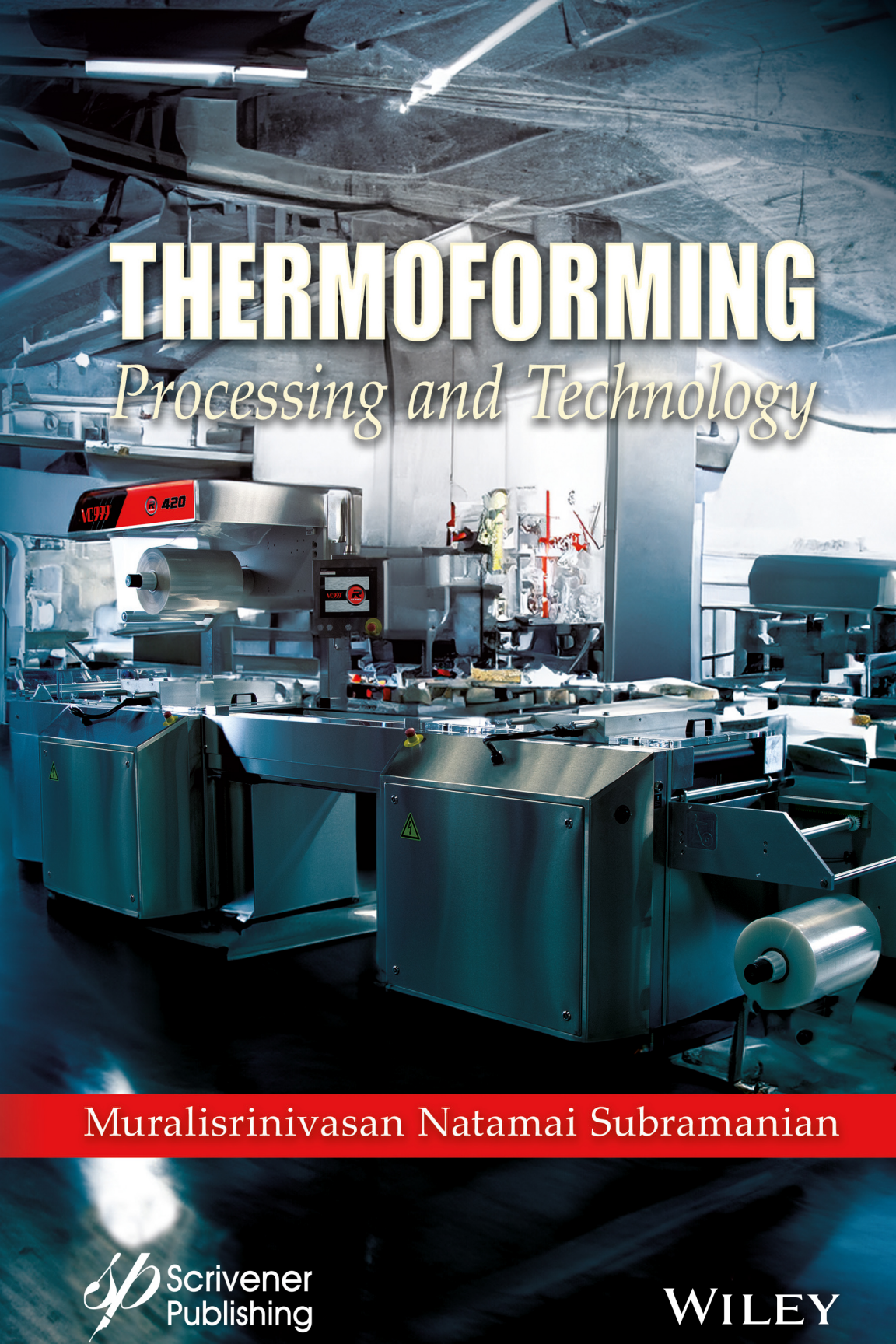
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Muralisrinivasan Natamai Subramanian

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Preface

The field of thermoforming is experiencing rapid development driven by commercial factors. Today, millions of tons of polymers are manufactured for use in various applications, both as commodity and specialty polymers.

