance. They enable structural reorganization, partial self-healing, and, under certain conditions, material reprocessing (REN, DONG 2024, CERDAN et al. 2024). Cross-linking is thus a crucial tool for tailoring polymer structure and properties. Controlling the type and density of linkages allows for the production of materials ranging from soft, highly elastic elastomers to rigid, chemically resistant thermosets. Modern development in cross-linked materials focuses on combining high durability and performance with capabilities for self-healing, structural reorganization, and more efficient recycling (SHAPIRO et al. 2024).

## Plastics

Plastics are materials primarily composed of a polymer or a mixture of polymers, with functional properties that can be modified through additives such as plasticizers, stabilizers, fillers, pigments, flame retardants, antioxidants and functional (e.g., antimicrobial) additives. The properties of plastics depend on the chemical structure and macromolecular architecture, molar mass, degree of crystallinity and cross-linking, type of additives, and processing conditions. These factors enable the production of materials with varying degrees of rigidity, flexibility, strength, and chemical and thermal resistance (URTEKIN, KODAL 2024). They can be classified according to various criteria. Based on mechanical behavior at service temperature, a distinction is made primarily between rigid plastics, referred to in the Central European literature as plastomers, and elastomers, whereas behavior upon heating distinguishes thermoplastics from thermosets. These are independent criteria; therefore, the terms should not be treated as synonyms (JONES et al. 2009). It should also be noted that in English-language industrial usage the term "plastomer" usually denotes very-low-density ethylene-α-olefin copolymers, which is why the term "rigid plastics" is used preferentially below. Rigid plastics (plastomers) may undergo permanent deformation once the yield point is exceeded, whereas elastomers are characterized by the ability to undergo large, largely reversible elastic deformations. This group includes, among others, polyethylene, polypropylene, PVC, polystyrene, PMMA, polyamides, and polycarbonates, while elastomers include natural rubber, synthetic rubbers, and silicone and polyurethane elastomers (KODAL 2023). Thermoplastics soften or melt when heated, allowing them to be repeatedly molded, provided they do not undergo significant degradation. This stems from their structure, which is based primarily on linear or branched chains rather than a permanent covalent network. Key thermoplastics include polyethylene, polypropylene, PVC, polystyrene, PET, PMMA, polyamides, polycarbonate, PTFE, and PEEK. Their ability to undergo repeated processing allows for methods such as extrusion, injection molding, thermoforming, and calendering, while also facilitating mechanical recycling.

Limitations include a reduction in stiffness and strength as temperature rises, as well as susceptibility to creep. During curing, thermosets form a permanent, three-dimensional covalent network that restricts macromolecular mobility and prevents the material from remelting; further heating ultimately leads to degradation. This group includes, among others, cured epoxy, phenol-formaldehyde, and melamine-formaldehyde resins, as well as certain polyester resins. They typically exhibit high stiffness, dimensional stability, and resistance to heat and chemicals. Due to their permanent network structure, they cannot undergo conventional mechanical recycling via remelting (HESS et al. 2013). A distinct group consists of thermoplastic elastomers (TPEs), which combine the high flexibility of elastomers with the processability of thermoplastics. Their properties arise from the presence of reversible physical domains or other interactions that create a temporary network structure. Upon heating, this structure weakens, enabling molding, whereas it reforms during cooling. TPEs are used, for example, in the automotive, medical and electronics sectors and in sealing applications.

## Antimicrobial (bactericidal) additives for plastics

Among the additives listed in Section Plastics, a growing group consists of functional additives, which impart new properties to plastics rather than merely improving their processing or durability. A representative example is antimicrobial additives, which link polymer formulation (Section Plastics) with processing (Section Basic plastics processing methods) and end-of-life management (Section Plastics recycling: Material recycling, feedstock recycling, and energy recovery): they must withstand processing temperatures, remain active in the polymer matrix, comply with regulations on materials in contact with food or the human body, and should not hinder subsequent recycling. Strictly speaking, the term "bactericidal" refers to agents that kill bacteria, whereas "biostatic" agents only inhibit microbial growth; therefore, the broader term "antimicrobial" is used below for additives acting against bacteria and/or fungi.

Antimicrobial additives in plastics play a crucial role in preventing the growth of microorganisms on the surface of polymer materials. Their use is particularly important in sectors such as food packaging, medicine, and the manufacture of consumer goods, where hygiene and microbiological safety are priorities. The functions of antimicrobial additives include inhibiting bacterial and fungal growth on plastic surfaces, thereby preventing the formation of biofilms and microbiological contamination, extending product shelf life by protecting against microbial degradation, enhancing material safety (especially in medical and food-related applications), and supporting the functional properties of plastics,

such as in smart or biodegradable packaging (CHANDRA et al. 2025, SU et al. 2025, SOLIHAT et al. 2024, HOSSEINI et al. 2024).

Incorporating additives into the polymer matrix of packaging materials aims to inhibit microbial growth on the surface of food products, thereby extending shelf life and ultimately helping to reduce food waste. Organic acids and their salts (e.g., sorbic, benzoic and propionic acid), as well as phenolic compounds and isothiocyanates, are among the most commonly used additives with biocidal or biostatic properties; however, their migration into food must be controlled to ensure consumer safety (JIDEANI, VOGT 2016, MAHMUD, KHAN 2018).

Other examples include natural antimicrobial agents, such as essential oils, animal-derived enzymes (e.g., lysozyme) and natural polymers (e.g., chitosan), as well as inorganic agents, such as silver nanoparticles, titanium dioxide ($TiO_2$) and cobalt oxide ($Co_3O_4$). The incorporation of metal and metal-oxide nanoparticle hybrids into polymer matrices is also attracting interest, as such materials can combine good antimicrobial activity with improved mechanical properties (ABUTALIB, RAJEH 2021, ALHARBI, RAJEH 2024, ALHUSSAIN et al. 2024).

