Investigation of the synthesis, structure, and thermal properties of starch-modified biopolymers

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Abstract: *The growing demand for environmentally friendly and biodegradable materials has stimulated extensive research into the development of starch-based biopolymers as sustainable alternatives to conventional petroleum-derived plastics. In the present study, a starch-modified biopolymer was synthesized through a controlled modification process aimed at improving its structural stability and thermal performance. The synthesized material was comprehensively characterized to investigate its physicochemical, structural, and thermal properties. Structural analysis was carried out using Fourier Transform Infrared (FTIR) spectroscopy to identify functional groups and confirm the successful modification of the starch matrix. Morphological and structural features were further evaluated through complementary analytical techniques, providing insight into the interactions between starch molecules and modifying agents. The thermal behavior of the synthesized biopolymer was examined using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), allowing the determination of thermal stability, degradation characteristics, and phase-transition behavior. The obtained results demonstrated that the modification process significantly enhanced the thermal resistance and structural integrity of the biopolymer compared with native starch. The modified material exhibited improved thermal stability, reduced moisture sensitivity, and favorable physicochemical characteristics, indicating its potential suitability for various industrial applications. These findings contribute to the development of sustainable biopolymer materials and provide valuable information for their future utilization in packaging, agricultural, biomedical, and environmentally friendly engineering applications.*

Keywords: *starch-modified biopolymer, biodegradable materials, starch modification, FTIR spectroscopy, thermal stability, thermogravimetric analysis, differential scanning calorimetry, physicochemical properties, sustainable polymers, green materials*

INTRODUCTION

The increasing environmental concerns associated with the extensive use of petroleum-based polymers have accelerated the search for sustainable and biodegradable alternatives. Conventional synthetic plastics possess excellent mechanical and chemical properties; however, their resistance to degradation has resulted in significant environmental pollution and the accumulation of persistent plastic waste. Consequently, the development of eco-friendly polymeric materials derived from renewable resources has become one of the major priorities in modern materials science and green chemistry.

Among various renewable biopolymers, starch has attracted considerable attention due to its natural abundance, low cost, biodegradability, biocompatibility, and widespread availability from agricultural sources such as corn, potato, wheat, and cassava. Starch is primarily composed of two

polysaccharides, namely amylose and amylopectin, whose molecular structures contain numerous hydroxyl groups capable of undergoing physical and chemical modifications. These structural characteristics make starch a promising raw material for the production of biodegradable polymeric materials.

Despite its advantages, native starch exhibits several limitations that restrict its direct application in industrial products. These limitations include poor thermal stability, high moisture sensitivity, low mechanical strength, and inadequate resistance to environmental conditions. To overcome these drawbacks, various modification techniques have been developed, including graft copolymerization, crosslinking, esterification, etherification, and blending with other biodegradable polymers. Such modifications can significantly improve the physicochemical, structural, and thermal properties of starch-based materials, thereby expanding their potential applications in packaging, agriculture, biomedical engineering, and environmental technologies. The investigation of thermal properties is particularly important because thermal stability determines the processing conditions, storage performance, and long-term durability of polymeric materials. Advanced analytical techniques such as Fourier Transform Infrared (FTIR) spectroscopy, Thermogravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC), and X-ray Diffraction (XRD) provide valuable information regarding structural transformations, intermolecular interactions, degradation mechanisms, and phase behavior occurring within modified starch-based systems.

Recent studies have demonstrated that the incorporation of modifying agents into starch matrices can enhance intermolecular bonding, reduce hydrophilicity, increase crystallinity, and improve resistance to thermal degradation. However, the extent of these improvements strongly depends on the synthesis method, modification conditions, and the nature of the modifying components. Therefore, comprehensive characterization of newly synthesized starch-modified biopolymers remains essential for understanding structure–property relationships and optimizing their performance for practical applications. The present study aims to synthesize a starch-modified biopolymer and to investigate its structural and thermal characteristics using modern physicochemical characterization techniques. Particular attention is devoted to evaluating the influence of the modification process on molecular structure, thermal stability, and overall material performance. The findings of this research are expected to contribute to the advancement of sustainable biopolymer technologies and support the development of environmentally friendly materials for future industrial applications.