The first edition of the book *Update on Troubleshooting in Thermoforming* was published nearly a decade ago by iSmithers Rapra, UK. The second edition, titled *Thermoforming – Processing and Technology*, aims to incorporate new and revised material on recent developments in thermoforming. This edition includes new, fully revised chapters and updated information on materials and processes.

The book is designed to provide practitioners and students with essential information on processing and technology in a concise and portable format. It is a valuable resource for polymer processors, engineers, technologists, and students, offering a comprehensive update on thermoforming. The book caters to both engineers and experts in physics and chemistry, providing introductory aspects, background information, and an overview of thermoforming processing and technology. The troubleshooting section includes flowcharts to assist in correcting thermoforming processes.

Thermoforming – Processing and Technology offers a complete account of thermoplastics, covering properties and forming, with chapters providing perspective on the technologies involved. The book is practical and mechanistic in its approach, making it useful for both industry professionals and academics. It serves as a self-contained reference manual and is engaging, accessible, and attractively presented. It would be a valuable addition to any research group with an interest in polymers, particularly in the field of thermoforming.

I am deeply thankful to the people who have made significant sacrifices of their personal time to prepare the book. This includes my parents who raised me, my wife Himachalaganga, and my children Venkatasubramanian, Amrutha and Sailesh. I am also grateful to those who have supported me in my education and career, including my professors and teachers. Above all Lord Natarajar, who brought me to this world, and my Guru,

Thiruchendur Subramanya Swamy, who provided his knowledge to write this book. Furthermore, I would like to express my gratitude to Mr. Martin Scrivener and his team at Scrivener Publishing for their invaluable assistance in bringing this book to fruition.

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Madurai, India

1

Introduction

Thermoforming was one of the earliest methods for fabricating thermoplastic materials. This involves shaping thermoplastic sheets into distinct parts. The United States has contributed to plastic processing methods. However, most of these techniques originated in Europe. It was not until the mid-twentieth century that a comprehensive understanding of its true nature was achieved [1].

Thermoforming has undergone significant growth and development with the introduction of cellulosic sheet materials, followed by acrylic and vinyl. In the 1890s, baby rattles and teething rings were thermoformed, but growth was slow until the 1930s, when roll-fed machines were developed in Europe. This process made significant progress in the 1950s using high-impact polystyrene for manufacturing containers and lids in the dairy industry. In addition, it has been used in the production of signage, exhibits, toys, and packaging materials. Initially, the thermoforming industry was limited by the lack of suitable sheet materials and forming equipment. However, in recent years, the process has rapidly advanced due to its advantages such as low machine and mold costs, low temperature and pressure requirements, ease of forming large parts, and fast mold cycles [2].

The emergence of plastics, synthetic materials that showcase human creativity and ingenuity, coincided with this understanding. Among the various methods utilized for processing plastics, thermoforming is a widely used technique for shaping extruded sheets into desired forms. This process is commonly used to produce large parts with low production volumes. It is a more cost-effective alternative to injection molding, which incurs higher expenses due to substantial fixed costs.

Thermoforming is a straightforward processing technology [2]. This involves modifying polymeric materials or systems to enhance their usefulness. Thermoforming is a cost-effective alternative to other plastic molding and forming methods. The process discussed here is often associated with the production of packaging materials such as blister packs and disposable

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coffee cup lids. However, it is important to note that the cost and time benefits of this process can be extended to a wide range of products in various industries.

Thermoplastics dominate the global polymer market and account for 85% of all polymers [3]. Most thermoplastic production focuses on large-volume, low-cost commodity resins, such as polyethylene, polypropylene, polystyrene, and polyvinyl chloride. Engineering plastics, such as acrylics, acrylonitrile-butadiene-styrene (ABS), and high-impact polystyrene (HIPS), are chosen for their performance and cost-effectiveness. However, there is an increasing demand for high-performance materials, which has led to the utilization of engineering plastics such as polyacetal (POM), polyamides (PAs), and polycarbonate (PC), and polyesters such as polyethylene terephthalate (PET), polybutylene terephthalate (PBT), and polypropylene oxide, as well as their blends. Polymers such as liquid crystalline polymers, polyetheretherketone (PEEK), and fluoropolymers are commonly used in high-temperature applications [4].

