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Starch Biocomposite Reinforced With Chemically Modified *Hibiscus esculentus* Biofibers

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ABSTRACT

The global proliferation of non-biodegradable plastics in landfills and marine ecosystem represents a critical environmental crisis. To mitigate this, present study explores the development of sustainable, starch based bio composites. Starch biocomposites was fabricated using corn starch matrix cross-linked with urea-formaldehyde and reinforced with chemically modified *Hibiscus esculentus* biofibers. The mechanical and structural properties of cross-linked starch matrix and resulting biocomposite were comprehensively evaluated by universal testing machine, Fourier transform infrared spectroscopy, thermogravimetry, scanning electron microscopy, and X ray diffraction. Mechanical testing revealed that while the cross-linked starch matrix achieved tensile, compressive and flexural strengths of 11.26, 21.93, and 35.51 MPa, respectively. However, the incorporation of 15 wt% modified fibers in matrix significantly enhanced these properties to 17.2, 37.64, and 67.5 MPa. Thermal analysis indicated a substantial increase in stability; the final degradation temperature rose from 525°C (neat corn starch) to 671°C for the fiber reinforced biocomposites. Furthermore, the biocomposite demonstrated superior resistance to water and acid–base environments compare to starch matrix alone. In flammability tests of biocomposites, magnesium hydroxide fillers outperformed zinc borate in providing flame-retardant properties. These findings highlight the potential of starch fiber sustainable biocomposites as high performance, biodegradable alternatives to synthetic plastics, supporting the transition toward a circular economy.

1 | Introduction

Sustainable and circular bioeconomies have emerged as new frameworks which can drive future growth and development in a global bioeconomic model. With increasing concerns over depleting fossil fuels, coupled with the escalating issues of climate change, plastic waste and carbon footprint awareness, interest in ecofriendly materials has risen in both research and commercial settings [1]. The global plastic market was worth USD 764.32 billion in 2025 and is projected to grow by 4.1% annually for the next five years [2]. Synthetic plastic products have resulted in huge accumulations of plastic waste which impart environmental toxicity and are non-biodegradable in nature [3]. By 2050, environmental scientists project that 12,000 million tonnes of plastic waste will be accumulated in landfills worldwide [4]. Thus, the non-biodegradable nature of synthetic plastics and

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Highlights

- Starch biocomposites are eco-friendly alternatives to synthetic plastics.
- 15% fiber loading yields 37.6 MPa compressive and 67.5 MPa flexural strength.
- Biocomposites dielectric parameters exhibit low values when compared to matrix.
- Biodegradability studies confirm 40% weight loss within a seven-week period.

criteria for a cleaner and safer environment has motivated researchers toward sustainable and biodegradable composite materials which have the potential to exhibit high performance along with environmentally friendly features [5–7].

For the last decade, there have been significant advances in using natural biopolymers to create sustainable materials [6, 7]. Biopolymers and biofibers have emerged as promising and excellent alternatives for developing new material systems and formats which have potential applications in packaging, medical, construction, energy, and automotive sectors [5–7]. In the quest for sustainable materials, crosslinked starch stands out as an innovative, eco-friendly alternative to traditional plastics [8, 9]. Made from natural grains, crosslinked starch embodies circular economy principles by turning waste or under valorised by-products into valuable resources which in turn boosts both the mechanical properties and environmental responsibility of biocomposites [8, 9]. Starch is a favored biopolymer for industrial use due to its wide availability, non-toxicity, and its chemical structure allows it to form a strong polymeric matrix [8–10]. With heat, shear, and addition of a plasticizer, starch can even be transformed into a thermoplastic-like material, which enhances some of its natural properties and makes it easier to process [8–11]. However, starch materials have limitations, including poor melting processability, high water solubility, mechanical strength, and barrier properties which hinder their broader applications [12]. However, starch polymeric materials have a couple of downsides as they are hydrophilic and have poor mechanical strength [13]. Modification of starch with cross-linkers such as phenol-formaldehyde, urea-formaldehyde, plasticizers such as glycerine, and other polyol compounds are known to be effective in increasing its strength [14–16]. Further, blending with other materials and by adding cellulosic biofibers as fillers offer promising ways to improve the technological potential of starch-based products [5, 15]. Mixing starch with other polymers reduces its biodegradability, and thus there is a need for biodegradable fillers. Different researchers used various natural fibers such as Saccharum, sisal, coconut, coir, and husk as reinforcing agents in starch biocomposite and evaluated different properties of these biocomposites [5, 17, 18]. Singha et al. studied the raw and alkaline treated okra fiber reinforced starch biocomposites. It was found that the mechanical properties of the biocomposite were increased by the incorporation of fibers in the starch matrix as a reinforcing agent [6, 15]. Zhang et al. demonstrated that thermoplastic starch with sugarcane cellulose formed a highly compatible material which has a tensile strength of 3.75 MPa [11]. Their TPS/corn-starch cellulose film also exhibited a high degradation temperature of 325°C. However, their study also noted a substantial increase in water absorption from 6.2% to 42.3% as cellulose filler content in TPS resin increased from 0% to 25%. Behra and his co-authors found that adding 10 wt% cellulose and soy waste optimized the tensile and flexural strength of TPS/soy pulp composites [19]. In another study, sugar palm fiber that exhibits a range of applications improved composite performance due to changes to surface structure orientation, distribution, and composition of fiber [20].

Further, to increase fiber-matrix interface, the surface of natural fibers has been modified using various methods like NaOH treatment, silane modification, grafting, bleaching, acetylation, and benzoylation [21]. Alkaline treatment and grafting are widely used methods for surface modification of natural fibers [22]. Reddy et al. studied the alkaline treatment of various natural fibers such as Tapsi natural bark, *Cordia dichotoma*, and *Balanites aegyptiaca*, which was used for composite preparation [23, 24]. Furthermore, grafting is another widely used technique for surface modification of natural fibers, and it enhances the various properties of surface modified fiber reinforced composites [22]. Surface modified natural fibers played an important role in the polymer matrix that is to transfer stress from the weak matrix to strong fibers [25]. In recent years, research has focused on improving various properties of natural/modified cellulosic fiber reinforced starch biocomposites. This approach has been widely reported by researchers globally [23]. In view of this, we fabricated the starch biocomposites reinforced with chemically modified *Hibiscus esculentus* biofibers, which have not been reported in the literature, and the fabricated biocomposites were evaluated for different properties.

