

Electrical and Thermal Properties of Polymer Nanocomposites

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Abstract

Biodegradable polymers has inherent drawbacks, such as limited thermal stability and electrical conductivity, which hinder their widespread application in various fields, including electronic devices. These challenges result in less-than-optimal electrical and thermal properties when compared to standalone biodegradable polymers. Various techniques, such as co-polymerization, cross-linking and blending, with other polymers, can address and enhance the electrical and thermal properties of biodegradable polymers. Among these methods, the creation of nanocomposites emerges as very important approach to significantly improve the overall characteristics and applications of biodegradable polymers. This article provides a comprehensive overview of the electrical and thermal properties of biodegradable polymers. Additionally, it delves into the discussion of biodegradable polymer nanocomposites, encompassing blends of polymers, inorganic materials, and other nanomaterials.

Keywords: Polymer Composite; Thermal;Electrical Properties; Conductivity.

1. INTRODUCTION

Polymers, versatile materials with the potential to substitute for metals, glass, and traditional materials [1–3], offer a range of benefits, such as being flexible, lightweight, and cost-effective. They find extensive applications in energy, biomedical and optoelectronics fields [4-6]. Both organic and coordination polymers hold promise for further applications. The term "biodegradable polymers" was introduced in 1980, gaining significant traction. The standardas defines biodegradable composites as those capable of degrading >89% of their mass in a biological environment over six months.

The term "biodegradable" ensures the environmental reliability of products without causing harm. Biodegradable materials, as defined by standards, must exhibit 70% degradation within 30 days under anaerobic conditions [7-9]. The synthesis of biodegradable polymer composites involves combining biodegradable polymers with reinforcing materials to enhance their mechanical, thermal, and electrical properties. Common biodegradable polymers include PLA, PHB, and PCL. Various methods, such as melt blending, solution casting, and in situ polymerization, are employed to incorporate reinforcing agents like natural fibers, nanoparticles, or other polymers. The goal is to achieve a synergistic balance between the biodegradable matrix and reinforcing materials, optimizing both performance and environmental impact. These composites find applications in eco-friendly packaging, biomedical devices, and agricultural materials, contributing to sustainable practices in materials science.

Materials derived from natural sources, such as polysaccharides (e.g., cellulose, lignin, starch, chitin/chitosan) or proteins (e.g., collagen, silk fibril (SF)), contrast with synthetic polymers obtained from fossil oil or petroleum.

Natural polymers and composites are materials derived from renewable resources found in nature. These materials offer environmentally friendly alternatives to synthetic polymers and composites, often characterized by their biodegradability and sustainability. Here's an overview of natural polymers and composites: Cellulose used for Paper, textiles, cellulose acetate, and as a reinforcement in composites. Chitinused for wound dressings, drug delivery systems, and as a reinforcement in composites. Starchused for

food packaging, biodegradable plastics, and as a thickening agent. Proteins (e.g., Collagen, Silk)used for biomedical scaffolds, textiles, and cosmetic surgery.

Hydrolysis of poly(vinyl acetate) [10] enables the synthesis of a water-soluble polymer like PVA, which boasts attributes such as high transparency, strength, flexibility, and biocompatibility. Despite its elevated density of –OH groups, shaping PVA through conventional methods like melting proves challenging. Nevertheless, it easily lends itself to blending with other materials through a straightforward mixing procedure. PVA-based materials have found extensive application in resistance random access memory. Another noteworthy water-soluble polymer is PVP, synthesized through the radical polymerization of Nvinylpyrrolidone [11]. Its versatile properties have led to its utilization in various applications, including wearable tech, including gas sensors. Good intrinsic biocompatibility and enzymatic degradability of natural polymers allow for extensive use in biomedical applications (**Figure 1**) [12].

Fig 1: Various biodegradable linkage and structure of it [12]. Reproduced with the permission with Wiley.