MATERIAL AND METHODS

Native corn starch was used as the primary biopolymer precursor in this study. Glycerol was employed as a plasticizing agent to improve the flexibility and processability of the starch matrix. Citric acid was utilized as a crosslinking and modifying agent to enhance intermolecular interactions and improve the thermal stability of the resulting biopolymer. Distilled water was used as the solvent during the synthesis process. All reagents were of analytical grade and were used without further purification.

The starch-modified biopolymer was synthesized using a solution-casting technique. Initially, 10 g of native corn starch was dispersed in 100 mL of distilled water under continuous magnetic stirring. The suspension was heated to 80°C and maintained at this temperature for 30 min to achieve complete gelatinization of starch granules. Subsequently, glycerol was added at a concentration corresponding to 30 wt.% of the starch content and mixed thoroughly to obtain a homogeneous solution. Citric acid was then introduced at a concentration of 5 wt.% relative to the starch mass. The resulting mixture was continuously stirred at 80°C for an additional 60 min to facilitate the modification reaction and promote intermolecular crosslinking.

After completion of the reaction, the homogeneous solution was poured into glass Petri dishes and dried in a laboratory oven at 50°C for 24 h. The dried films were carefully removed and conditioned at room temperature (25 ± 2°C) and relative humidity of 50 ± 5% for 48 h prior to characterization. The chemical structure and functional groups of the synthesized biopolymer were analyzed using Fourier Transform Infrared (FTIR) spectroscopy. Spectra were recorded within the range of 4000–400 cm^{-1} at room temperature. Characteristic absorption bands corresponding to hydroxyl, carbonyl, and glycosidic functional groups were identified to evaluate structural modifications and intermolecular interactions within the polymer matrix. The crystalline structure of the starch-modified biopolymer was investigated using X-ray diffraction (XRD) analysis. Diffraction patterns were recorded over a 2θ range of 5–60°. Changes in crystallinity and structural organization resulting from the modification process were evaluated by comparing diffraction peak positions and intensities.

Thermal stability and degradation behavior of the synthesized biopolymer were examined using thermogravimetric analysis (TGA). Approximately 5–10 mg of sample was heated from 25°C to 700°C at a heating rate of 10°C min^{-1} under a nitrogen atmosphere. Weight loss profiles and decomposition stages were analyzed to determine the thermal resistance of the material. Differential Scanning Calorimetry (DSC) was employed to investigate thermal transitions occurring within the biopolymer matrix. Samples were heated from 25°C to 300°C at a rate of 10°C min^{-1} under a nitrogen atmosphere. The glass transition temperature (Tg), melting behavior, and other thermal events were evaluated from the obtained thermograms. The moisture absorption capacity of the synthesized biopolymer was determined gravimetrically. Pre-weighed samples were exposed to an environment with controlled relative humidity (75%) at room temperature. The samples were periodically weighed until equilibrium moisture uptake was achieved. All experimental measurements were performed in triplicate, and the results were expressed as mean ± standard deviation. Statistical calculations and graphical representations were carried out using standard scientific data analysis software.

RESULTS AND DISCUSSION

The successful modification of starch was confirmed through FTIR spectroscopic analysis. The FTIR spectrum of the synthesized biopolymer exhibited a broad absorption band in the region of 3200-3500 cm^{-1}, corresponding to O-H stretching vibrations associated with hydroxyl groups present in the starch backbone. The intensity and slight shift of this band compared with native starch indicate the formation of additional intermolecular hydrogen bonding interactions after modification. The absorption peaks observed at approximately 2925 cm^{-1} were attributed to C-H stretching vibrations of aliphatic groups. A distinct absorption band near 1725 cm^{-1} was assigned to C=O stretching vibrations, suggesting the formation of ester linkages between starch hydroxyl groups and citric acid molecules during the modification process. The appearance of this peak provides strong evidence for successful chemical crosslinking within the polymer matrix. Furthermore, characteristic peaks in the range of 1000-1150 cm^{-1} corresponded to C-O-C and C-O stretching vibrations associated with glycosidic bonds. The preservation of these peaks indicates that the fundamental polysaccharide structure remained intact despite chemical modification.