As a result, the present study aims to create and characterize sustainable starch biocomposite reinforced with chemically modified *Hibiscus esculentus* biofibers. However, to the best of our knowledge, no information is available on the fabrication and preparation of chemically modified *Hibiscus esculentus* biofibers reinforced starch composites. The fabricated biocomposites were studied by FT-IR, FE-scanning electron microscopy (SEM), X-RD, thermogravimetry (TGA), LCR impedance analyzer, and oxygen index analyzer techniques. Biocomposites are evaluated for mechanical, thermal, flame retardant, dielectric, acid–base resistance, and biodegradable properties. Mechanical, thermal, and acid–base resistance of biocomposites were found to be better as compared to crosslinked starch matrix. This approach alleviates issues around waste management and has the potential to contribute to economic growth in low-income countries whilst promoting the adoption of eco-friendly materials.

2 | Experimental Sections

2.1 | Materials

Corn starch (99% purity), magnesium hydroxide $Mg(OH)_2$, zinc borate ($Zn_3B_2O_6$), urea $CO(NH_2)_2$, formaldehyde (HCHO), acrylonitrile (AN), and sodium hydroxide (NaOH) were supplied by CDH, New Delhi, India. Acetone, hydrochloric acid (HCl), hydrogen peroxide (H_2O_2), dimethyl sulfoxide (DMSO), and ascorbic acid were supplied by E-Merck, Mumbai, India. Distilled water was used for experimental work. *Hibiscus esculentus* (HE)

biofibers were extracted from HE plant stems obtained from the Kangra region of Himachal Pradesh.

2.2 | Extraction of *Hibiscus esculentus* (HE) Biofibers

Hibiscus esculentus biofibers were obtained from HE plants stem by a water retting process as reported in the literature [24]. HE biofibers were extracted from the bast of plants having excellent fiber quality was collected and then these were immersed in running fresh water for maximum of 1 month so that waxes and outer covering layer on the stems were removed. The stems were then taken out and rubbed gently in order to remove the cementing materials and separating the fibers from the stem. The fibers thus obtained were washed with mild detergent to remove other associated impurities and these were then dried in hot air oven maintained at 65°C for 24 h. HE biofibers were soxhlet extracted with acetone for the removal of waxes, fatty acids, lipids and low molecular weight phenolic compounds. The soxhlet-extracted HE biofibers were subsequently washed with double distilled water and re-dried in oven at 60°C for 48 h.

2.3 | Chemical Modification of *Hibiscus esculentus* Biofibers

Chemical modification of soxhlet-extracted HE biofibers was carried out by graft copolymerization technique using acrylonitrile (AN) vinyl monomer. Grafting was optimized based on monomer concentration, initiator concentration, time and temperature to achieve maximum graft yield as reported in our previous studies [25]. HE biofibers were graft copolymerized by using AN monomer using ascorbic acid and hydrogen peroxide as a redox activator. For the activation of reaction sites, 0.5 g of HE biofibers was submerged in distilled water for 24 h in a round bottom flask (RBF). HE-g-poly (acrylonitrile) graft copolymer was prepared by taking 0.5 g of HE biofibers in RBF fitted with a stirrer (RBF) in which a determined amount of ascorbic acid and hydrogen peroxide was added. This reaction mixture was then placed in an oil bath and its temperature was maintained at 45.0°C ± 0.1°C. Afterwards, the determined amount of AN monomer was added and the reaction was conducted for the given time. During the grafting reaction, a non-grafted poly (AN) homopolymer was also associated with the grafted product which was extracted by soxhlet extraction with dimethyl sulfoxide for 12 h. Soxhlet-extracted samples were then rinsed with deionized water and desiccated at 70°C in a hot air oven. Maximum grafted HE biofibers were then transferred to a ball milling apparatus to convert them into microfibers and these were used for the fabrication of starch biocomposites.

2.4 | Fabrication of Chemically Modified HE Biofibers Reinforced Starch Biocomposites

The chemically modified fiber-reinforced composites were fabricated using urea–formaldehyde (UF) as cross-linker. Starch matrix and biocomposites were prepared by preparing a thick slurry of starch which was stirred at 60°C for 30 min. UF was used as cross-linker for manufacturing of matrix and biocomposites. Matrix and biocomposites were fabricated using a 12 wt% loading of urea-formaldehyde resin as reported in our previous studies [6]. An iron die of dimension 15 cm × 15 cm × 1 cm was used for preparation of starch biocomposites and for easy processing of biocomposites iron die interior surfaces were coated with oleic acid to prevent the material from sticking to the molds walls. Optimized concentration of UF cross linker was used for the preparation of starch and its biocomposites with modified cellulosic biofibers. The biocomposites sheets were prepared by reinforcing chemically modified HE fibers in particle form with different percent loading from 5% to 25% by w/w ratio. The semi-solid paste was poured into previously described iron die 15 cm × 15 cm × 1 cm and allowed to pre-cure for 24 h. Afterwards, the pre-cured biocomposites were subjected to pressure of 100 kg/cm^2 by carver hydraulic press at 90°C for 1 h.

2.5 | Fabrication of Flame Retardants Starch Biocomposites

Flame retardant biocomposites were prepared by adding magnesium hydroxide and zinc borate to them. The flame-retardant starch matrix was prepared by adding magnesium hydroxide and zinc borate at 10%, 20%, and 30% w/w ratio. For preparation of flame-retardant composites with maximum mechanical properties were taken and 30% w/w ratio of $Mg(OH)_2$ and ($Zn_3B_2O_6$) was added to them.