Thermoforming presents numerous advantages over alternative thermoplastic fabrication techniques. These advantages encompass several aspects, such as the ability to fabricate components with a large surface area, reduced expenses for molds and equipment due to its low-pressure requirement, the capability to produce extremely thin-walled parts, increased production rates for high-volume thin-walled products, and the ability to manufacture low-volume heavy-gauge products at lower tooling costs [5].

This realization coincided with the advancement of plastics, which are synthetic materials that showcase human ingenuity and resourcefulness. The process involves shaping the thermoplastic sheets into precise components. Thermoforming has gained considerable importance as a method for processing plastic sheets, particularly for producing larger components [6].

Thermoplastics, which have gained significant popularity in the global polymer market, are exceptionally suitable for thermoforming processes because of their ability to be produced in high volumes at lower costs. This versatile procedure can be used for any thermoplastic sheet material, which demonstrates the necessary dimensional stability and impact resistance. Thermoforming presents numerous advantages over alternative thermoplastic fabrication techniques.

The market for thermoforming is experiencing growth due to its increasing use in the production of complex shapes and a wider range of materials. Thermoforming is widely regarded as a viable and economically advantageous alternative to various plastic molding and forming methods.

The development of applications has largely been brought about by the introduction of new manufacturing methods. New methods have encouraged the development of new forming machines and techniques. This has brought the thermoforming industry to a new level in terms of processing technology.

2

Polymers

2.1 Introduction

Polymers have experienced steady market growth and are widely acknowledged as a significant category of materials. These materials possess characteristics such as affordability, ease of manipulation, and versatility, rendering them suitable for a diverse array of applications. These applications encompass a wide range of household items, packaging materials, advanced fibers, medical devices, and wearable electronics. The application of polymers has greatly enhanced our standard of living and sparked revolutionary progress in various sectors [1, 2].

The prevalence of synthetic polymers can be attributed to the fact that 90% of these polymers are derived from finite fossil feedstock. The incorporation of these materials into diverse products is driven by their exceptional stability, processability, versatile mechanical properties, and durability. Although the terms plastics and polymers are often used interchangeably, it is crucial to acknowledge that there is a subtle distinction between them [3, 4].

Polymer engineering encompasses the technological processes used for the complete synthesis of meticulously regulated macromolecules. The objective of polymer engineering is to attain mastery over the physical characteristics of macromolecules, encompassing factors such as molecular weight, molecular weight distribution, end functionality, tacticity, stereochemistry, block sequence, and block topology. Polymers find applications in a wide range of consumer products such as carpets, furniture, glues, and clothing. In addition, they play a crucial role in advanced engineering, particularly in the development of materials used in the aerospace industry. Therefore, the utilization of polymers and their constituent monomers is important in our daily lives [5].

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2.2 Physics and Chemistry of Polymers

The study of polymer materials is a complex and intriguing subject in physics and chemistry. The structure of a polymer is determined by the number and type of repeating units it contains. Polymer science investigates the characteristics, composition, and behavior of these substances at the atomic, molecular, and macroscopic levels. This multidisciplinary field combines concepts from biology, engineering, chemistry, and physics to understand and manipulate material properties for specific purposes. Many polymeric materials exhibit emergent properties, which are unique characteristics arising from the interaction of their constituent monomers.

One particularly fascinating aspect of chemistry and polymer science is the ability to transition materials between different phases, particularly in relation to the monomers. These transitions allow the manipulation of materials for real-world applications. This process is not only scientifically intriguing, but also essential for the development of new and innovative materials with a wide range of uses in modern technology and everyday life. This is particularly true for monomers that form polymers [6, 7].