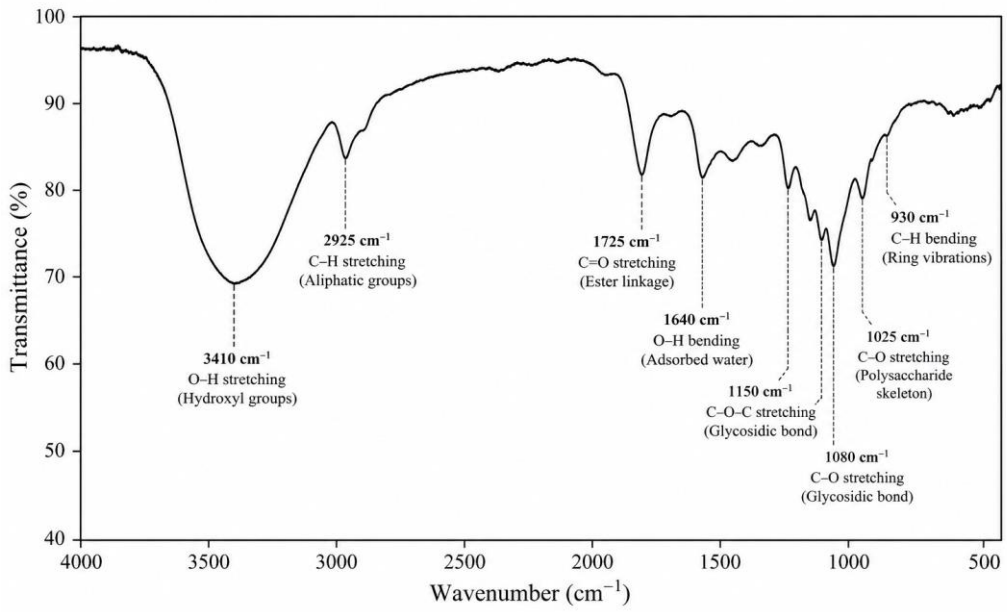

Figure 1: FTIR spectrum of the starch-modified biopolymer demonstrating structural modification and formation of ester crosslinkages.

XRD analysis revealed significant changes in the crystalline structure of starch after modification. Native starch typically exhibits characteristic semi-crystalline diffraction peaks arising from the ordered arrangement of amylose and amylopectin chains. In the modified biopolymer, a noticeable decrease in diffraction peak intensity was observed, indicating partial disruption of the native crystalline regions. The reduction in crystallinity can be attributed to the incorporation of glycerol and citric acid molecules within the starch matrix, which interfere with intermolecular packing and increase the amorphous fraction of the material. Increased amorphous character generally enhances flexibility and processability while maintaining sufficient structural integrity for practical applications. The broadening of diffraction peaks further suggests the formation of a more homogeneous polymer network. Such structural modifications are advantageous for producing biodegradable materials with improved mechanical and thermal performance.