3 | Characterization of Chemically Modified Cellulosic Fibers Reinforced Starch Biocomposites

Functional groups analysis of native starch, cross-linked starch matrix and chemically modified HE microfiber reinforced starch biocomposites was conducted using Perkin-Elmer Fourier transform infrared spectroscopy spectrophotometer (Shelton, U.S.A). Samples were mixed with potassium bromide and converted into pellets which was scanned in the transmittance mode from 4000 to 500 cm^{-1} with a resolution of 2 cm^{-1}. Thermal analysis of starch, starch matrix and its modified fibers reinforced biocomposites was analyzed using an Ex-Star TG/DTA 6300 (Hitachi High-Tech Science Corporation, Tokyo, Japan). Matrix and biocomposites specimen were heated from 10°C to 800°C at a heating rate of 10°C/minute to capture decomposition and phase transitions. Crystallinity and phase composition were assessed with Philips 1710 X-ray diffractometer (Netherlands, Eindhoven). Samples were crushed into powdered form and were scanned from 5° to 50° 2Θ step of 2Θ per minute using 40 kV and generator settings. Surface morphology of the starch matrix, chemically modified HE microfiber-reinforced composites specimens were examined at high magnification using-SEM (FEI Quanta 250F, Netherlands, Eindhoven) to assess fiber dispersion, interfacial interactions and material degradation features.

3.1 | Assessment of Mechanical, Flammability and Dielectric Studies of Fabricated Starch Biocomposites

Hounsfield universal testing machine (H25KS, Bedfordshire, United Kingdom) was employed to assess various mechanical

properties of biocomposite samples. Biocomposite specimens (10×1×0.5) cm were evaluated using standardized American testing methods. Biocomposite mechanical properties such as tensile properties were assessed according to ASTM D3039, compressive properties per ASTM D 3410, and flexural properties following ASTM D 790. Flammability studies of starch matrix and its biocomposites were conducted using an Oxygen Index Analyzer using ASTM D-2863-77. Dynisco 230 (Massachusetts, USA) (limited oxygen index) LOI-smoke, Alpha technologies model was used for flammability studies. The LOI test of matrix and starch biocomposites prepared with different flame retardants such as magnesium hydroxide and zinc borate were performed as per standard mentioned above. For LOI test, specimens measuring 10 cm in length, 6 cm in width, and 3 cm in thickness were used. Each specimen was mounted vertically in the holder such that it was positioned at 100 mm below the top of the glass column. LOI was determined as the lowest oxygen concentration at which a 5 cm section of the specimen could burn continuously or remain a flame for 180 s. Each sample was tested three times at varying flow rates, using sections between 3 cm and 5 cm in length.

Dielectric properties of starch matrix and biocomposites samples were measured at 25°C across a frequency of 1 kHz to 1 MHz range using LCR impedance analyzer (Wayne Kerr model 6520A, Sussex, United Kingdom). For dielectric properties, samples of starch matrix and modified HE fibers reinforced biocomposites were cut into (10 mm × 10 mm × 2 mm) rectangular pieces. Each specimen was coated on both faces with silver paste and air dried. Afterwards, on dried samples, copper wires were attached to the opposing faces to serve as electrodes.

3.2 | Assessment of Water Uptake, Acid–Base Resistance and Biodegradability Behavior of Biocomposites

Starch and biocomposites samples were dried in oven for 24 h at 60°C. After drying, their water uptake behavior was evaluated by immersing pre-weights specimens in 100 mL of D.W. for 24 h at 25°C. Following immersion, the samples were removed from the water. These samples were then gently wiped with cotton cloth to remove surface water and weighed again. Water uptake percentage was calculated using the formula as follows:

$$\%\,\text{Water uptake} = \frac{W_2 - W_1}{W_1} \times 100 \tag{1}$$

where W_1 is the initial dry weight and W_2 is the weight after immersion.

For acid–base resistance studies of biocomposites, 1 N HCl and NaOH solutions were used for different time intervals. Weight loss was monitored at various time intervals and final weights were recorded. The percentage of weight loss was determined by the following formula:

$$\%\,\text{Weight loss} = \frac{W_1 - W_2}{W_1} \times 100 \tag{2}$$

where W_1 represents the initial weight of biocomposite sample and W_2 denotes the weight after specified time interval.

Biodegradability studies of chemically modified HE fibers reinforced biocomposites was assessed using soil burial method. Test samples were buried approximately 20 cm deep in natural soil for 120 days. The soil used contained a diverse population of microorganism capable of degrading various organic materials. Prior to burial, the initial weights (W_i) of each sample was recorded. Subsequently, the samples were retrieved (W_f) at a regular interval of 1 week. Percent biodegradability of samples was determined as follows:

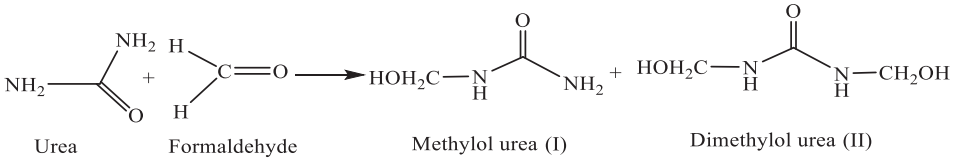
$$\%\,\text{Biodegradability} = \frac{W_i - W_f}{W_i} \times 100 \tag{3}$$

4 | Results and Discussion

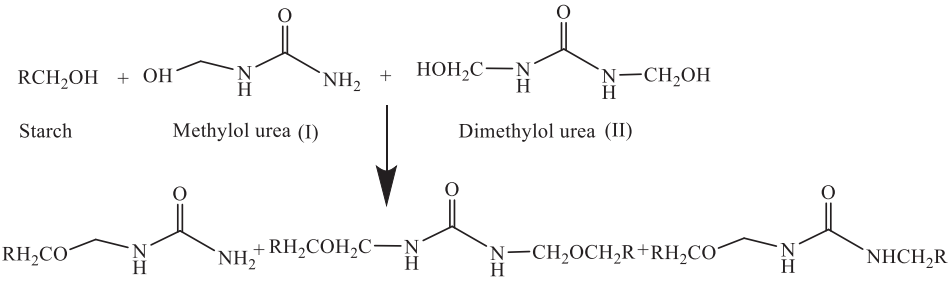
4.1 | Proposed Mechanism for Synthesis of Cross-Linker and Starch Matrix Biocomposites

