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THE INFLUENCE OF CHEMICAL COMPOSITION ON THE THERMAL STABILITY OF POLYMERIC MATERIALS

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Annotation

Thermal stability is one of the most critical performance characteristics of polymeric materials, determining their applicability in engineering, industrial, and high-temperature environments. The chemical composition of polymers plays a decisive role in governing their resistance to thermal degradation, structural decomposition, and loss of mechanical properties under elevated temperatures. This article presents a comprehensive scientific analysis of how the chemical structure, molecular architecture, bonding energy, and the presence of functional groups influence the thermal stability of polymeric materials. Special attention is given to the role of backbone structure, side-chain chemistry, crosslinking density, copolymerization, and the incorporation of additives such as stabilizers, fillers, and flame retardants. The methodological framework of the study is based on comparative analysis of experimental thermal analysis techniques, including thermogravimetric analysis and differential scanning calorimetry, supported by theoretical interpretations rooted in polymer chemistry and materials science. The relevance of the topic is justified by the growing demand for thermally stable polymers in aerospace, electronics, construction, and energy sectors. The article identifies key challenges related to thermal degradation mechanisms and proposes scientifically grounded solutions and recommendations for improving thermal resistance through rational chemical design. The findings contribute to the advancement of polymer science by providing a holistic understanding of the chemical factors that control thermal stability and by offering practical guidelines for the development of high-performance polymeric materials.

Keywords

polymeric materials, thermal stability, chemical composition, thermal degradation, molecular structure, polymer chemistry

Introduction. Polymeric materials have become indispensable in modern technology due to their versatility, lightweight nature, cost-effectiveness, and tunable physical and chemical properties. From packaging and consumer goods to advanced aerospace and biomedical applications, polymers have replaced traditional materials such as metals and ceramics in many domains. However, despite their numerous advantages, polymers are often limited by their relatively low thermal stability, which restricts their use in high-temperature environments. Thermal stability refers to the ability of a polymeric material to retain its chemical structure and functional properties when exposed to elevated temperatures over a certain period. Understanding the factors that influence thermal stability is therefore a central issue in polymer science and engineering. Among the various factors affecting thermal behavior, chemical composition occupies a fundamental position. The intrinsic thermal resistance of a polymer is primarily dictated by the nature of its chemical bonds, molecular backbone, side groups, and intermolecular interactions. Small changes in chemical structure can result in significant differences in degradation temperature, decomposition pathways, and char formation.[107] Consequently, the rational design of polymer chemistry offers a powerful approach to enhancing thermal stability without compromising other essential properties. Polymers are classified into thermoplastics and thermosetting plastics. Thermoplastics consist mainly of linear high-molecular-weight polymers or copolymers such as polyethylene, polystyrene, and polyvinyl chloride. Their composition often includes plasticizers and pigments. Plasticizers increase the flexibility and processability of polymers at elevated temperatures, making molded products more elastic and resistant to low temperatures. However, thermoplastics generally lose their mechanical strength at temperatures above 60–100 °C due to their limited thermal stability. The present article aims to provide an in-depth examination of the influence of chemical composition on the thermal stability of polymeric materials. Unlike studies that focus on isolated aspects, this work adopts an integrative perspective, linking molecular-level chemistry with macroscopic thermal behavior. The article is structured to address the relevance of the topic, identify existing problems, describe the methodological approaches used to study thermal stability, analyze key chemical factors, propose solutions and scientific recommendations, and summarize the main conclusions.