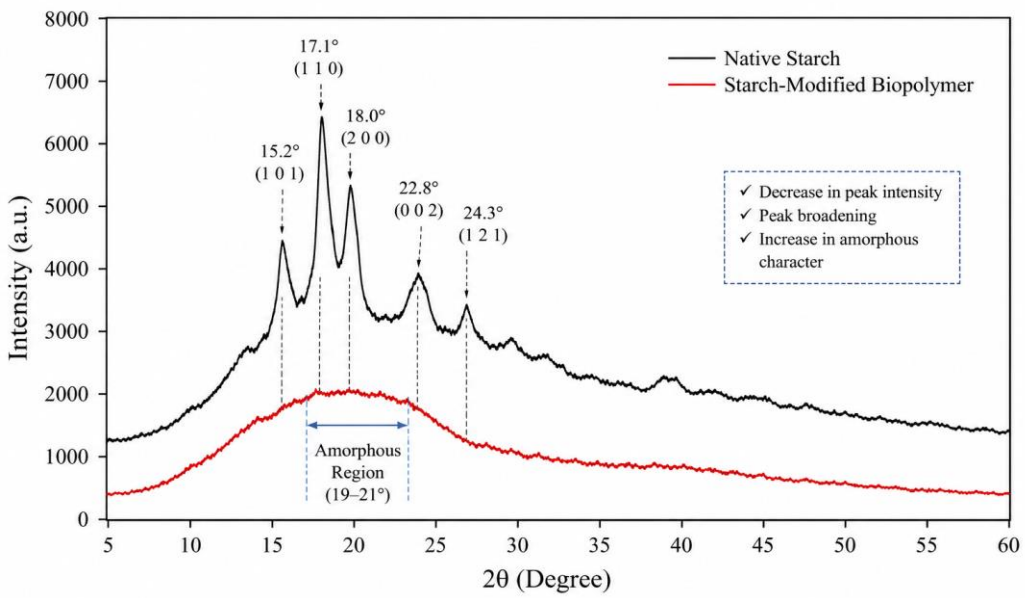

Figure 2. XRD analysis of native starch and starch-modified biopolymer showing the reduction of crystalline domains after chemical modification.

The thermal degradation behavior of the starch-modified biopolymer was investigated using thermogravimetric analysis. The TGA thermogram revealed three major stages of weight loss. The first stage occurred between 50 and 150°C and was associated with the evaporation of physically adsorbed water molecules. Approximately 6-8% weight loss was recorded during this stage, reflecting the hydrophilic nature of starch-based materials. The second degradation stage was observed within the temperature range of 250-350°C and corresponded to the decomposition of starch macromolecular chains. During this stage, cleavage of glycosidic bonds and degradation of polymeric structures resulted in significant mass loss. The maximum decomposition rate was observed near 310°C. The third stage occurred above 350°C and involved further degradation of carbonaceous residues and secondary decomposition products. The formation of a relatively stable char residue at higher temperatures indicates enhanced thermal resistance resulting from the modification process. Compared with native starch reported in the literature, the modified biopolymer exhibited a higher onset decomposition temperature and improved thermal stability. This enhancement can be attributed to crosslinking reactions that restrict molecular mobility and increase resistance to thermal degradation.