Urea-formaldehyde (UF) cross-linker was synthesized following a previously reported method in the literature [26] and the reaction is proposed to proceed through the mechanism shown in Scheme 1. The reaction between urea and formaldehyde typically yields methylol urea (I) and dimethylol urea (II) as depicted. The formation rates of these products are influenced by temperature, pH, and formaldehyde to urea ratio. To facilitate the controlled synthesis of dimethylol urea, a slightly alkaline medium (pH of 7–8) is preferred. In the next step, the synthesized cross-linker has been used for the production of the cross-linked starch matrix and its biocomposites. Scheme 2 illustrates the reaction pathways for synthesizing UF cross-linked starch matrix. During both the pre-curing and curing stages, the hydroxy groups within the starch act as the active sites for cross-linking with UF. The primary hydroxy group located at carbon six position in starch is understood to be more reactive than its secondary hydroxy counterparts. Consequently, it is the primary hydroxy groups that are predominantly involved in this cross-linking reaction, and this is further supported by literature [27].

Cross-linking was optimized to achieve a balance of mechanical strength and biodegradability. Figure 1 shows the impact of UF on the tensile strength (TS) of the starch matrix. From Figure 1, it can be determined that the TS of the matrix increases with increasing UF content. This is attributed to enhanced covalent bonding between the hydroxy groups present in the starch and



SCHEME 1 | Synthetic pathway for formation of Urea–formaldehyde cross-linker.



SCHEME 2 | Cross-linked starch using Urea–formaldehyde.

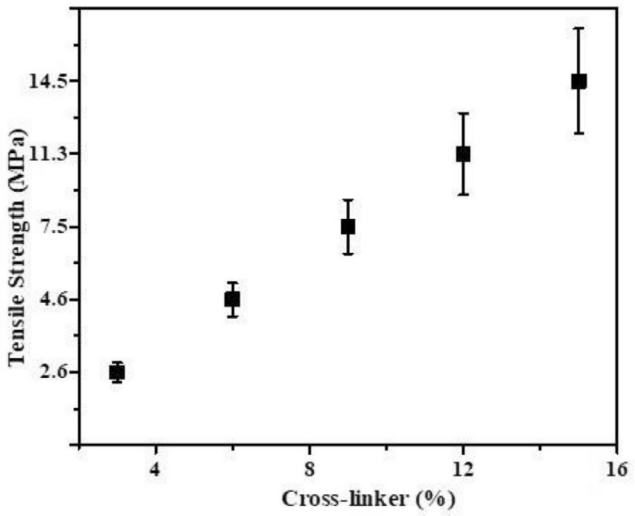


FIGURE 1 | Impact of UF on the tensile strength (TS) of starch matrix.

UF. While increasing the crosslinker concentration consistently boosted the TS of the matrix, it also led to a reduction of biodegradability. Thus, a 12% crosslinker concentration was chosen as optimal for preparing the matrix and for subsequent biocomposite production.

4.2 | Chemical Composition of Starch Biocomposites

FT-IR spectra for starch, UF cross-linked starch matrix, raw HE fibers reinforced starch biocomposites and chemically modified HE fibers reinforced composites are shown in Figure 2. From the FT-IR spectra, it can be observed that starch shows a broad band between 3200 and 3600 cm^{-1} due to O—H and a band at 2928 cm^{-1} C—H stretching. FT-IR shows a band at 1644 cm^{-1} assigned to O—H bending, while C—O bond stretching was evident through bands at 1157, 1080 and 1020 cm^{-1} [22]. In case of the matrix, a decrease in the intensity of the broad band due to O—H stretching at 3200–3600 cm^{-1} and C═O stretching vibration band at 1650 cm^{-1} due to amide functional group was observed [27].

While, in cross-linked starch matrix bands at 1555 cm^{-1}, 1385 cm^{-1} and 1255 cm^{-1} was due to be due to evidence of N—H bending in amide, N—O stretching and C—N stretching, respectively. Further, the strong band at 1380 cm^{-1} indicates CH_2 bending and the band at 1260 cm^{-1} was due to C—N vibrations in the amine of the cross-linked matrix. In the case of both raw and chemically modified HE fibers reinforced starch composites, an additional band at 1735 cm^{-1} was observed. This band is characteristic of C═O stretching vibrations of carboxyl groups found in hemicelluloses present in fiber. Furthermore, for chemically modified starch composites, a distinct band at 2245 cm^{-1} appeared due to stretching vibrations of the nitrile group of acrylonitrile monomer used for chemical modification [25].

4.3 | Phase Composition and Crystallinity of Starch Biocomposites

Figure 3 illustrates the X ray diffraction patterns for starch, UF cross-linked matrix and its biocomposites reinforced with chemically modified HE fibers. Starch displays its characteristic strong diffraction peaks at 15.0°, 17.2°, 17.8°, 22.8°, and 23.5° and weak intensity diffraction peaks at 11.4°, 20.1° and 26.3°.

While, UF cross-linked starch exhibits new peaks at 20.5° and 22.2°. This indicates a disruption of the starch's original crystalline structure. Furthermore, the X-ray diffractograms of modified fiber-reinforced starch composites reveal a more intense and prominent peak at 22.5°. This enhanced peak is attributed to the presence of crystalline cellulose which is present in the reinforcing fiber [24].