Polymer molecules consist of a sequence of monomers that are joined by chemical bonds. The orientations of these bonds between successive monomers are correlated with those of adjacent monomers and crossing energy barriers is necessary for a bond to change its orientation. The arrangement of monomers within a polymer significantly affects its characteristics. Describing the behavior of materials at different length scales, from atomic interactions to macroscopic properties, is challenging. The development of polymer materials with specific properties is crucial for numerous technological advancements.

Even small variations in the arrangement of monomers can lead to significant differences in the material behavior. Polymers are highly versatile due to their flexible design, structure, and chemical composition, allowing them to exhibit a wide range of properties that can be tailored to meet specific requirements [8].

2.3 Natural Polymers

Natural polymers, which are associated with biopolymers, are formed through metabolic processes in living organisms [9]. These polymers consist of monomeric units that are linked by covalent bonds. Examples of natural polymers include proteins such as collagen and silk fibroin as well

as polysaccharides such as chitosan, alginate, hyaluronic acid, and cellulose [10]. These polymers play important roles in nature, including the preservation and transmission of genetic information and the storage of cellular energy. One of their key advantages is their ability to biodegrade, with the released CO_2 rapidly absorbed by agricultural crops and soil. Among polysaccharide biopolymers, cellulose is particularly abundant and is present in approximately 33% of all plant components [11, 12]. Other notable natural polymers include chitin/chitosan, starch, and lignin. Chitosan, alginate, cellulose, lignocellulose, starch, and PVA are among the most promising and frequently studied natural polymers, either as standalone materials or in combination with other advanced materials [13].

2.4 Synthetic Polymers

Synthetic polymers belong to a distinct class of polymers derived from crude oil, petrochemicals, natural gas, or biomass. These polymers possess a wide range of desirable characteristics such as low density, high durability, and resistance to deterioration. In addition to their advantages in terms of weight and cost, polymer products offer enhanced durability that can help prevent damage during transportation. Furthermore, many polymers exhibit corrosion resistance, making them well suited for use in harsh environments, such as chemical manufacturing facilities [14].

Polymerization, which involves chemically bonding monomers to form long chains, is utilized to produce synthetic polymers, which are subsequently used in various manufacturing processes. Synthetic polymeric networks consist of repeatable inert units and are generally superior to natural polymers in terms of mechanical properties and immunogenic responses [15].

Synthetic polymers offer tailored structures and properties through the appropriate design of their functional groups. These advantages ensure predictable, reproducible, and adjustable properties, which can vary according to specific applications. For example, the degradation rate of synthetic polymers can be altered by manipulating their chemical compositions, crystallinities, and molecular weights.

The ability to process and shape polymers enables the efficient mass production of a diverse range of items. Techniques, such as injection molding, extrusion, blow molding, and thermoforming, facilitate the creation of complex designs and ensure reliable quality. The lightweight nature of plastic products contributes to reducing shipping expenses and energy

consumption. Moreover, manufacturing products from plastics is often more cost-effective than manufacturing conventional materials [16].

2.5 Polymerization Methods

During the polymerization process, monomers undergo chemical bonding to form extensive chains or networks, resulting in the development of unique polymer properties. This chemical reaction, known as a polymerization reaction, leads to the formation of high-molecular-weight molecules from the monomers [17]. The structural features of polymers, such as linear, branched, or network configurations, are determined by the arrangement of monomers and the types of chemical bonds that connect them. The ability to manipulate the structure and composition of polymers is crucial in various industries and applications. Two primary approaches are utilized in the production of polymers: addition and condensation polymerization. Both mechanisms can be used in the polymerization of the same monomer or different monomers can be used to create the same polymer through both approaches, provided that suitable functional groups are available for each individual polymerization. Addition and condensation polymerizations are both essential in the creation of diverse polymers, fibers, rubbers, and other materials that have extensive applications in everyday life and industry. The selection of specific monomers and the desired characteristics of the final polymer product determine the appropriate polymerization method [18, 19].