Zinc compounds constitute an interesting group of microbial growth inhibitors. Zinc oxide, including its nanoform, is included in the Union list of substances authorised for the manufacture of plastic materials intended for contact with food (Regulation (EU) No 10/2011), following a favourable safety assessment by the European Food Safety Authority (EFSA) for use in unplasticised polymers. It should be noted, however, that this authorisation concerns the use of ZnO as a technical additive, whereas articles for which a biocidal function is claimed are additionally subject to the Biocidal Products Regulation (Regulation (EU) No 528/2012). ZnO exhibits antibacterial activity against both Gram-positive (G+) bacteria, such as *Staphylococcus aureus*, and Gram-negative (G−) bacteria, such as *Salmonella* Typhimurium and *Escherichia coli*, while its antifungal activity is relatively weak. The addition of ZnO nanoparticles to polyethylene–ethylene vinyl acetate (PE–EVA) blends has been shown to improve the antibacterial resistance of the material (GALLI et al. 2020).

A complex zinc–ammonium salt has proven to be a promising antimicrobial (antibacterial and antifungal) additive for nanocellulose–polypropylene composites intended for packaging applications. The salt has a crystalline structure composed of two main phases: ammonium tetrachlorozincate, $[NH_4]_2ZnCl_4$, and diamminezinc chloride, $Zn(NH_3)_2Cl_2$. Its addition increased the thermal stability of the composites, and the composite samples inhibited the growth of Gram-positive and Gram-negative bacteria as well as fungi; the inhibitory effect increased with the content of the salt in the polymer matrix (ZIELIŃSKA et al. 2025).

Table 3

Main classes of antimicrobial additives for plastics

| Class | Examples | Mode of action | Advantages | Limitations |
|---|---|---|---|---|
| Organic acids and their salts | Sorbic, benzoic, propionic acid | Penetration of the cell membrane by undissociated acid and acidification of the cytoplasm; mainly biostatic | Low cost, established use in food applications | Limited thermal stability, migration, narrow spectrum of activity |
| Natural agents | Essential oils, lysozyme, chitosan, tannic acid | Membrane disruption, enzymatic lysis of the cell wall, electrostatic interactions | Bio-based origin, consumer acceptance | Volatility, thermal sensitivity, effect on odor and taste, variable composition |
| Metal and metal-oxide nanoparticles | Ag, ZnO, $TiO_2$, $Co_3O_4$ | Release of metal ions, generation of reactive oxygen species (photocatalytic for $TiO_2$), membrane damage | Broad spectrum, high thermal stability, long-lasting effect | Nanoparticle migration and safety, regulatory constraints, possible effect on color and transparency |
| Metal complexes and salts | Complex zinc–ammonium salt | Release of $Zn^{2+}$ ions; antibacterial and antifungal activity | Activity increasing with content; improved thermal stability of composites | Limited data on migration and long-term performance |

Source: own elaboration based on JIDEANI, VOGT (2016), MAHMUD, KHAN (2018), GALLI et al. (2020), ABUTALIB, RAJEH (2021), HOSSEINI et al. (2024), SOLIHAT et al. (2024), SU et al. (2025) and ZIELIŃSKA et al. (2025).

The main classes of antimicrobial additives are compared in Table 3. From the perspective of polymer technology, the choice of an additive is a compromise between antimicrobial efficacy, thermal stability during processing, migration and regulatory compliance, and its effect on mechanical and optical properties. Organic and natural agents are often volatile or thermally sensitive, which limits their use in high-temperature processes such as extrusion or injection molding, whereas inorganic agents are more thermally stable but raise questions about nanoparticle release and long-term safety (CHANDRA et al. 2025, SU et al. 2025). An issue that is still insufficiently addressed in the literature is the fate of antimicrobial additives at the end of life: their presence may affect the quality of recyclates and their suitability for food-contact applications, and in biodegradable materials it may slow down the intended biodegradation (LOGAN et al. 2024, MUZATA et al. 2024). Integrating antimicrobial functionality with design for recycling is therefore an important direction for further research.

## Basic plastics processing methods

Plastics processing encompasses the technological processes used to impart specific shapes, dimensions, and functional properties to polymer materials. For thermoplastics, the key stages include material preparation, plasticization, transport and homogenization, shaping, and structural stabilization during cooling. In the processing of thermosetting plastics, however, shaping may be combined with cross-linking, resulting in the formation of a permanent three-dimensional structure. The process dynamics depend on factors such as the polymer's properties, including viscosity, glass transition and melting temperatures, thermal stability, and crystallization behavior, as well as temperature, pressure, shear rate, and the material's residence time in the equipment (OSSWALD, HERNÁNDEZ-ORTIZ 2006). For hygroscopic polymers, drying is a crucial step, as the presence of moisture can lead to hydrolytic degradation (TADMOR, GOGOS 2006).

Extrusion is a continuous process in which material is conveyed, plasticized, and homogenized, and then shaped by a die that imparts a specific cross-sectional profile. This method is primarily used in the production of pipes, profiles, films, and sheets, as well as in the preparation of polymer blends and composites (EDELEVA et al. 2023). Single-screw extruders are mainly used for conveying and plasticizing material, whereas twin-screw extruders provide more intensive mixing and are particularly suitable for processing blends, composites, and materials containing fillers. Process parameters, such as temperature and screw rotational speed, influence the degree of plasticization, homogenization, and the potential for material degradation. Modern extrusion solutions also encompass process modeling, parameter optimization, and technologies aimed at processing recycled materials (CUNHA et al. 2022). Injection molding is a cyclic process designed primarily for the production of three-dimensional products with complex geometries. Plasticized polymer is injected under pressure into a closed mold, followed by holding pressure, cooling, and removal of the finished product (NAROWSKI, WILCZYŃSKI 2024). Component quality is primarily influenced by material and mold temperatures, injection pressure and speed, and cooling time. Flow conditions and thermal history can determine macromolecule orientation, crystallization, and the formation of internal stresses and molding defects. This technology is widely used in the production of automotive components, packaging, electronic equipment, and consumer goods (ZHOU, HRYMAK 2024). Compression molding involves shaping material within a closed mold under the influence of heat and pressure. It is particularly significant in the processing of thermosets, elastomers, and composites, as cross-linking, leading to permanent shape fixation, can occur during the process. The method is used, among other applications, to manufacture components from epoxy, phenol-formaldehyde, and polyester resins, as well as fiber-reinforced composites. Its advantages include