2. POLYMERS NANOCOMPOSITES

2.1 Dielectric Properties

Dielectric materials refer to electrical insulator materials that can undergo polarization when subjected to an applied electric field. This polarization is characterized by a high electrical polarization resulting from the interaction of electric charges within the material under the influence of an electric field [13]. As insulators, these materials impede the flow of electric charges. The dielectric polarization generates positive charges aligned with the electric field and negatively charges moving opposite to the field direction. The performance of material's is quantified by its dielectric constant, representing its ability to store electrical

charge. High-k materials are suitable for applications like gate dielectrics in metal–oxide–silicon (MOS) semicondutor, while low-k materials are essential for electrical insulation.

Fig 2: Dielectric properties of the Polymer nanocomposites [15]. Reproduced with the Permission of American Chemical Society.

The electrical properties make the polymer applicable in surface, capacitance, and dielectric resonators. In a parallel plate capacitor, the capacitance (C) is determined by the dielectric constant (ϵ) , the area (A) , and the distance between electrodes (d), expressed as $C = \varepsilon A/d$. Various factors influence the dielectric properties of polymer layers, including composition, atomic number, size, porosity, thickness of the thin film, flaws, operating frequency, and doping concentration. Cellulose ion-gel and cellulose-based materials, such as cellulose nanocrystals (CNC), exhibit dielectric properties suitable for applications like flexible field-effect transistors (FETs) and ultralow-power electronics [14]. Enhancements in cellulose performance can be achieved through methods such as incorporating cellulose derivatives, like cyanoethyl cellulose-containing barium strontium titanate (BST) nanoparticles. Chitosan, when combined with high-k materials like Y_2O_3 nanoparticles, presents improved dielectric and electrical performance, reducing current leakage. Polyvinyl alcohol (PVA) with a dielectric constant of 6-7 in the Hz-MHz range surpasses other biodegradable polymers. Introducing inorganic fillers like Au NPs/graphene oxide (GO), GO, and MoS2 enhances electrical properties. Composite films of consisting of graphite and poly(butylene succinate) demonstrate significantly increased dielectric constants. Biodegradable polymers like polylactic acid (PLA) blended with various dielectric materials such as $TiO₂$, BaTiO₃ nanowires, $Al₂O₃$, carbon nanotubes, reduced graphene oxide (rGO), and others are explored for applications such as sensors, energy harvesters, and tissue scaffolds, with improvements in dielectric properties attributed to mechanisms like a decrease in energy band gap. In summary, the incorporation of diverse dielectric materials into polymers enhances their electrical and dielectric properties as shown in **Figure 2**, making them suitable for a wide range of electronic applications [15].