4.4 | Thermal Properties of Starch Biocomposites

The initial degradation of starch is attributed to dehydration, glycogen formation and depolymerization. Figure 4a represents the thermal analysis of starch. Native starch began to decompose at 277°C (initial decomposition temperature, IDT) and completely decomposes at 525°C (final decomposition temperature FDT), respectively. Starch exhibited a two-stage decomposition within the temperature ranges of 275°C–318°C and 318°C–525°C, corresponding to 74.5% and 24.5% wt. loss. The initial stage involves dehydration, whereas second stage involves decomposition due to depolymerization.

Figure 4b shows the thermal analysis of UF crosslinked starch matrix which shows two stage decompositions. However, the first stage decomposition for cross linked matrix begins at a lower temperature which is due to presence of UF crosslinker [28]. The IDT and FDT for UF crosslinked starch were determined to be 200°C and 637°C, respectively. The two-stage decomposition observed for the crosslinked starch matrix occurs between 200°C and 330°C with 55% weight loss and 340°C–637°C, accounting for a 45% weight loss.

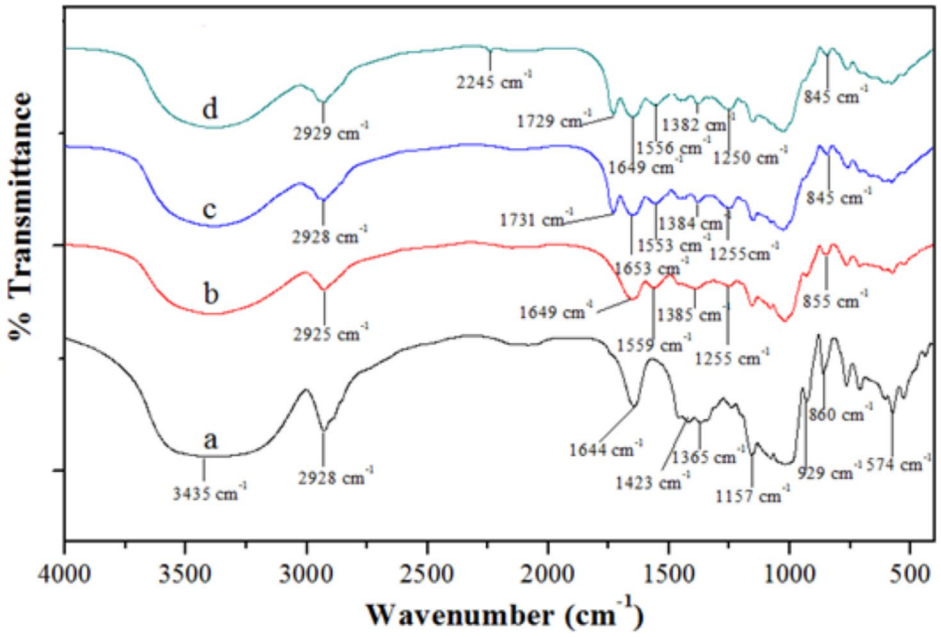


FIGURE 2 | FT-IR spectra of (a) corn starch, (b) UF cross-linked starch matrix, (c) raw fiber reinforced starch composites, (d) chemically modified fiber reinforced composites.

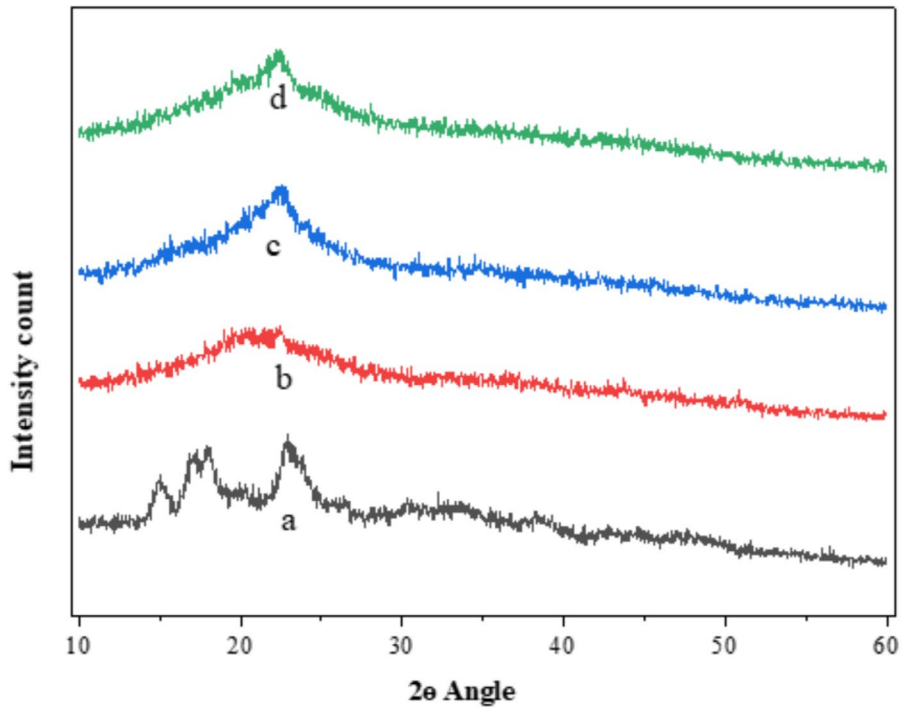


FIGURE 3 | X-RD pattern of (a) corn starch (b) UF cross-linked starch matrix (c) raw fiber reinforced composites (d) poly (AN) grafted fiber reinforced composites.

Figure 4c,d presents the thermal analysis of UF crosslinked starch composites reinforced with raw fibers and chemically modified HE fibers reinforced starch composites. For raw fibers reinforced starch composites, IDT and FDT were determined to be 200°C and 657°C. For chemically modified HE fibers reinforced starch composites, IDT and FDT were determined to be 200°C and 671°C. The thermal analysis indicates two-stage decomposition for chemically modified HE fibers reinforced starch composites. For chemically modified HE fibers reinforced starch composites, the first stage decomposition occurs between 200°C and 355°C with 50% weight loss and 356°C–671°C, accounting for a 40% weight loss. Based on TGA/DTA data, both the starch matrix and biocomposites show improved thermal resistance. This enhancement is attributed to the formation of covalent bonds via cross-linking and the reinforcing effect of incorporated fibers. The data further revealed that the FDT's of fabricated biocomposites were higher than starch as well as UF cross-linked starch matrix. This improved thermal stability may be due to the polymeric grafted

chains onto cellulosic fibers which are capable of withstanding higher temperatures [25].