the ability to mold high-viscosity materials and large components, while its limitation is a longer cycle time compared to injection molding (TATARA 2024). Thermoforming involves heating a thermoplastic sheet or film to a temperature that allows for deformation, followed by shaping it using vacuum, compressed air, or a mold plunger (WINHARD et al. 2024). This method is primarily used to produce packaging, trays, containers, housings, and technical components (SUBRAMANIAN 2024). A significant challenge is achieving uniform material thickness distribution, which depends on temperature, mold geometry, and deformation conditions (MINUPALA et al. 2024). Calendering is a continuous material-forming process utilizing rotating rollers. The plasticized polymer passes through the gap between the rollers, forming a layer of a specific thickness. The process is primarily used to produce films, sheets, and coatings, particularly from PVC and elastomeric materials. Product quality is influenced by factors such as roller temperature, rotational speed, gap size, and material viscosity (OSSWALD, HERNÁNDEZ-ORTIZ 2006). Spinning is the fundamental method for producing fibers and filaments. The polymer is formed through a spinneret, then solidifies and often undergoes stretching, which orients the macromolecules along the fiber axis and improves its mechanical properties. Depending on the forming method, distinctions are made between melt spinning, dry spinning, and wet spinning. Melt spinning is used for materials such as polyesters, polyamides, and polyolefins, whereas solution-based methods are employed for polymers that are difficult to process from the melt (HUFENUS et al. 2020). Rotational molding, or rotomolding, is primarily used to produce large, hollow thermoplastic products. The polymer, usually in powder form, is placed in a mold that rotates around two axes while being heated. The material melts and coats the inner surface of the mold, subsequently solidifying during cooling (KELLY-WALLEY et al. 2024). This technology enables the production of large-scale components with relatively low pressure and internal stress levels. It is used to manufacture items such as tanks, containers, housings, and vehicle components, and the most commonly used material is polyethylene. The application of pressure and the appropriate selection of process parameters can further influence the cycle time and the properties of the resulting products (ORTEGA et al. 2024).

The choice of processing technology depends on material properties, product geometry, production scale, and the required quality and dimensional accuracy (Table 4). Extrusion is particularly suitable for the continuous production of products with a constant cross-section; injection molding for complex three-dimensional parts; compression molding for thermosets and composites; thermoforming for sheets and films; calendering for wide layers; spinning for fibers; and rotational molding for large hollow products (SUBRAMANIAN 2024). Regardless of the technology, processing conditions influence not only the shape but also the structure and properties of the material. Modern processing increasingly employs process modeling, parameter monitoring, and technologies that enable the efficient processing of recycled materials (CUNHA et al. 2022).

Table 4

Comparison of the basic plastics processing methods

| Method | Process type | Typical materials | Typical products | Advantages | Limitations |
|---|---|---|---|---|---|
| Extrusion | Continuous | Thermoplastics, compounds, recyclates | Pipes, profiles, films, sheets, granulate | High output; compounding and recycling possible | Only constant cross-section; risk of degradation |
| Injection molding | Cyclic | Thermoplastics; also thermosets and elastomers | Complex 3D parts | High precision and automation, short cycles | Expensive molds; internal stresses; economical for large series |
| Compression molding | Cyclic | Thermosets, elastomers, composites | Large parts, composite components | Suitable for high-viscosity materials and large parts | Long cycles, limited geometric complexity |
| Thermo-forming | Cyclic | Thermoplastic sheets and films | Packaging, trays, housings | Low tooling costs | Non-uniform wall thickness, trimming waste |
| Calendering | Continuous | PVC, elastomers | Films, sheets, coatings | Wide layers of uniform thickness | High investment costs, limited range of materials |
| Spinning | Continuous | PET, PA, PP; solution spinning for non-meltable polymers | Fibers, filaments | Molecular orientation and high strength along the fiber axis | Solvent recovery in solution methods |
| Rotational molding | Cyclic | Mainly PE (powder) | Large hollow products, tanks | Low stresses, inexpensive molds | Long cycles, limited range of materials |

Source: own elaboration based on Osswald, Hernández-Ortiz (2006), Tadmor, Gogos (2006), Hufenus et al. (2020), Cunha et al. (2022), Kelly-Walley et al. (2024), Subramanian (2024), Tatara (2024) and Zhou, Hrymak (2024).