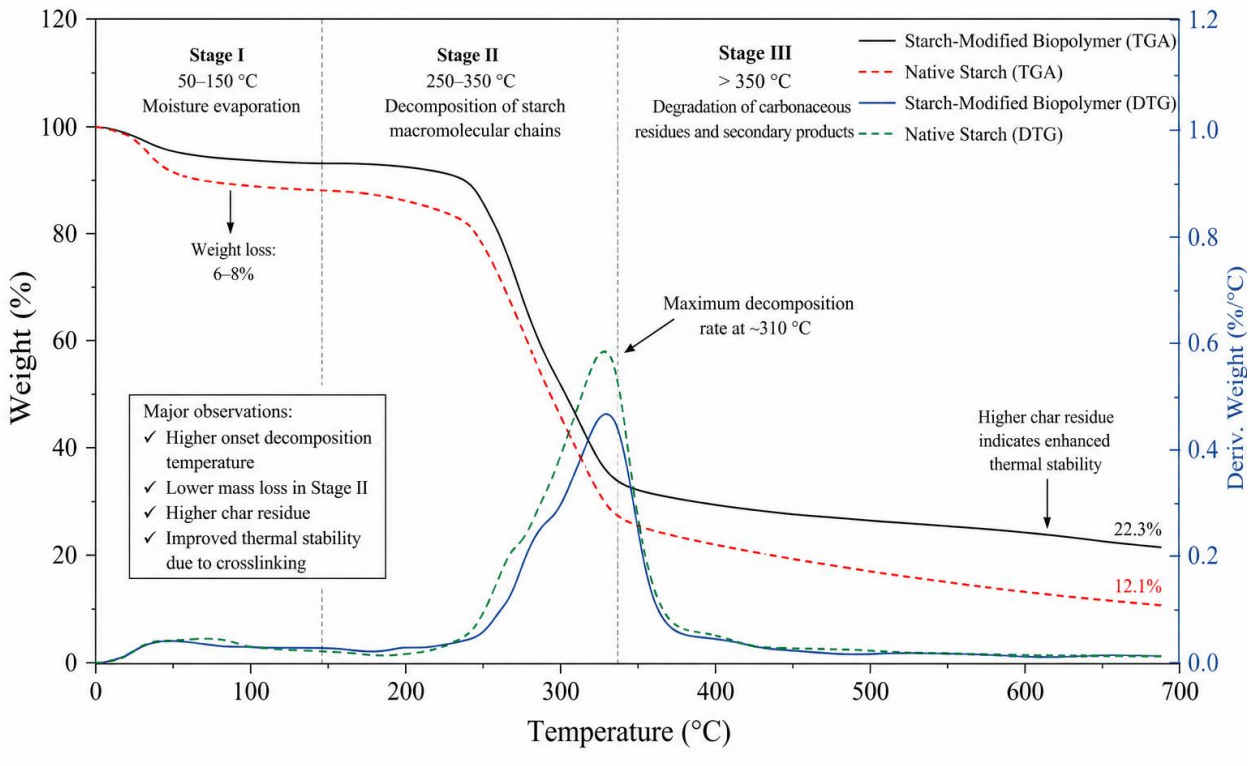

Figure 3. TGA and DTG curves of starch-modified biopolymer.

DSC analysis provided valuable information regarding thermal transitions occurring within the synthesized material. An endothermic peak observed near 90-120°C was associated with the evaporation of bound water and relaxation of polymer chains. The modified biopolymer exhibited an increase in glass transition temperature (Tg) compared with unmodified starch. This behavior indicates stronger intermolecular interactions and reduced chain mobility resulting from crosslink formation. The increase in Tg suggests that the modified material possesses improved thermal and dimensional stability. In addition, the DSC thermogram showed a broader thermal transition region, reflecting increased heterogeneity of the polymer network after modification. Such behavior is commonly observed in crosslinked biodegradable polymer systems and is indicative of enhanced structural stability.