4.5 | Morphological Properties

SEM analyzed the morphology of raw fiber and modified fiber as shown in Figure 5. It can be observed from the SEM images that the surface of raw fiber is smoother and the surface of modified fiber is rougher or uneven, which confirms the modification of cellulosic fibers. SEM analysis of starch, crosslinked starch matrix, modified HE fibers reinforced starch composite, and biodegraded biocomposite samples has been shown in Figure 6a–e. In Figure 6a, it can be observed that starch shows polyhedral or polygon shaped granules. While the crosslinked starch matrix shows a smooth surface with no visible pores and cracks.

Furthermore, SEM images of fiber reinforced starch composite show excellent fiber dispersion and thorough

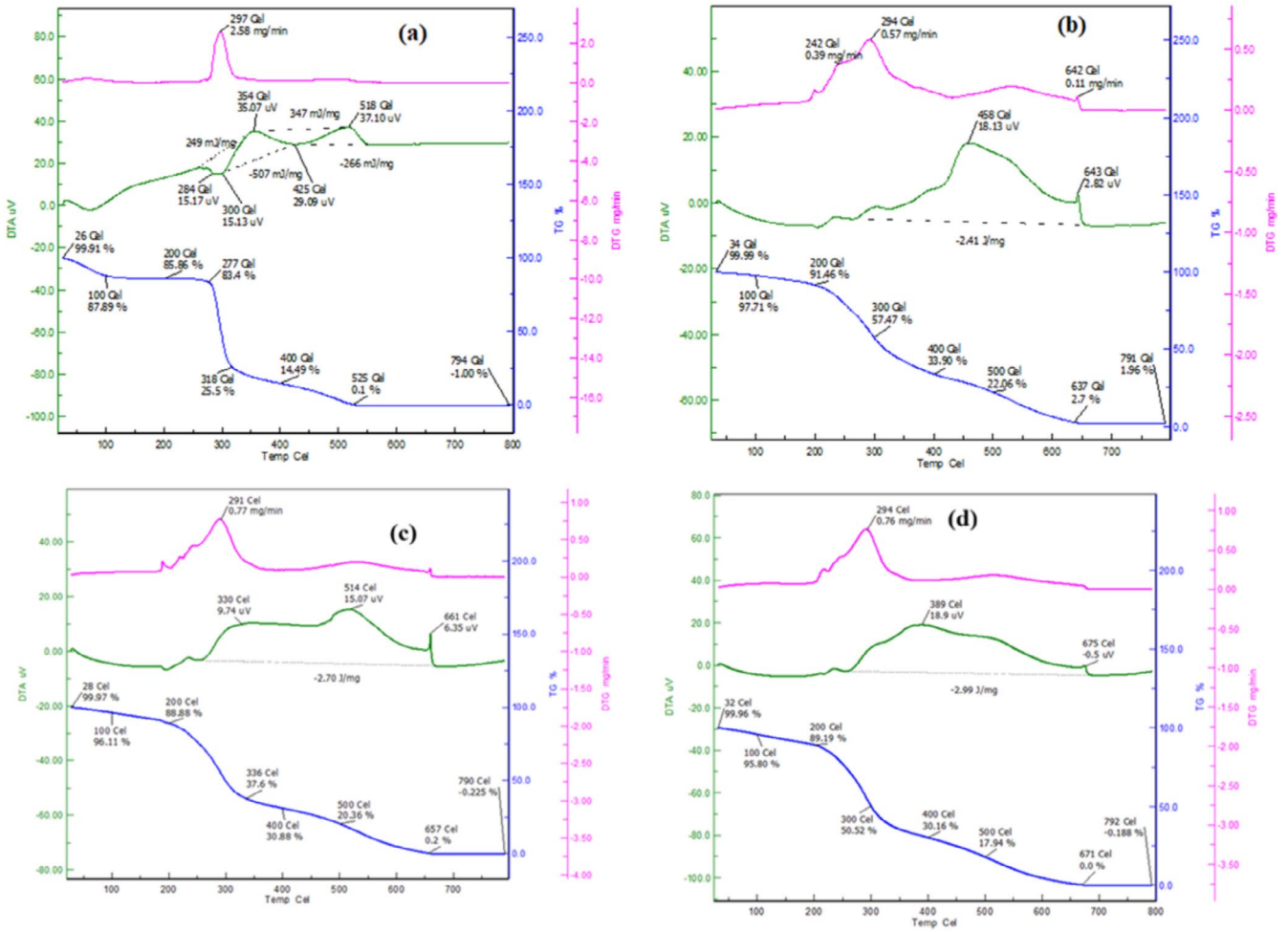


FIGURE 4 | Thermogram of (a) native starch (b) UF cross linked starch matrix and (c) raw HE fiber reinforced starch biocomposites (d) modified HE fiber reinforced starch biocomposites.

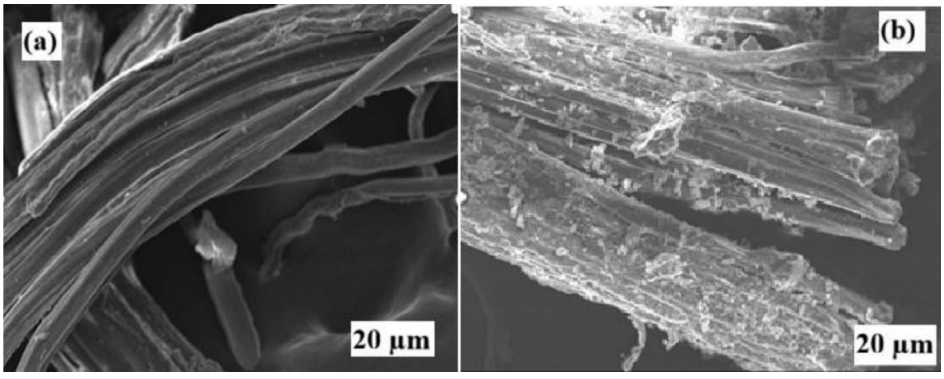


FIGURE 5 | SEM images of (a) natural HE fiber (b) modified HE fiber.