## Applications of polymers

Polymers are among the most important groups of materials used in modern technology and industry. Their widespread application stems from the ability to modify their chemical structure, macromolecular architecture, and morphology, enabling the production of materials with diverse mechanical, thermal, chemical, and functional properties. Factors determining these properties include the type of structural units, molar mass, chain branching and cross-linking, tacticity, degree of crystallinity, and intermolecular interactions (Simunec et al. 2023). Polyolefins, primarily polyethylene (PE) and polypropylene (PP), constitute one of the most significant industrial groups. They are characterized by low density,

hydrophobicity, good chemical resistance, and ease of processing. The properties of polyethylene depend largely on chain architecture. Low-Density Polyethylene (LDPE), which features extensive branching, exhibits greater flexibility and lower rigidity, making it suitable primarily for the production of films and packaging. In contrast, Linear Low-Density Polyethylene (LLDPE) combines good ductility with mechanical strength, while the more linear High-Density Polyethylene (HDPE) is characterized by higher crystallinity, rigidity, and resistance to deformation, enabling its use in applications such as containers, pipes, and technical components. Ultra-High-Molecular-Weight Polyethylene (UHMWPE), owing to its exceptionally high molar mass, is distinguished by superior abrasion and impact resistance (ZAKARIA et al. 2024). Polypropylene is characterized by greater rigidity than polyethylene, good chemical resistance, and favorable fatigue resistance. It finds application in packaging, automotive components, fibers, household appliances, and medical devices (HOSSAIN et al. 2024). Vinyl polymers constitute a significant group, with polyvinyl chloride (PVC), polystyrene (PS), poly(methyl methacrylate) (PMMA), and poly(vinyl acetate) (PVAc) being of particular importance. The properties of this group depend primarily on the type of substituents attached to the carbon backbone. PVC can exist as a rigid or flexible material, depending on the use of plasticizers, and is used, among other things, for the production of pipes, profiles, wire insulation, and films (MNYANGO, HLANGOTHI 2026). PS is a rigid yet relatively brittle aromatic polymer, whereas its foamed variants, such as Expanded Polystyrene (EPS) and Extruded Polystyrene (XPS), are widely used as thermal insulation materials (SINGH et al. 2025). Rubbers and elastomers are characterized by their ability to undergo significant, largely reversible deformations. Their properties depend on chain flexibility and the degree of cross-linking; in the case of rubbers, vulcanization plays a crucial role. Important elastomers include natural rubber and synthetic rubbers such as Butadiene Rubber (BR), Styrene-Butadiene Rubber (SBR), Nitrile-Butadiene Rubber (NBR), Chloroprene Rubber (CR), and Ethylene Propylene Diene Monomer (EPDM). They are primarily used in the production of tires, gaskets, hoses, anti-vibration components, and abrasion-resistant products. Individual varieties are selected depending on the required resistance to oils, fuels, ozone, UV radiation and aging (WHBA et al. 2024). Another important group are polyesters, including Polyethylene Terephthalate (PET), Polybutylene Terephthalate (PBT), Polylactic Acid (PLA) and Polycaprolactone (PCL) (NTRIVALA et al. 2025). PET is characterized by high mechanical strength, dimensional stability and good barrier properties, which is why it is widely used in the production of packaging, bottles, films and fibers. The ability to crystallize and the related changes in the structure of the material are important for the properties of PET (DI LORENZO 2024). PLA and PCL are biodegradable polyesters (PLA mainly under industrial composting conditions) that are important, among others, in packaging, additive technologies

and biomedicine (KHOURI et al. 2024). The properties of these materials depend, among others, on molar mass, stereochemistry and degree of crystallinity (NTRIVALA et al. 2025). Polyamides such as Polyamide 6 (PA 6) and Polyamide 6,6 (PA 6,6) contain amide moieties that enable the formation of hydrogen bonds between the chains. Thanks to this, they are characterized by high mechanical strength, abrasion resistance and favorable thermal stability. However, their important feature is water absorption, which can change mechanical properties and dimensional stability. Polyamides are used, among others, for the production of fibers, machine components, car parts, gears and other structural elements (ARIOLI et al. 2024). Polycarbonates, especially materials based on bisphenol A, combine high impact resistance, stiffness, transparency and dimensional stability, thanks to which they are used, among others, in electronics, automotive, optical technology and protective products (CHERNIKOVA, BELETSKAYA 2024). A wide range of properties is represented by polyurethanes (PU), whose properties can be shaped by the selection of soft and hard segments and the degree of cross-linking. They can come in the form of flexible and rigid foams, elastomers, adhesives, coatings and sealants (WU et al. 2025). Epoxy resins and unsaturated polyester resins are thermosetting materials. After hardening, they create durable spatial networks characterized by high stiffness, chemical resistance and thermal stability. They are widely used as adhesives, coatings and matrices for glass or carbon fiber reinforced composites (VERMA et al. 2025, EZEH 2024). A special group are high-performance polymers, designed to operate at elevated temperatures, aggressive chemical environments or under high loads. These include, among others: Polyether Ether Ketone (PEEK), Polyetherimide (PEI), Polyphenylene Sulfide (PPS), Polyether Ketone Ketone (PEKK) and Polytetrafluoroethylene (PTFE). PEEK is characterized by high mechanical, chemical and thermal resistance, PPS is characterized by high dimensional stability and chemical resistance, while PTFE is distinguished by exceptional chemical resistance, hydrophobicity and a very low coefficient of friction. These materials are used, among others, in aviation, automotive, electronics, energy and medicine (SIMUNEC et al. 2023).

The variation in properties among different polymer groups stems directly from their molecular structure and morphology. The non-polar chains of polyolefins contribute to low density and water resistance; polar polyamide groups enhance inter-chain interactions; and the presence of aromatic rings can increase rigidity and thermal resistance (ARIOLI et al. 2024). Conversely, flexible chains and a suitably selected degree of cross-linking enable the achievement of elastomeric properties (WHBA et al. 2024, WU et al. 2025). Crystallinity, which can enhance rigidity, strength, and chemical resistance, and cross-linking, which improves dimensional stability and heat resistance but precludes conventional remelting, also play significant roles (VERMA et al. 2025). Selecting a polymer for a specific application requires considering not