2.2 Thermal Conductivity Properties of Polymer Composites

The thermal conductivity of polymer composites is a critical property influencing their performance in diverse applications. By incorporating fillers like nanoparticles, carbon fibers, or ceramics, the composite's thermal conductivity can be significantly enhanced. The dispersion and alignment of these fillers within the polymer matrix impact heat transfer. Achieving an optimal filler concentration and distribution is crucial. Enhanced thermal conductivity makes these composites valuable in industries such as electronics, where efficient heat dissipation is vital. Tailoring the thermal properties of polymer composites plays a pivotal role in advancing materials for applications ranging from aerospace to energy-efficient electronics [16]. The resulting PLA/CNCfs fibrous membrane demonstrated an elevated thermal conductivity of 0.27 W⁻¹•m⁻¹•K⁻¹. Additionally, a biodegradable composite of PLA/poly(butylene adipate-co-butylene terephthalate)/carbon nanofiber (PLA/PBAT/CNF) was processed using a melt extrusion-stretching method [17]. The PLA/PBAT/CNF composite, containing 10 wt.% CNF, exhibited an in-plane TC of 1.53 W−1•m−1•K−1, showcasing a notable 31.9% increase in thermal conductivity compared to the biocomposite without CNF. Metallic nanoparticles exhibit significantly heightened thermal conductivity compared to conventional materials. This enhanced thermal conductivity is attributed to the unique properties of metallic nanoparticles, including their high electron mobility and efficient heat transfer capabilities. The small size of these nanoparticles allows for improved phonon transport, contributing to the efficient transmission of thermal energy. Due to these characteristics, metallic nanoparticles find applications in various fields, particularly in the development of advanced materials such as nanocomposites, where their exceptional thermal conductivity properties play a crucial role [18]. This heightened thermal conductivity makes metallic nanoparticles valuable in enhancing the performance of materials used in electronic devices, heat transfer applications, and other technologies where efficient thermal management is essential. The preparation of metallic polymer composites involves combining metallic nanoparticles with polymer matrices to create materials with enhanced properties. The process typically begins with the selection of suitable metallic nanoparticles, such as silver, gold, or copper, known for their excellent thermal and electrical conductivity. Various methods can be employed for the preparation of metallic polymer composites, including solution blending, in situ polymerization, and melt blending. In solution blending, metallic nanoparticles are dispersed within a polymer solution, followed by solvent removal to obtain a composite material. In in situ polymerization, the metallic nanoparticles are synthesized directly within the polymer matrix during the polymerization process. Melt blending involves the mixing of metallic nanoparticles with molten polymer followed by cooling and solidification. The key to successful metallic polymer composite preparation lies in achieving a homogeneous dispersion of metallic nanoparticles within the polymer matrix [19]. This ensures the creation of a composite material with uniform properties and effective interaction between the metallic phase and the polymer. The choice of preparation method, nanoparticle size, and concentration play crucial roles in determining the final properties of the composite. Metallic polymer composites find applications in various fields, including electronics, aerospace, and biomedical engineering, owing to their unique combination of metallic and polymeric characteristics, such as enhanced conductivity, mechanical strength, and biocompatibility. **Fig 3** shows the thermal conductivity proeprties of biodegradable polymer nanocomposite [20].

Fig 3: Thermal conductivity properties of biodegradable polymer composites [20]. Reproduced with the permission of Elsevier.

2.3 Electrical Conductivity

The electrical conductivity of biodegradable polymer composites is a key parameter that determines their suitability for various applications, especially in electronic devices. Biodegradable polymers, inherently insulating in nature, can be enhanced with the addition of conductive fillers or through specific processing techniques to improve their electrical conductivity [21]. Several factors influence the electrical conductivity of biodegradable polymer composites:

Conductive Fillers: The addition of conductive materials such as metallic nanoparticles (e.g., silver nanoparticles), carbon-based materials (e.g., graphene, carbon nanotubes), or conductive polymers (e.g., polyaniline) can significantly enhance the electrical conductivity of biodegradable polymer composites.

Concentration of Fillers: The amount or concentration of conductive fillers in the polymer matrix plays a crucial role. Higher concentrations often result in increased electrical conductivity, but there is typically an optimal loading beyond which further increases may not lead to significant improvements.

Dispersion and Alignment: The uniform dispersion and alignment of conductive fillers within the polymer matrix are critical for achieving effective percolation networks, which facilitate the flow of electrons and enhance electrical conductivity.

Processing Techniques: Various processing methods, such as melt blending, solution casting, or electrospinning, can influence the composite's microstructure and, consequently, its electrical properties.

Polymer Matrix: The choice of biodegradable polymer as the matrix also affects electrical conductivity. Some polymers inherently have better charge transport properties, while others may require modifications for improved conductivity.

Environmental Conditions: The electrical conductivity of biodegradable polymer composites may be influenced by environmental conditions, such as humidity and temperature.

In summary, tailoring the electrical conductivity of biodegradable polymer composites involves a careful selection of conductive fillers, optimizing their concentration, ensuring proper dispersion, employing suitable processing techniques, and considering the specific application requirements [22]. These conductive biodegradable polymer composites find applications in areas such as electronic skins, sensors, and other electronic devices where both electrical performance and biodegradability are essential.