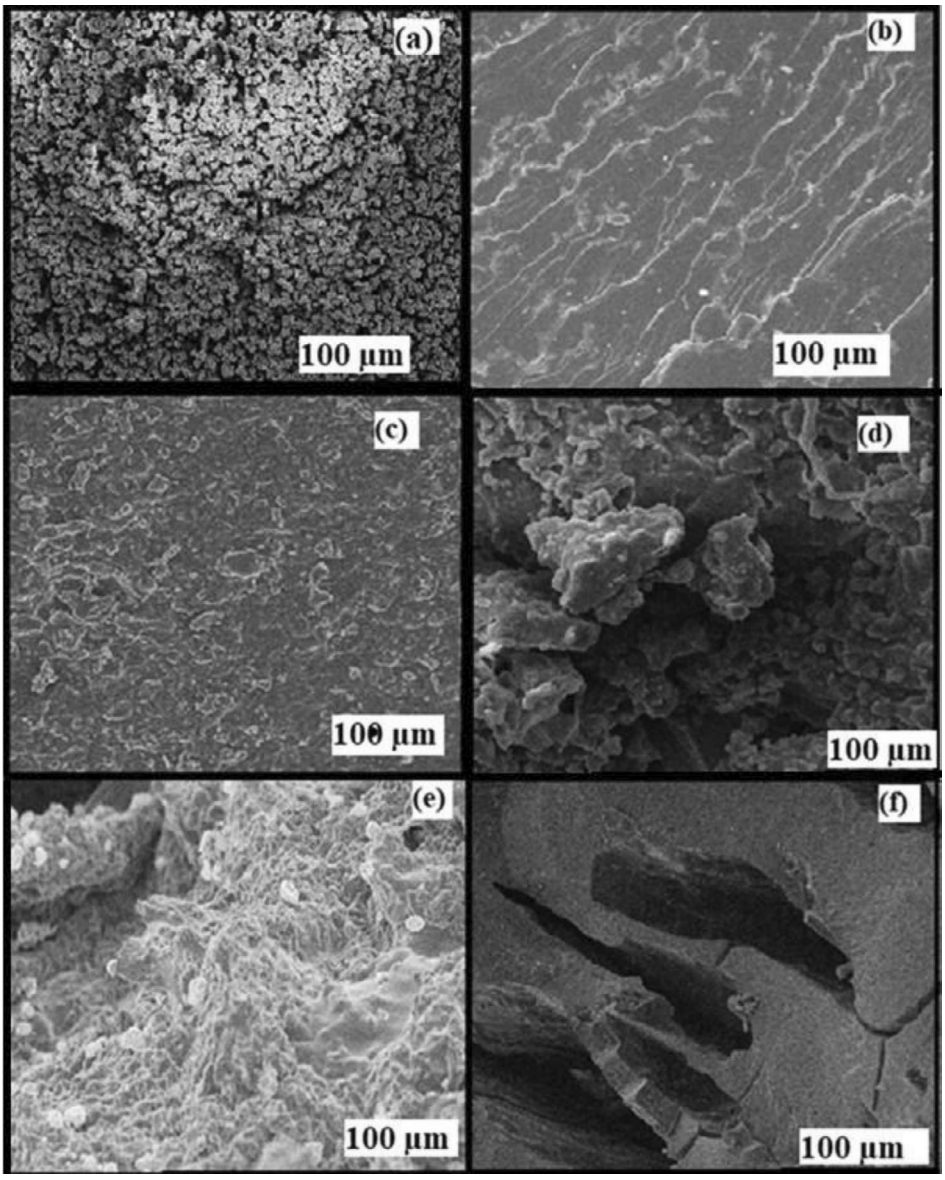


FIGURE 6 | SEM images of (a) starch (b) UF cross-linked starch matrix (c) modified HE fiber reinforced composites (d–f) modified HE reinforced composites reinforced at three different stages of biodegradation.

mixing within the crosslinked starch matrix. Figure 6d–f illustrates the morphological changes on the surface of starch matrix and biocomposites during various stages of biodegradation. SEM images clearly indicate that the biodegrading matrix surface becomes significantly rougher compared to non-biodegraded samples, providing strong evidence of biodegradation.

4.6 | Mechanical Properties of Chemically Modified HE Fibers Reinforced Starch Biocomposites

Figure 7 illustrates tensile, compressive, and flexural strengths of the biocomposites containing varying weight percentages of chemically modified HE fibers. The mechanical properties of modified HE fibers biocomposites were significantly impacted by the interfacial interaction between the matrix and fibers. Notably, biocomposites reinforced with chemically modified

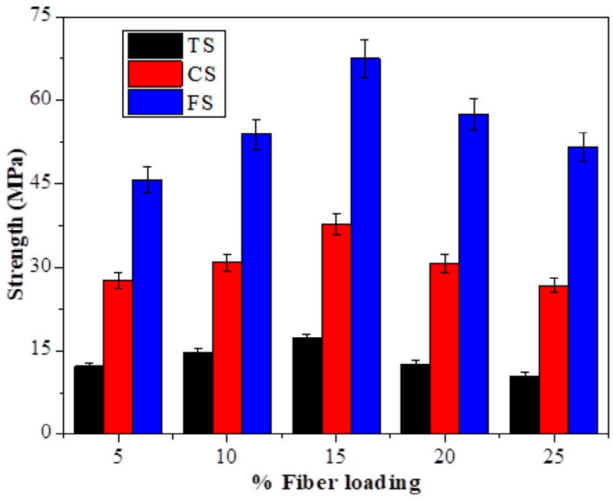


FIGURE 7 | TS, CS, and FS results of modified HE fibers reinforced starch biocomposites.