Table 5

Main groups of polymers: structure, properties, applications and end-of-life options

| Group | Representative polymers | Key structural features | Characteristic properties | Typical applications | Main end-of-life options |
|---|---|---|---|---|---|
| Polyolefins | LDPE, LLDPE, HDPE, UHMWPE, PP | Non-polar C–C backbone; branching and tacticity control crystallinity | Low density, hydrophobicity, chemical resistance | Films, packaging, pipes, containers, automotive parts | Mechanical recycling; pyrolysis of mixed streams |
| Vinyl polymers | PVC, PS, PMMA, PVAc | C–C backbone with polar or aromatic substituents | Governed by substituents; PVC rigid or plasticized; PS rigid but brittle | Pipes, profiles, cable insulation, thermal insulation (EPS, XPS), optical parts | Mechanical recycling; depolymerization to monomer (PMMA, PS); HCl release from PVC in thermal processes |
| Elastomers | NR, BR, SBR, NBR, CR, EPDM | Flexible chains, low cross-link density (vulcanization) | Large, largely reversible deformations | Tires, gaskets, hoses, anti-vibration parts | Devulcanization, ground rubber, pyrolysis, energy recovery |
| Polyesters | PET, PBT, PLA, PCL | Ester bonds in the main chain; ability to crystallize | Strength and barrier properties (PET); biodegradability (PLA, PCL) | Bottles, fibers, films, packaging, biomedicine | Mechanical recycling; glycolysis, methanolysis, hydrolysis; composting (PLA, PCL) |
| Polyamides | PA 6, PA 6,6 | Amide groups forming inter-chain hydrogen bonds | Strength, abrasion resistance, water absorption | Fibers, gears, machine and automotive parts | Mechanical recycling; depolymerization (e.g., PA 6 to caprolactam) |
| Polycarbonates | Bisphenol A polycarbonate | Aromatic carbonate backbone | Impact resistance, transparency, dimensional stability | Electronics, optical and protective products | Mechanical recycling; alcoholysis |
| Polyurethanes | Flexible and rigid PU | Soft and hard segments; variable cross-linking | Tunable from elastomers to rigid foams | Foams, adhesives, coatings, sealants | Glycolysis (polyol recovery), energy recovery |
| Thermosetting resins | Epoxy, unsaturated polyester | Dense covalent networks | Stiffness, chemical and thermal resistance; not remeltable | Adhesives, coatings, composite matrices | Limited: grinding to fillers, solvolysis, pyrolysis with fiber recovery |
| High-performance polymers | PEEK, PEI, PPS, PEKK, PTFE | Aromatic or fluorinated backbones | High thermal and chemical resistance | Aerospace, automotive, electronics, medicine | Mainly mechanical recycling of production scrap |

Source: own elaboration based on the literature discussed in Sections Applications of polymers and Plastics recycling: Material recycling, feedstock recycling, and energy recovery.

only mechanical properties but also operating temperature, chemical and environmental resistance, dimensional stability, electrical properties, wear resistance, and the potential for processing and end-of-life management (MNYANGO, HLANGOTHI 2026). Consequently, the modern development of polymer materials encompasses both the optimization of performance characteristics and the design of materials with regard to durability, degradation, the use of renewable feedstocks, and recyclability (SIMUNEC et al. 2023). The relationships between structure, properties, applications and end-of-life options of the main groups of polymers discussed above are summarized in Table 5. The comparison indicates that the chemical nature of the main chain determines not only service properties but also the available recycling routes, which is further discussed in Sections Plastics recycling: Material recycling, feedstock recycling, and energy recovery and Critical synthesis and research gaps.

## Plastics lastics recycling: Material recycling, feedstock recycling, and energy recovery

The growing production and consumption of plastics are leading to an increase in the volume of polymer waste, the management of which poses a significant environmental and technological challenge. Modern waste management strategies aim to move away from the linear model in favor of a circular economy, in which the largest possible proportion of material remains in circulation (HU et al. 2024). Following the terminology of ISO 15270:2008 and the waste hierarchy of the EU Waste Framework Directive, which ranks prevention, preparing for re-use and recycling above other recovery (including energy recovery) and disposal (Directive 2008/98/EC), the primary approaches to plastic waste management include:

• material recycling – also known as mechanical recycling, involves reprocessing plastic without intentionally breaking down its chemical structure. For thermoplastics, this process typically encompasses sorting, shredding, cleaning, drying, and reprocessing, often utilizing extrusion and granulation. The resulting regranulate can be used to manufacture new products. Proper sorting is crucial, as the presence of different or incompatible polymers and contaminants can impair the properties of the recyclate (MUZATA et al. 2024). Additives such as colorants, plasticizers, stabilizers, and fillers also present challenges. Repeated processing can cause chain degradation, oxidation, or cross-linking, leading to changes in molar mass, viscosity, and mechanical properties (LOGAN et al. 2024). Techniques such as compatibilization and modification of recyclates are employed for mixtures and multi-material waste. Upcycling is another developing approach, aiming to produce materials with higher utility value (MUZATA et al. 2024);

• feedstock recycling – also referred to as chemical recycling, involves the deliberate breakdown of polymers into monomers, oligomers, or other chemical compounds suitable for reuse. It is particularly significant for polymers containing cleavable bonds, such as polyesters, polyamides, and polycarbonates. A prime example is PET, which can undergo hydrolysis, glycolysis, or methanolysis to yield raw materials that can be used in the resynthesis of the polymer (HU et al. 2024). Feedstock recycling also encompasses thermochemical processes, primarily pyrolysis and gasification (SCHADE et al. 2024, VUPPALADADIYAM et al. 2024). It should be emphasized that, under EU law, thermochemical outputs may be counted as recycling only when they are used as chemical feedstock (e.g., for the production of new monomers or polymers), since the reprocessing of waste into materials intended to be used as fuels is excluded from the legal definition of recycling (Directive 2008/98/EC);

• energy recovery – is a distinct waste management method aimed at utilizing the energy content of waste, typically through incineration with heat recovery and electricity generation (BRUNNER, MORF 2025). The high calorific value of many plastics allows them to serve as fuel in suitably equipped facilities. However, the process requires effective emission control and flue gas treatment, particularly when dealing with PVC-containing waste, due to the potential formation of hydrogen chloride (VUPPALADADIYAM et al. 2024). Assessing the viability of energy recovery requires considering not only the energy yield but also the environmental and economic aspects of the entire process (JUNG et al. 2024). Since energy recovery does not preserve the material or allow for the recovery of raw materials for new polymer production, it should serve as a supplementary solution within the waste management hierarchy, applied primarily to waste fractions for which material or feedstock recycling is technically or economically unfeasible (VLASOPOULOS et al. 2023).