[107] Billmeyer, F. W. Textbook of Polymer Science. Wiley, New York, 2017

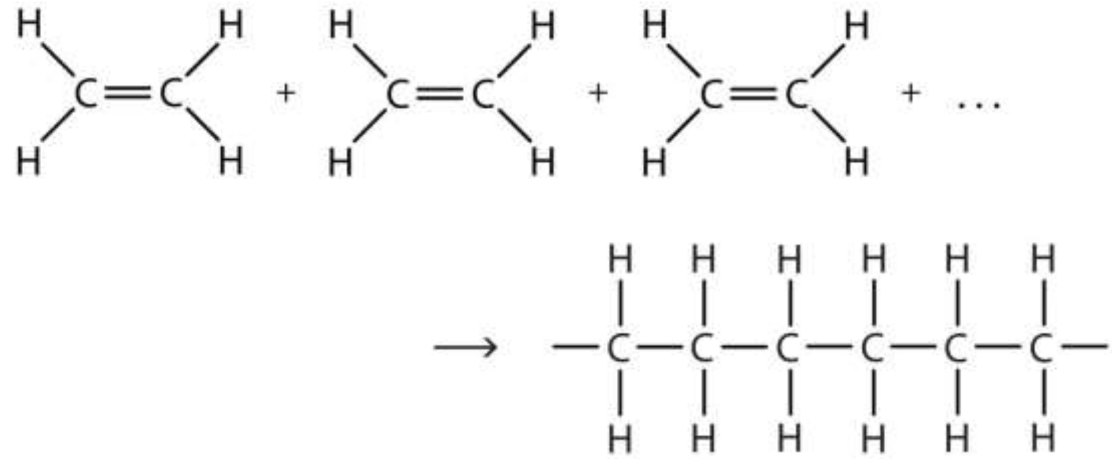

Figure 1. Polymer chemical structure.

Relevance and Scientific Significance of the Topic. The relevance of investigating the thermal stability of polymers has increased significantly in recent decades due to rapid technological progress and increasingly demanding operating conditions. High-performance polymers are now required to function reliably under extreme thermal loads in aerospace structures, automotive components, electronic devices, and energy systems. In such applications, thermal degradation can lead to catastrophic failure, loss of mechanical integrity, and safety hazards. From a scientific perspective, thermal stability is closely linked to the fundamental principles of polymer chemistry, including bond dissociation energy, molecular mobility, and thermodynamic stability. Advances in synthetic chemistry have enabled the creation of polymers with tailored chemical structures, making it possible to systematically study the relationship between composition and thermal behavior. Furthermore, the growing emphasis on sustainability and recyclability has introduced new challenges, as environmentally friendly polymers often exhibit lower thermal resistance compared to traditional materials. Thus, the study of chemical composition as a determinant of thermal stability is not only relevant for practical applications but also essential for advancing theoretical understanding and guiding future material design.

Problem Statement. Despite extensive research in polymer science, several unresolved problems remain regarding the thermal stability of polymeric materials. One major challenge is the trade-off between thermal stability and other desirable properties such as processability, flexibility, and biodegradability. Polymers with rigid aromatic backbones often exhibit high thermal resistance but are difficult to process, whereas flexible aliphatic polymers are easier to manufacture but degrade at lower temperatures. Another problem lies in the complexity of thermal degradation mechanisms. Polymers can undergo a variety of degradation processes, including chain scission, depolymerization, crosslinking, oxidation, and

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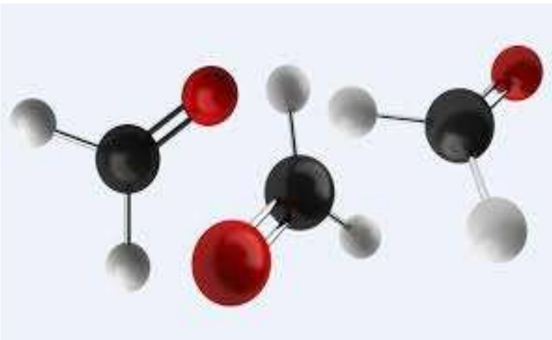
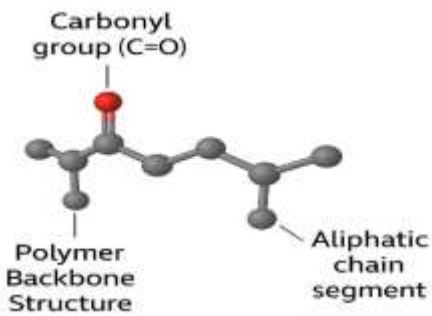
volatilization, depending on their chemical composition and environmental conditions. Predicting these processes based solely on chemical structure remains difficult, particularly for complex copolymers and composite systems.[108] Furthermore, the influence of additives and fillers on thermal stability is not always straightforward. While certain stabilizers can significantly enhance thermal resistance, their effectiveness depends on compatibility, dispersion, and interaction with the polymer matrix. In some cases, additives may even accelerate degradation if improperly selected. At present, polymer-based materials are widely used in the national economy. In our republic, the application of polymers contributes significantly to the development of various industrial sectors. However, in many cases, the physical and mechanical properties of basic polymers such as polyethylene, polypropylene, polyamide, and others are insufficient for their effective use in different fields. The incorporation of various modifiers into polymer systems (PE, PP) leads to an improvement in their properties. In particular, extensive use is being made of modification processes aimed at developing new modified polymer materials and enhancing their physicochemical properties.