2.5.1 Addition Polymerization

In this process, the reaction between monomers containing double or triple bonds leads to the formation of polymer chains. This involves the breaking of the double or triple bonds and the subsequent connection of the monomers without the production of any byproducts. The double bonds of the monomers react without releasing any molecules. These reactions occur *via* the addition of monomer molecules *via* unsaturated (double) bonds [20].

The initiation of the reaction can be achieved using chemical molecules, such as azo compounds or peroxides, or through physical sources, such as heat or electromagnetic radiation. These initiators create radicals, anions, or cations in the monomer. Depending on the type of initiation, addition polymerization can be classified as radical, anionic, cationic, or

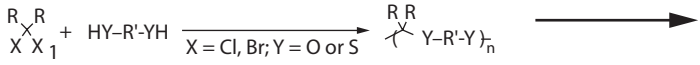
coordination polymerization. All addition polymerizations involve three stages: initiation, propagation, and termination [18, 21].

In the case of addition polymerization, a reactive center such as a radical, an anion, or a cation must first be created on a molecule that contains a double bond. New monomer molecules are then successively added to this active molecule, creating a new active center for further addition. This process continues until the reaction is terminated by other reactions or events. Termination results in the formation of "dead" polymer, which is no longer capable of further reaction. During these reactions, addition must be initiated and typically involves a termination reaction. No small molecules, such as water or alcohol, are released during this process [22].

The most common type of addition polymerization is free-radical polymerization. Most radical polymerizations require an initiator to generate the initial active radical and initiate a chain of addition reactions. The most common initiation reaction is the thermal decomposition of molecules containing weak bonds such as peroxides (–OO–) or azo compounds (–N=N–). Addition polymerization is generally rapid and can be moderately or highly exothermic. Additionally, polymerization of an individual chain is completed quickly, resulting in the formation of high-molecular-weight products even in the early stages. The concentration of monomers in the medium slowly decreased over time [23]. The most significant group of addition polymerizations involves the combination of monomers, such as ethylene, propylene, styrene, and vinyl chloride, which give rise to polyethylene, polypropylene, polystyrene, and polyvinylchloride, respectively.

2.5.2 Condensation Polymerization

The homogeneous two-component polycondensation reaction holds significant historical importance in the field of polymer science. Achieving a consistently high degree of polymerization (DP) is a crucial consideration in polymer synthesis, as the desired physical properties often arise from high molecular weights. Condensation polymerization involves the reaction between two distinct functional groups present in monomers. This process entails the elimination of small molecules, such as water, alcohol, or ammonia, while simultaneously forming a polymer chain from monomers that possess two or more functional groups, such as –OH and –COOH. The reaction occurs in multiple phases, with each phase releasing a small molecule, hence earning the designation of a "condensation" reaction [24] and presented in Equation (2.1).



(2.1)

It is applicable to monomers that possess functional groups, such as -COOH, -COOR, -COOOC-, -COCl, -OH, -NH2, -CHO, -NCO, and epoxy. In condensation polymerization, the reactive groups located at the ends of each monomer react with one another. Consequently, a growing chain is formed with reactive groups at both ends, and when two chains combine, the length of the chain immediately increases.

However, the increase in the molecular weight of the product in condensation polymerization is slow due to the addition of growing chains to each other, leading to a depletion of monomers at the initial stages. Condensation polymerization is typically characterized by its slow rate, limited by equilibrium, and slightly exothermic nature [25].

In condensation polymerization, two functional groups form a bond by releasing a small molecule such as H_2O. While there are some condensation reactions where no molecule release occurs, such as polyurethane polymerization, nylon 6 is an example of a polymer with repeating units $-NH(CH_2)_5CO-$. It can be synthesized through either condensation of 6-aminocaproic acid or addition polymerization of caprolactam [26].

Furthermore, there have been recent advancements in polymerization techniques, including click polymerization, atom transfer radical polymerization (ATRP), and reversible addition-fragmentation chain transfer polymerization (RAFT). These techniques employ specialized catalysts and agents to produce polymers with controlled molecular weights, offering new possibilities for polymer design [27–29].