The choice of technology depends primarily on the polymer type, waste purity and homogeneity, the presence of additives, and the feasibility of sorting and further utilization (LUO et al. 2024). Pyrolysis, i.e., thermal decomposition in the absence of oxygen, enables the conversion of waste, particularly polyolefins, into liquid, gaseous, and solid products, including hydrocarbon mixtures (LAGHEZZA et al. 2024). The process dynamics and product composition depend on factors such as temperature, residence time, reactor type, and the use of a catalyst (GAO et al. 2024). Gasification leads to more extensive material conversion, yielding synthesis gas composed mainly of carbon monoxide and hydrogen, which can serve as fuel or a chemical feedstock (VUPPALADADIYAM et al. 2024). For waste containing PVC, the formation of hydrogen chloride must be taken into account, necessitating appropriate purification of the process products. Consequently, the pyrolysis of halogen-containing waste requires careful process design, emission control, and the management or recovery of halogens (MA et al. 2024). In addition to conventional thermochemical methods, processes

enabling the more selective conversion of polymers into monomers and low-molecular-weight products are also being developed. Examples include light-driven processes capable of depolymerizing specific materials and recovering compounds with potential value as raw materials (WIMBERGER et al. 2024). Thus, the development of chemical recycling encompasses both depolymerization processes aimed at monomer recovery and thermochemical technologies capable of processing more complex waste streams (SCHADE et al. 2024). Material recycling is most beneficial for clean, homogeneous thermoplastic streams, as it allows for the preservation of material value with relatively little transformation (LOGAN et al. 2024). Feedstock recycling, on the other hand, can enable the management of waste that is difficult to process mechanically, such as polymer mixtures and certain multilayer materials, though it typically entails greater technological complexity and higher energy demands (LUO et al. 2024). Energy recovery remains a solution for waste fractions where higher levels of recovery are neither feasible nor efficient (VLASOPOULOS et al. 2023).

Table 6

Comparison of the main routes of plastic waste management

| Criterion | Mechanical recycling | Chemical recycling: depolymerization | Chemical recycling: pyrolysis, gasification | Energy recovery |
|---|---|---|---|---|
| Principle | Reprocessing without intentional change of chemical structure | Selective cleavage of main-chain bonds to monomers or oligomers | Thermal cracking to hydrocarbon mixtures or synthesis gas | Combustion with heat and/or electricity recovery |
| Suitable waste streams | Clean, sorted, homogeneous thermoplastics | PET, PA, PC, PU; PMMA | Mixed and contaminated polyolefins, multilayer materials | Residual, non-recyclable fractions |
| Products | Regranulate | Monomers of virgin-like quality | Pyrolysis oil, gas, char; syngas | Heat, electricity |
| Energy demand and complexity | Low | Medium to high (reagents, purification) | High (elevated temperatures, product upgrading) | Net energy recovery |
| Main limitations | Degradation, contaminants and additives; downcycling | Limited to specific chemistries; purification costs | Low selectivity; HCl from PVC; only feedstock use counts as recycling | Loss of material; emissions and flue gas treatment |
| Position in the waste hierarchy | Recycling | Recycling | Recycling only when products are used as chemical feedstock | Other recovery |

Source: own elaboration based on Directive 2008/98/EC, ISO 15270:2008, HU et al. (2024), LOGAN et al. (2024), LUO et al. (2024), SCHADE et al. (2024), VUPPALADADIYAM et al. (2024) and VLASOPOULOS et al. (2023).

A comparison of the waste management routes (Table 6) shows that none of them is universally superior; they should be regarded as complementary elements of an integrated system in which the route is selected according to the properties of a given waste stream (Fig. 2). Mechanical recycling has the lowest energy demand and, for clean and homogeneous streams, usually the most favorable environmental profile, but repeated processing and contamination lead to a gradual loss of properties, which often results in downcycling (LOGAN et al. 2024, MUZATA et al. 2024). Depolymerization can provide monomers of virgin-like quality, but it is technically and economically justified mainly for polymers with cleavable heteroatom-containing main chains, such as PET, polyamides, polycarbonates and polyurethanes. For polyolefins, which constitute the largest share of plastic waste, the C–C backbone makes selective depolymerization difficult, and thermochemical processes yielding hydrocarbon mixtures predominate (CLARK, SHAVER 2024, GAO et al. 2024, LOHMANN et al. 2024). Moreover, the environmental benefit of chemical recycling is not self-evident and depends on process yields, energy demand and the end use of the products.