3 CONCLUSIONS

The fundamental physical mechanisms for customizing the thermal conductivity of both polymers and polymer nanocomposites are discussed in this chapter. The key advancements in research over the past two decades can be summarized as follows:

Enhanced Crystallinity or Chain Alignment: Thermal conductivity is generally increased when polymer chains are better aligned or have more crystallinity. To further increase thermal conductivity, particular polymer species with distinct chain architectures must be chosen. Higher heat conductivity is associated with stronger stretching and bending strengths of backbone bonds, but lower dihedral-angle strength can dramatically lower it. Furthermore, heat conductivity tends to decrease with increasing side chain weight or number density, and side chain shape can affect side chain length in different ways.

Inter-Chain Coupling: By strengthening inter-chain coupling via processes like covalent cross-links and H-bonds, virgin polymers' thermal conductivity can be raised. This improvement is explained by elements like increased inter-chain "thermal bridges," decreased rotation of

Functionalization of Nano-Fillers: To prevent nano-filler aggregation, functionalization is often employed. However, surface functionalization aimed at hindering aggregation can result in larger interfacial thermal resistance. The challenge is to simultaneously reduce interfacial thermal resistance while suppressing the aggregation of nano-fillers.

Filler Network Formation: When fillers are equally dispersed in nanocomposites, thermal conductivity first rises gradually until the filler concentration surpasses the percolation threshold. After that, it increases quickly before finally saturating the filler network and convergeing to a constant number. The difficulty is in creating a 3D network with the least amount of single fillers, therefore hybrid fillers are frequently used. It is still difficult to determine the ideal concentration ratio for hybrid fillers that will maximize thermal conductivity between the two fillers.

The 3D Fillers' effectiveness: When it comes to improving thermal conductivity, three-dimensional (3D) fillers—such as expanded graphite (EG), carbon fibers (CF), graphene fibers (GF), and 3D boron nitride nanosheets (3DBNNS) aerogel—may work better than hybrid fillers.

Despite significant progress in the past two decades, there is still much work to be done to fully understand and further enhance the thermal conductivity of polymers and polymer nanocomposites, given their technical importance.In this chapter, the focus is on exploring the electrical and thermal properties aspects of nanocomposites involving biodegradable polymers. The electrical properties of biodegradable polymer nanocomposites are significantly influenced by the fabrication process. While various methods exist for synthesizing and fabricating polymer nanocomposites, achieving high conductivity, specifically a low percolation threshold, remains a challenging task. The absence of well-defined procedures for characterizing the electrical and thermal properties aspects of biodegradable polymers poses a challenge. However, there is the potential for substantial progress in evaluating the material's properties, ensuring significant advancements and benefits in this field.

REFERENCES

[1] Sownthari K, Suthanthiraraj SA.:Preparation and properties of biodegradable polymer-layered silicate nanocomposite electrolytes for zinc based batteries. Electrochim Acta. 174, 885–92, 2015

[2] Kashi S, Gupta RK, Baum T, Kao N, Bhattacharya SN.: Dielectric properties and electromagnetic interference shielding effectiveness of graphene-based biodegradable nanocomposites. Mater Des. 109, 68–78, 2016.

[3] Zheng N, Xu Y, Zhao Q, Xie T.: Dynamic Covalent Polymer Networks: A Molecular Platform for Designing Functions beyond Chemical Recycling and Self-Healing. Chem Rev, 121,1716–45, 2021.

[4] Peng X, Dong K, Wu Z, Wang J, Wang ZL.: A review on emerging biodegradable polymers for environmentally benign transient electronic skins. J Mater Sci, 56, 16765–89, 2021.

[5] Martina M, Hutmacher DW. Biodegradable polymers applied in tissue engineering research: a review. Polym Int. 56, 145–57, 2007.

[6] Kaur D, Bharti A, Sharma T, Madhu C.: Dielectric Properties of ZnO-Based Nanocomposites and Their Potential Applications. Int J Opt, 2021, 1–20, 2021.

[7] Abdelhamid HN.: Zinc hydroxide nitrate nanosheets conversion into hierarchical zeolitic imidazolate frameworks nanocomposite and their application for CO2 sorption. Mater Today Chem, 15, 100-222, 2020.