Methodology. The methodological approach employed in this study is based on a comprehensive review and comparative analysis of experimental and theoretical investigations reported in the scientific literature. Thermal stability is primarily evaluated using thermogravimetric analysis, which provides information on weight loss as a function of temperature, and differential scanning calorimetry, which reveals thermal transitions such as glass transition, melting, and crystallization. These techniques are complemented by spectroscopic methods, including infrared spectroscopy and nuclear magnetic resonance, to identify chemical changes during thermal exposure. In addition to experimental data, theoretical considerations derived from polymer chemistry are used to interpret observed thermal behavior. Bond dissociation energies, resonance stabilization, and molecular rigidity are analyzed in relation to degradation temperatures. This combined methodological framework allows for a robust assessment of how chemical composition governs thermal stability.





[108] Sperling, L. H. Introduction to Physical Polymer Science. Wiley, 2016

Figure 2. Schematic representation of a polymer.

Influence of Polymer Backbone Structure. The polymer backbone is the primary structural element determining thermal stability. Polymers with carbon–carbon backbones, such as polyethylene and polypropylene, generally exhibit lower thermal stability due to the relatively low bond dissociation energy of C–C bonds and the susceptibility of tertiary carbon atoms to oxidation. In contrast, polymers containing heteroatoms such as oxygen, nitrogen, or sulfur in the backbone may display either enhanced or reduced thermal stability depending on the specific bonding environment. Aromatic polymers represent a distinct class characterized by high thermal resistance. The presence of aromatic rings in the backbone, as observed in polyimides, polyether ether ketone, and polyphenylene sulfide, introduces rigidity and resonance stabilization, which increases resistance to thermal degradation. The delocalized π-electron system in aromatic structures requires higher energy to disrupt, resulting in elevated decomposition temperatures.[109]

Role of Side Chains and Functional Groups. Side chains and functional groups attached to the polymer backbone significantly influence thermal behavior. Bulky side groups can restrict molecular mobility, thereby increasing glass transition temperature and thermal stability. However, they may also introduce steric strain that facilitates degradation under certain conditions. Functional groups such as hydroxyl, ester, amide, and ether groups can participate in intermolecular hydrogen bonding, which enhances thermal resistance by stabilizing the polymer structure. Conversely, thermally labile groups, including peroxides and weakly bonded substituents, can act as initiation sites for degradation.

Effect of Molecular Weight and Crosslinking. Molecular weight is another critical factor influencing thermal stability. High-molecular-weight polymers generally exhibit greater thermal resistance due to reduced chain mobility and a lower concentration of chain ends, which are more susceptible to degradation. Crosslinking further enhances thermal stability by forming a three-dimensional network that restricts chain motion and inhibits volatilization of degradation products. Thermosetting polymers, such as epoxy resins and phenolic resins, demonstrate superior thermal stability compared to thermoplastics due to their highly crosslinked structures. However, excessive crosslinking can lead to brittleness and processing difficulties.[110]

Influence of Copolymerization and Blending. Copolymerization offers a versatile strategy for tailoring thermal stability by combining monomers with

[109] Mark, J. E. Polymer Data Handbook. Oxford University Press, 2009.
[110] Gedde, U. W. Polymer Physics. Springer, 1999.

complementary properties. Random, block, and graft copolymers can exhibit thermal behavior distinct from their homopolymer counterparts. The incorporation of thermally stable monomer units can increase degradation temperature, while flexible segments improve processability. Polymer blending is another approach, though its effectiveness depends on miscibility and interfacial interactions. Phase separation can create weak points that compromise thermal stability.