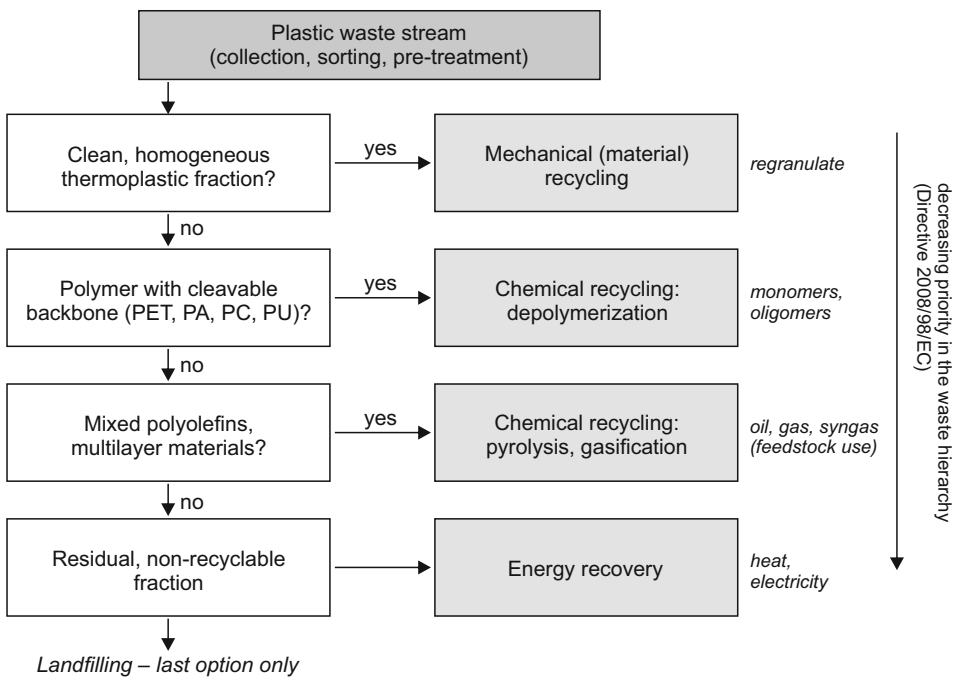



Fig. 2. Simplified scheme for selecting the plastic waste management route according to the properties of the waste stream and the waste hierarchy
Source: own elaboration based on Directive 2008/98/EC, ISO 15270:2008, LUO et al. (2024) and SCHADE et al. (2024).

The comparative assessment of recycling routes should therefore be based on life cycle assessment (LCA) and techno-economic analysis performed with consistent system boundaries (VLASOPOULOS et al. 2023, JUNG et al. 2024, LUO et al. 2024); such comparable data are still scarce.

## Prospects and development directions of plastics technology

The development of plastics is being dynamically shaped by growing environmental, technological, and social demands. Key directions in plastics technology development are expected to include:

**• bioplastics and biopolymers**

The term "bioplastics" covers two partly overlapping groups of materials: bio-based plastics, produced wholly or partly from renewable raw materials such as plant starch, cellulose or vegetable oils, which are not necessarily biodegradable (e.g., bio-PE, bio-PET), and biodegradable plastics, which may also be fossil-based (e.g., PCL). Examples include PLA (polylactic acid) and PHA (polyhydroxyalkanoates), which are both bio-based and biodegradable; PLA decomposes mainly under industrial composting conditions, whereas PHA can also biodegrade in natural environments. Bioplastics have the potential to reduce reliance on fossil fuels and limit greenhouse gas emissions. In applications such as food packaging, medicine, and agriculture, bioplastics offer eco-friendly alternatives, although their production and mechanical properties still require optimization (GHASEMLOU et al. 2024).

**• chemical recycling of plastics**

Chemical recycling involves processes that break down plastics into their basic monomers or other chemical compounds, which can then be reused to manufacture new polymers. Methods such as pyrolysis (thermal decomposition in the absence of oxygen), gasification, and depolymerization enable the recovery of raw materials from waste that is difficult to process mechanically. While chemical recycling can significantly improve resource efficiency and reduce the volume of waste sent to landfills, it requires advanced technologies and is costly (see Section Plastics recycling: Material recycling, feedstock recycling, and energy recovery Table 6) (BABAEI et al. 2024, FRISA-RUBIO et al. 2021).

**• nanocomposites in plastics**

Nanocomposites are materials in which conventional plastics are enhanced with nanoparticles, such as carbon nanotubes, graphene, nanoclays, or silica and metal-oxide nanoparticles. This allows for significant improvements in mechanical properties (strength, hardness), thermal properties (high-temperature resistance),

electrical properties (conductivity), and barrier properties (protection against gases and moisture). Nanocomposites are used in the automotive, electronics, packaging, and medical industries. Challenges include, among others, the uniform dispersion of nanoparticles and the safety of their use (YADAV et al. 2025b, LI et al. 2024).

**• microbial biodegradation of plastics**

Microbial biodegradation involves the breakdown of plastics by microorganisms, such as bacteria and fungi, or enzymes that decompose polymers into simpler organic compounds. Research focuses on identifying and engineering microorganisms capable of efficiently degrading common plastics such as polypropylene (PP), polyethylene (PE) and poly(ethylene terephthalate) (PET); however, the biodegradation of polyolefins, whose C–C backbones are highly resistant to enzymatic attack, remains very slow and is still far from technological application. Modern approaches also include creating microbial consortia and enhancing biodegradation through the use of nanomaterials. This technology could significantly contribute to reducing plastic pollution in the environment (YADAV et al. 2025a, SUTKAR, DHULAP 2025).

**• intelligent and functional plastics**

Intelligent plastics are materials that respond to external stimuli, such as changes in temperature, light, pH, or humidity. Examples include self-healing plastics, which can restore their integrity after damage (PENG et al. 2023), and chromogenic materials, which change color in response to temperature, light or pH. Applications include active packaging that can provide information about product freshness, medicine (e.g., drug carriers that respond to body conditions), and flexible electronics. These technologies combine advanced polymer chemistry with electronics and sensors (PUČNIK et al. 2024, REGMI et al. 2025, ARIJENIWA et al. 2024).

**• 3D printing and additive technologies in plastics**

3D printing enables the production of complex plastic structures layer by layer, enabling rapid prototyping and product customization. Various polymers are used, including biodegradable polymers and composites. 3D printing has the potential to reduce production waste and enable material recycling by reusing plastic waste. Applications include medicine (implants, prosthetics), the automotive and aerospace industries, and the production of tools and spare parts (PARK et al. 2022, MALIK, KUMAR 2024, OYINLOLA et al. 2023).