2.6 Polymer Molecules in Thermoforming

The behavior of polymeric materials is influenced by the chemical composition and physical structure of both the penetrant molecule and polymer itself. These factors play a crucial role in determining the mobility of the chain segments, presence of defects, and interactions that govern the extent of sorption and molecular mobility of the penetrant within the polymer.

Anisotropy, or directional dependence, occurs in polymers when the links of the polymeric chain align in the direction of stretching. In thermoforming, anisotropy is associated with the temperature at which a transition between two or more phases occurs as well as the temperature at which a change of state, such as melting, occurs. The molecular structure of

the polymer contributes to these transitions, which depend on the monomer structure, degree of orientation, and extent of stretching at specific temperatures. It is important to note that a given transition in polymers can arise from either the amorphous or the crystalline phase.

Generally, polymers exhibit significant changes in their physical properties as a function of temperature. The theory of rubber elasticity states that strained elastomers with a low degree of crosslinking exhibit a combination of orientation and segmental motion. However, in stretched amorphous polymers, segmental motion is absent because it can only exist below the glass transition temperature. This resulted in a frozen-in orientation. By subjecting amorphous linear polymers to strain at temperatures above the glass transition temperature, they can be brought into an anisotropic state. Once cooled below the glass transition temperature, the polymer remains in the stretched state even when unloaded.

In mechanical applications, the amorphous regions between crystallites largely determine the response to stress, giving polymers desirable qualities such as ductility and toughness. In electronic applications, it is believed that tie molecules spanning adjacent crystalline lamellae can improve field-effect charge carrier mobility [30].

2.7 Classification

Polymers are classified on the basis of their unique properties, characteristics, or attributes. The objective of this categorization is to methodically arrange these elements and their connections, promoting comprehension and enabling a deeper investigation within each specific category.

2.8 Primary Classification

In the field of polymer science, plastics can be classified into two fundamental groups: homopolymers and copolymers, which are distinguished by their distinct molecular structures.

2.8.1 Homopolymers

Homopolymers possess a consistent and uniform structure throughout their composition because they are composed of identical repeating units of a single monomer. Despite their uniformity, the properties of

homopolymers can still be modified by adjusting various factors, such as the processing parameters, molecular weight, or monomer structure [31].

The chemical structure of homopolymers is relatively straightforward, allowing relatively easy synthesis. Depending on the specific monomer and polymerization conditions, homopolymers can exhibit varying degrees of crystallinities. Higher levels of crystallinity can enhance mechanical properties but may reduce transparency. The homogeneous structure of homopolymers generally makes them more suitable for processing, making them applicable to a range of production techniques, including injection molding, extrusion, blow molding, and thermoforming. Additionally, homopolymers typically possess high thermal stability, enabling them to withstand high temperatures without significant degradation. This thermal resistance makes them valuable for applications that require heat resistance [32].

Homopolymers are known for their inherent rigidity, which is attributed to their high elastic modulus. This characteristic renders them particularly advantageous in scenarios where maintaining structural integrity is of utmost importance. Additionally, many homopolymers exhibit exceptional optical clarity, making them highly suitable for applications that necessitate transparency and visual acuity, such as display screens, optical lenses, and transparent packaging materials. Moreover, homopolymers generally offer a more cost-effective solution compared to copolymers or more intricate polymers due to their straightforward chemical composition and ease of production. However, it is crucial to acknowledge that homopolymers possess a limited range of properties, which can be perceived as a drawback [33].

2.8.2 Copolymers

The blending of polymeric substances is a cost-effective and straightforward method to create new materials with enhanced mechanical properties. It is anticipated that copolymers will exhibit a wider melting temperature range and a sigmoidal relationship between their crystallinity and temperature. When two polymer surfaces that are not soluble in each other come into contact, it is expected that their surface functionality will arrange or structure themselves in a way that minimizes free energy. Understanding the structure of polymer/polymer interfaces is crucial in various areas such as adhesion, polymer blends, and nanocomposites [34].