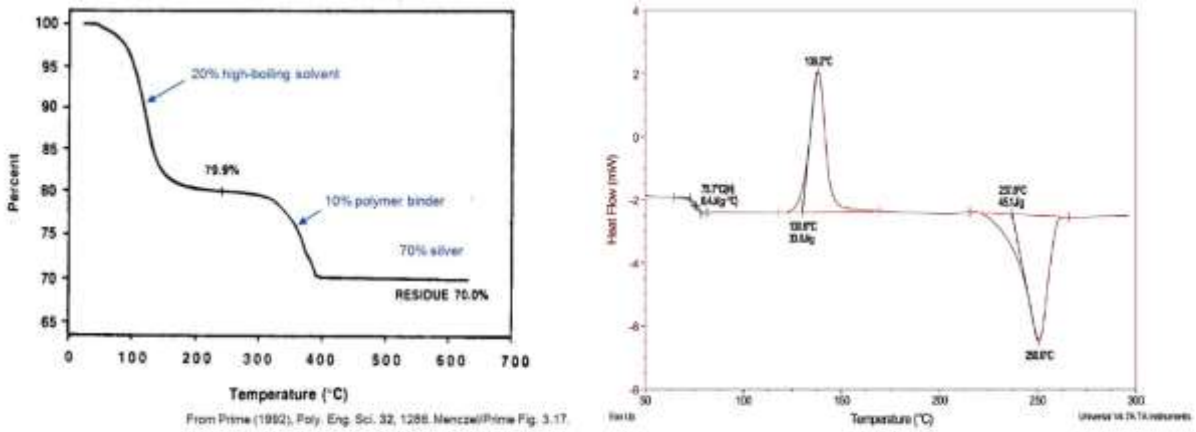


Figure 3. a) TGA polymer b) DSC polymer

Role of Additives and Fillers. Additives play a crucial role in enhancing the thermal stability of polymeric materials. Thermal stabilizers, antioxidants, and flame retardants can delay degradation by scavenging free radicals, forming protective char layers, or absorbing heat. Inorganic fillers such as silica, clay, and carbon-based materials can improve thermal resistance by acting as heat barriers and reinforcing the polymer matrix. However, the effectiveness of additives is highly dependent on their dispersion and compatibility. Poorly dispersed fillers may act as stress concentrators and initiate degradation.[111]

Proposed Solutions and Scientific Recommendations. Based on the analysis presented, several solutions can be proposed to improve the thermal stability of polymeric materials. Rational chemical design should prioritize the incorporation of high-energy bonds, aromatic structures, and stable functional groups. Controlled crosslinking and copolymerization strategies can balance thermal resistance with processability. From a scientific perspective, future research should focus on developing predictive models that link chemical composition to thermal behavior. Advanced characterization techniques and molecular simulations can provide deeper insights into degradation mechanisms. Additionally, the development of environmentally friendly stabilizers and sustainable polymers with enhanced thermal stability remains a key challenge.

Conclusion. The thermal stability of polymeric materials is fundamentally governed by their chemical composition. Factors such as backbone structure, side

[111] Odian, G. Principles of Polymerization. Wiley-Interscience, 2004.

chains, molecular weight, crosslinking, and the presence of additives collectively determine resistance to thermal degradation. A thorough understanding of these relationships enables the rational design of polymers with improved performance under high-temperature conditions. This article has demonstrated that chemical composition is not merely one of many factors but the central determinant of thermal stability. By integrating experimental observations with theoretical principles, the study provides a comprehensive framework for advancing polymer science and developing next-generation thermally stable materials.

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