[8] El-Bery HM, Abdelhamid HN.: Photocatalytic hydrogen generation via water splitting using ZIF-67 derived Co3O4@C/TiO2. J Environ Chem Eng, 9, 105702, 2021.

[9] Ching-Li Huang, Yu-Chieh Pao, Shi-Yen Chen, Jhih-Yang Hsu, Chia-Lin Tsai, Yen-Ju Cheng.: Synthesis of Asymmetric Benzotrithiophene/Benzotriselenophene Building Blocks and Their Donor–Acceptor Copolymers: Chalcogen Effect on Face-on/Edge-on Orientations and Charge Transport. Macromolecules. 56 (17) , 6722-6732, 2023.

[10] Sung Yun Son, Taiho Park, Wei You.: Understanding of Face-On Crystallites Transitioning to Edge-On Crystallites in Thiophene-Based Conjugated Polymers. Chemistry of Materials, 33 (12) , 4541-4550, 2021.

[11] Milani MA, Gonzlez D, Quijada R, Basso NR, Cerrada ML, Azambuja DS, Galland GB.: Polypropylene/graphene nanosheet nanocomposites by in situ polymerization: synthesis, characterization and fundamental properties. Compos Sci Technol.84,1–7, 2013.

[12] Jerika AC, Helen T, Yangju L, Yu Z, Zhenan B.: Integrating Emerging Polymer Chemistries for the Advancement of Recyclable, Biodegradable, and Biocompatible Electronics. Advanced Sciences. 8, 2101233, 2021.

[13] Ali S, Bae J, Lee CH, Choi KH, Doh YH.: All-printed and highly stable organic resistive switching device based on graphene quantum dots and polyvinylpyrrolidone composite. Org Electron. 25, 225–31, 2015.

[14] Hosseini NR, Lee J-S.: Biocompatible and Flexible Chitosan-Based Resistive Switching Memory with Magnesium Electrodes. Adv Funct Mater. 25, 5586–92, 2015.

[16] Muhammad RA, Leni M, Riyanto R, Jaidan J, Zainuddin N, Ida S.: Dielectric Properties and Flexibility of Polyacrylonitrile/Graphene Oxide Composite Nanofibers. ACS Omega, 7, 33087–33096, 2022.

[17] Sun D, Gu T, Mao Y, Huang C, Qi X, Yang J, et al.: Fabricating High-Thermal-Conductivity, High-Strength, and High-Toughness Polylactic Acid-Based Blend Composites via Constructing Multioriented Microstructures. Biomacromolecules. 23, 1789–802, 2022.

[18] Liu Y, Wu K, Lu M, Shi J, Liang L, Lu M.: Enhanced thermal conductivity of bio-based epoxy-graphite nanocomposites with degradability by facile in-situ construction of microcapsules. Compos Part B Eng. 218, 108936, 2021.

[19] Patel GB, Singh NL, Singh F, Kulriya PK.: Effect of swift heavy ions irradiation on physicochemical and dielectric properties of chitosan and chitosan-Ag nanocomposites. Radiat Phys Chem. 181, 109288, 2021.

[20] Bekas D, Hou Y, Liu Y, Panesar A. 3D printing to enable multifunctionality in polymer-based composites: a review, Composites Part B: Engineering. 179, 107540, 2019.

[21] Congliang H, Xin Q, Ronggui Y.: Thermal conductivity of polymers and polymer nanocomposites. Material Science and Engineering R. 132, 1-22, 2018.

[22] Hirai T, Leolukman M, Liu CC, Han E, Kim YJ, Ishida Y, Hayakawa T, Kakimoto MA, Nealey PF, Gopalan P.: One-step direct-patterning template utilizing self-assembly of POSS-containing block copolymers. Adv Mater. 21, 1–5, 2009.

[23] Chen WC, Kuo SW, Lu CH, Chang FC.: Specific interactions and self-assembly structures through competitive interactions of crystalline-amorphous diblock copolymer/homopolymer blends: poly(-caprolactone) b-poly(4-vinyl pyridine)/poly(vinyl phenol). Macromolecules. 42, 3580–90, 2009.