These new multiphase materials can be obtained as blends, block copolymers, and graft copolymers, all of which typically consist of two or more polymeric phases in the solid state. It is important to differentiate these

materials from composite materials. Most homopolymer phases are insoluble in each other, resulting in materials with low strength due to the lack of interfacial adhesion [35].

Copolymers have a narrower range of compositions than blends, but they offer several advantages. The different segments in the copolymers are covalently bonded, eliminating the interface problem [36]. The molecular architecture of copolymers can be precisely controlled to produce novel materials. Copolymers can also strengthen blends of immiscible polymers by acting as emulsifiers and facilitating physical connections between the phases. This improves the interfacial adhesion and ability to transfer loads between components [37].

In an ordered copolymer, where structural units of a specific type are arranged in long sequences, crystallinity should disappear at a temperature slightly below the melting temperature of the pure polymer. The phase rule cannot be applied to the crystal-amorphous transformation in polymers because the free energy per unit amount of the amorphous "phase" is not a unique function of the composition [38].

The presence of copolymers at the interface between immiscible polymers has been widely recognized for their significant influence on interfacial properties, provided that an appropriate copolymer structure is utilized. The degree of toughening varies depending on the copolymer architecture and the interactions between the copolymer and polymer [39, 40].

2.8.2.1 Block Copolymers

Block copolymers are polymers that consist of two or more distinct sequences joined together by covalent bonds and have different chemical compositions. Blending different homopolymers together to form a block copolymer structure offers unique properties that cannot be achieved by simply blending individual homopolymer components. This is due to the ability of the block copolymer to segregate its chains, resulting in distinct characteristics. There are two types of block copolymers: coil–coil and rod–coil, with the latter having a rigid and inflexible rod-like segment [41].

Unlike homopolymers, block copolymers consist of distinct blocks of different monomers, rather than repeating units of the same monomer. Block copolymers are a fascinating group of polymeric materials that are of great interest in both the scientific and technological fields. These consist of sequences of different homopolymers within the same molecule. These block copolymers had distinct hard and soft blocks with substantially different compositions. In the strong segregation limit, they exhibit

highly ordered long-range organization, which is a result of the interplay between the thermodynamics of polymer interactions, configuration of domain-forming blocks, and minimization of free energy with the morphology of microphase-separated domains [42].

These blocks can vary in size, and their arrangement can result in different morphologies and properties, as depicted in Figure 2.1. Within a block copolymer, blocks can form distinct and specialized regions. This phase separation led to the formation of microdomains with unique characteristics. This property makes block copolymers important in industries, such as nanotechnology and the production of self-assembling materials.

These copolymers tend to separate into different phases on the nanoscale due to the repulsive interaction between their repeating units. This results in the formation of well-organized morphologies, such as alternating lamellae, gyroids, hexagonally packed cylinders, and body-centered cubic spheres. The equilibrium morphology and domain size of block copolymers depend on the balance between the enthalpic contribution associated with short-range segmental interactions and the entropic contribution associated with chain packing and distribution within the microdomains [43].

At equilibrium, a dense collection of monodisperse diblock copolymer chains is arranged in minimum free energy configurations (ordered). Lowering the temperature, i.e., increasing the energy parameter, favors a reduction in the A–B monomer contacts (disordered) [44]. To manipulate the phase behavior of block copolymers, factors such as the volume fraction of components, degree of polymerization, and segmental interaction parameters are considered. Another approach to modify the phase behavior of block copolymers is to blend them with other polymers such as homopolymers or other block copolymers. This blending introduces an additional degree of freedom into the system, resulting in a more complex and diverse phase behavior than that of a neat block copolymer. This enhanced behavior includes microphase separation, macrophase separation, order–order transition, and order–disorder transition. For instance, studies have been conducted on binary block copolymer blends where two

Figure 2.1 Schematic representation of block copolymer.