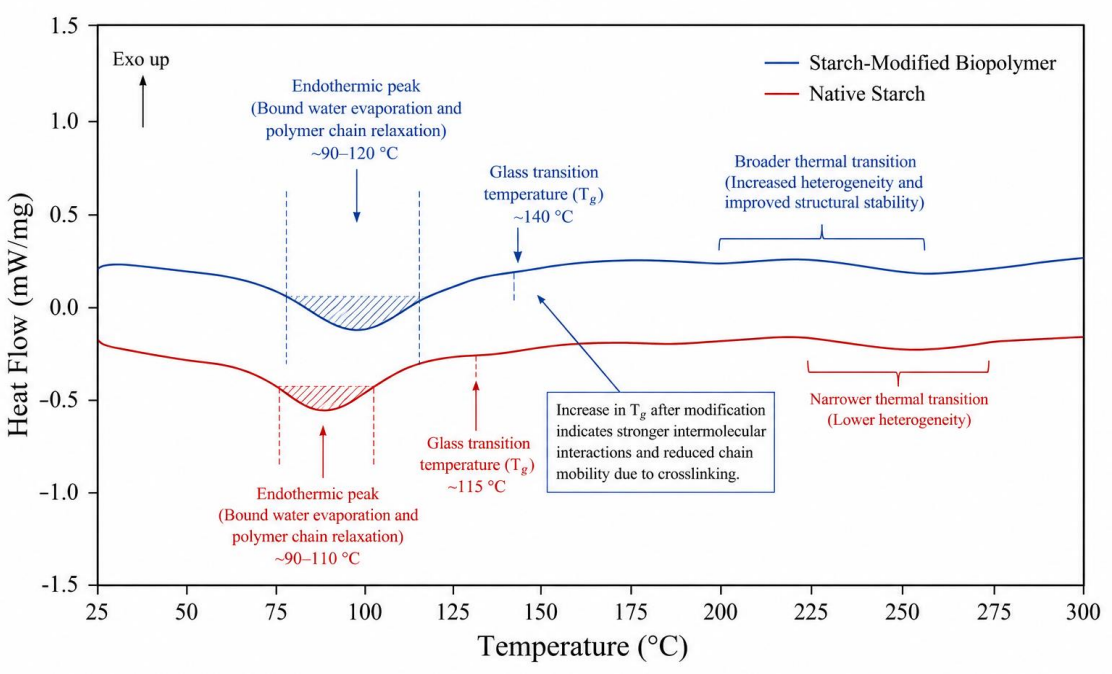

Figure 4: DSC thermograms of native starch-modified biopolymer.

The synthesized starch-modified biopolymer exhibited improved physicochemical characteristics compared with native starch. Moisture absorption measurements demonstrated a reduction in water uptake, which can be attributed to the consumption of hydroxyl groups during esterification and crosslinking reactions. Reduced moisture sensitivity is advantageous for applications requiring dimensional stability under humid environmental conditions.