The future of plastics will be shaped by the development of more environmentally friendly materials, advanced recycling technologies, functional and intelligent materials, and innovative production methods such as 3D printing. Challenges will include further optimizing material properties, production costs, and ensuring safety and sustainability.

## Critical synthesis and research gaps

The reviewed literature allows several cross-cutting observations to be formulated. First, the structure–synthesis–processing–application–end-of-life chain (Fig. 1) is strongly coupled: the same features that provide high performance – high molar mass, high crystallinity, dense covalent networks, multi-material constructions and functional additives – usually make reprocessing more difficult. This is most evident for thermosets and vulcanized elastomers, which cannot be remelted (SELVIN et al. 2024, SHAPIRO et al. 2024), and for multilayer packaging, which is difficult to separate (MUZATA et al. 2024). Second, the chemistry of the main chain largely determines the available recycling routes: polymers with cleavable heteroatom-containing linkages (polyesters, polyamides, polycarbonates, polyurethanes) can be depolymerized relatively selectively, whereas for polyolefins and other polymers with C–C backbones, chemical recycling relies mainly on less selective thermochemical processes (CLARK, SHAVER 2024, LOHMANN et al. 2024, SCHADE et al. 2024). Third, processing conditions not only shape the product but also determine its morphology and degradation history, and thus its service properties and suitability for subsequent recycling (CUNHA et al. 2022, BANERJEE 2023).

The main technological limitations identified in this review include: (i) the gradual deterioration of the properties of mechanically recycled materials due to chain scission, oxidation, cross-linking and contamination (LOGAN et al. 2024); (ii) the high energy demand, need for product upgrading and limited selectivity of pyrolysis and gasification, including the problem of halogens in PVC-containing waste (MA et al. 2024, VUPPALADADIYAM et al. 2024); (iii) the limited thermal stability and potential migration of functional additives, including antimicrobial agents (CHANDRA et al. 2025); and (iv) the still unsatisfactory balance between performance and cost of bio-based and biodegradable polymers (GHASEMLOU et al. 2024).

Unresolved scientific problems and research gaps include: the design of dynamic (covalent adaptable) networks that combine the durability of thermosets with reprocessability (CERDAN et al. 2024, REN, DONG 2024); catalytic and low-temperature routes for the selective conversion of polyolefins into monomers or high-value chemicals (GAO et al. 2024, WIMBERGER et al. 2024); a quantitative description of how additives and contaminants affect recyclate quality and how they should be accounted for in LCA (LOGAN et al. 2024); the long-term safety, release and end-of-life fate of nano-sized and antimicrobial additives (SU et al. 2025); efficient enzymatic and microbial degradation of non-hydrolysable polymers (SUTKAR, DHULAP 2025, YADAV et al. 2025a); and the lack of harmonized life cycle and techno-economic data enabling an objective comparison of mechanical recycling, chemical recycling and energy recovery (JUNG et al. 2024, LUO et al. 2024).

Areas requiring further development therefore include design for recycling (mono-material solutions, compatibilizers, reversible linkages), advanced sorting based on sensors and machine learning (PUČNIK et al. 2024), process modeling and monitoring enabling the processing of recyclates of variable quality (CUNHA et al. 2022, EDELEVA et al. 2023), and the integration of functional properties, such as antimicrobial activity or stimulus responsiveness, with recyclability and safety requirements. These directions are consistent with the increasing regulatory pressure in the European Union, including mandatory recycled-content targets for plastic packaging (Regulation (EU) 2025/40).

## Summary and conclusion

This review has provided an integrated overview of polymer materials technology, from macromolecular structure through synthesis and processing to applications and end-of-life management. The most important conclusions are as follows:

1. The physicomechanical and thermal properties of polymeric materials are determined by their chemical structure, chain architecture, molar mass distribution, tacticity, degree of crystallinity and cross-link density; the same parameters also determine processability and the available end-of-life options.

2. Chain-growth and step-growth mechanisms differ fundamentally in the relationship between conversion and molar mass, which dictates the choice of industrial technique: in chain-growth processes, heat removal and microstructure control (catalysts, controlled radical polymerization) are critical, whereas in polycondensation, the efficient removal of by-products is decisive.

3. Kinetic relationships – the steady-state kinetics of radical polymerization, the Mayo–Lewis equation and the Carothers equation – explain how initiator concentration, temperature, comonomer reactivity, conversion and stoichiometry control molar mass and composition, while complementary characterization methods (FTIR, NMR, SEC, DSC, TGA, DMA and standardized mechanical tests) link the synthesis conditions with the performance properties of the material.

4. Processing (extrusion, injection molding, thermoforming and other methods) shapes not only the geometry of a product but also its morphology, molecular orientation and degradation history, and thus its service properties and recyclability.

5. Functional additives, including antimicrobial agents, broaden the range of applications of plastics (e.g., in food packaging and medical products), but their thermal stability, migration, regulatory status and impact on recycling should be considered already at the design stage.

6. No single waste management route is universally optimal. Mechanical recycling should remain the preferred option for clean, homogeneous thermoplastic

streams; depolymerization is most promising for condensation polymers; thermochemical processes are suited to mixed polyolefin and multilayer waste; and energy recovery should be limited to residual fractions that cannot be recycled.

7. The main technological limitations and research gaps concern the quality of recyclates, the recycling of thermosets, elastomers and multilayer materials, the selective chemical recycling of polyolefins, the end-of-life fate of additives and the lack of comparable LCA and techno-economic data.

Further development of polymer materials technology will therefore require simultaneous optimization of performance, cost, safety and circularity, in which design for recycling, dynamic polymer networks, advanced sorting and bio-based materials are expected to play a key role.

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