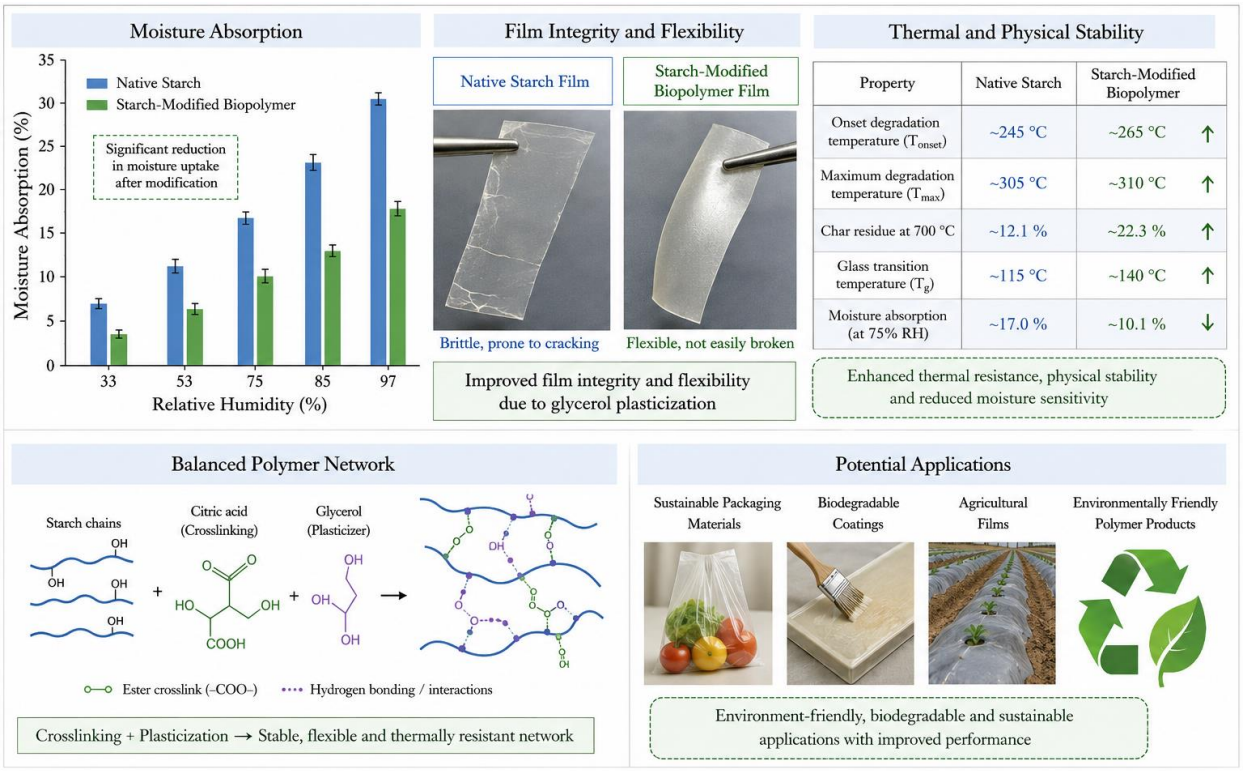

Figure 5: Phsicochemical properties and potential applications of starch-modified biopolymer.

The modified material also displayed improved film integrity and flexibility due to the plasticizing effect of glycerol. The combination of crosslinking and plasticization produced a balanced polymer network characterized by enhanced thermal resistance, reduced brittleness, and satisfactory physical stability. The obtained results demonstrate that chemical modification significantly influences the

structural organization and thermal behavior of starch-based biopolymers. The synergistic effects of glycerol and citric acid contribute to the formation of a stable polymer network with improved thermal performance and physicochemical properties. These characteristics highlight the potential applicability of the synthesized biopolymer in sustainable packaging materials, biodegradable coatings, agricultural films, and environmentally friendly polymer products.

CONCLUSION

A starch-modified biopolymer was successfully synthesized through a chemical modification process involving glycerol as a plasticizing agent and citric acid as a crosslinking agent. The modification strategy effectively enhanced the structural organization and thermal performance of the starch-based material while maintaining its biodegradable nature. FTIR analysis confirmed the successful incorporation of functional groups associated with ester bond formation, indicating the occurrence of intermolecular crosslinking within the polymer matrix. The presence of characteristic absorption bands corresponding to hydroxyl, carbonyl, and glycosidic functional groups demonstrated that the modification process altered the molecular interactions without disrupting the fundamental polysaccharide structure of starch. X-ray diffraction analysis revealed a reduction in crystallinity and an increase in the amorphous character of the modified biopolymer. These structural changes resulted from the incorporation of glycerol and citric acid molecules into the starch matrix, leading to improved homogeneity and flexibility of the polymer network. The formation of a partially amorphous structure is advantageous for processing and practical applications requiring enhanced mechanical performance.

Thermal characterization using TGA and DSC demonstrated a significant improvement in thermal stability after modification. The starch-modified biopolymer exhibited a higher onset degradation temperature, increased glass transition temperature, and greater residual mass at elevated temperatures compared with native starch. These findings indicate stronger intermolecular interactions and restricted molecular mobility resulting from effective crosslink formation. The enhanced thermal resistance suggests improved suitability for applications involving moderate thermal stress. Physicochemical investigations showed a reduction in moisture absorption and improved film integrity, flexibility, and dimensional stability. The synergistic effects of crosslinking and plasticization produced a balanced polymer structure with reduced brittleness and enhanced physical performance. Such improvements are particularly important for biodegradable materials intended for industrial and environmental applications. The results demonstrate that chemical modification is an effective approach for improving the structural, thermal, and physicochemical properties of starch-based biopolymers. The synthesized material exhibits promising characteristics for potential use in sustainable packaging systems, biodegradable coatings, agricultural films, and other environmentally friendly polymer products. Future studies may focus on optimizing formulation parameters and evaluating long-term mechanical, barrier, and biodegradation properties under various environmental conditions.

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