HE fibers demonstrated superior mechanical properties as compared to the matrix.

Starch matrix exhibited TS of 11.26 MPa, compressive strength (CS) 21.93 MPa and flexural strength (FS) of 35.51 MPa. In case of chemically modified HE fibers reinforced starch biocomposites exhibited TS of 12.24, 14.7, 17.2, 12.6, and 10.56 MPa at 5%, 10%, 15%, 20%, and 25% loading, respectively. Similarly, chemically modified HE fibers reinforced starch biocomposites exhibited CS of 27.7, 30.9, 37.64, 30.7, and 26.8 MPa at 5%, 10%, 15%, 20%, and 25% loading, respectively. Further, chemically modified HE fibers reinforced starch biocomposites exhibited FS of 45.73, 53.9, 67.5, 57.5, and 51.62 MPa at 5%, 10%, 15%, 20%, and 25% loading, respectively. Mechanical testing revealed that composites with 15% fiber loading by weight consistently achieved the maximum TS, CS, and FS. This enhanced performance may be due to improved load transfer from matrix to the reinforcing fibers. However, after 15% fiber loading, there is a decrease in TS, CS and FS due to agglomeration of fibers. As a result of agglomeration of grafted fibers, a poor fiber-matrix interface is developed and load cannot be transferred from matrix to fibers which results in the failure of composites at lower load. Reinforced biocomposites failure under longitudinal tensile load was due to breakage at a weaker point in reinforcement and load transfer to reinforcement which ultimately results in complete rupture of biocomposite [26]. Adhesive and stiffness characteristics of the reinforcement are paramount for straightness and buckling of fibers. Compression failure of biocomposites was typically instigated by abrupt and significant fiber buckling. The buckling is often preceded by debonding and micro-cracking, which constitutes the predominant failure mode for composites subjected to longitudinal compressive forces [29].

4.7 | Flammability Properties of Fabricated Starch Biocomposites

Flammability studies of starch matrix and chemically modified HE fibers reinforced starch biocomposites with different fire retardants have been displayed in Table 1. Biocomposites reinforced with chemically modified HE fibers show a higher limiting oxygen index (LOI) when contrasted with UF cross-linked starch matrix. The improved LOI in starch biocomposite containing chemically modified HE fibers is attributed to the enhanced high-temperature stability of grafted polymeric chains on fibers. These results align with the TGA results, further supporting the increased thermal stability of these biocomposites. Additionally, incorporating the fire retardants $Mg(OH)_2$ and $Zn_3B_2O_6$ also boosts the LOI. As the percentage of these retardants increases from 10% to 30% by weight, the LOI of starch matrix increases. Among both the fire retardants, magnesium hydroxide provides a more significant increase in fire retardancy than zinc borate, likely due to its superior thermal stability [30].

TABLE 1 | Impact of fire retardants on LOI of modified HE fibers reinforced UF crosslinked starch biocomposites.

Corn-starch: HE fiber ratio (% by weight)	Fire retardant (% by weight of corn starch matrix)	LOI
100% UF-cl-CS matrix		17
85% UF-cl-CS matrix +15% modified HE fibers		20
100% UF-cl-CS matrix	10% $Mg(OH)_2$	18
100% UF-cl-CS matrix	20% $Mg(OH)_2$	19
100% UF-cl-CS matrix	30% $Mg(OH)_2$	22
85% UF-cl-CS matrix +15% raw fiber	30% $Mg(OH)_2$	19
85% UF-cl-CS matrix +15% modified HE fibers	30% $Mg(OH)_2$	23
100% UF-cl-CS matrix	10% $Zn_3B_2O_6$	18
100% UF-cl-CS matrix	20% $Zn_3B_2O_6$	19
100% UF-cl-CS matrix	30% $Zn_3B_2O_6$	20
85% UF-cl-CS matrix +15% raw fiber	30% $Zn_3B_2O_6$	18
85% UF-cl-CS matrix +15% modified HE fibers	30% $Zn_3B_2O_6$	21

4.8 | Electrical Dielectric Properties: Dielectric Constant, Dissipation Factor and a. c. Conductivity

Optimized samples of UF crosslinked starch matrix and chemically modified HE fibers reinforced starch composites were analyzed for dielectric constant, dissipation factor (tanδ) and a. c. conductivity. It can be observed form Figure 8, dielectric constant of raw HE fiber reinforced composites exhibit a higher value as compared to crosslinked starch matrix-based composites. This is because dielectric constant is directly related to the polarizability of the molecules. The presence of raw fibers in starch matrix introduces a significant number of polar groups. These groups lead to increased dipole or orientation polarizability. Polarizability of a raw fiber composite is sum of electronic, atomic and orientation polarization which favors higher dielectric constant. Conversely, the dielectric constant decreases in chemically modified HE reinforced biocomposites. This reduction is attributed to a decrease in orientation polarization of grafted fibers. Chemical modification reduces the hydrophilicity of the fibers, which in turn lower their orientation polarization and subsequently the dielectric constant [31]. Therefore, chemically modified HE fiber reinforced composites show a lower dielectric constant compared to those with raw fibers. A similar trend was observed for the dissipation factor as a function of frequency. The dissipation factor generally decreases with increasing frequency. In the low frequency region, significant variation is apparent: chemically modified HE fiber reinforced composites exhibit the lowest dissipation factor, while raw fiber reinforced composites show the highest a given frequency.

This behavior is explained by the higher number of polar groups in raw fibers compared to grafted fibers which leads to increased orientation polarization and thus a higher dissipation factor. At higher frequencies, the orientation of polar groups becomes more challenging, causing a significant decrease in the dissipation factor. The a. c. conductivity of the composites, as a function

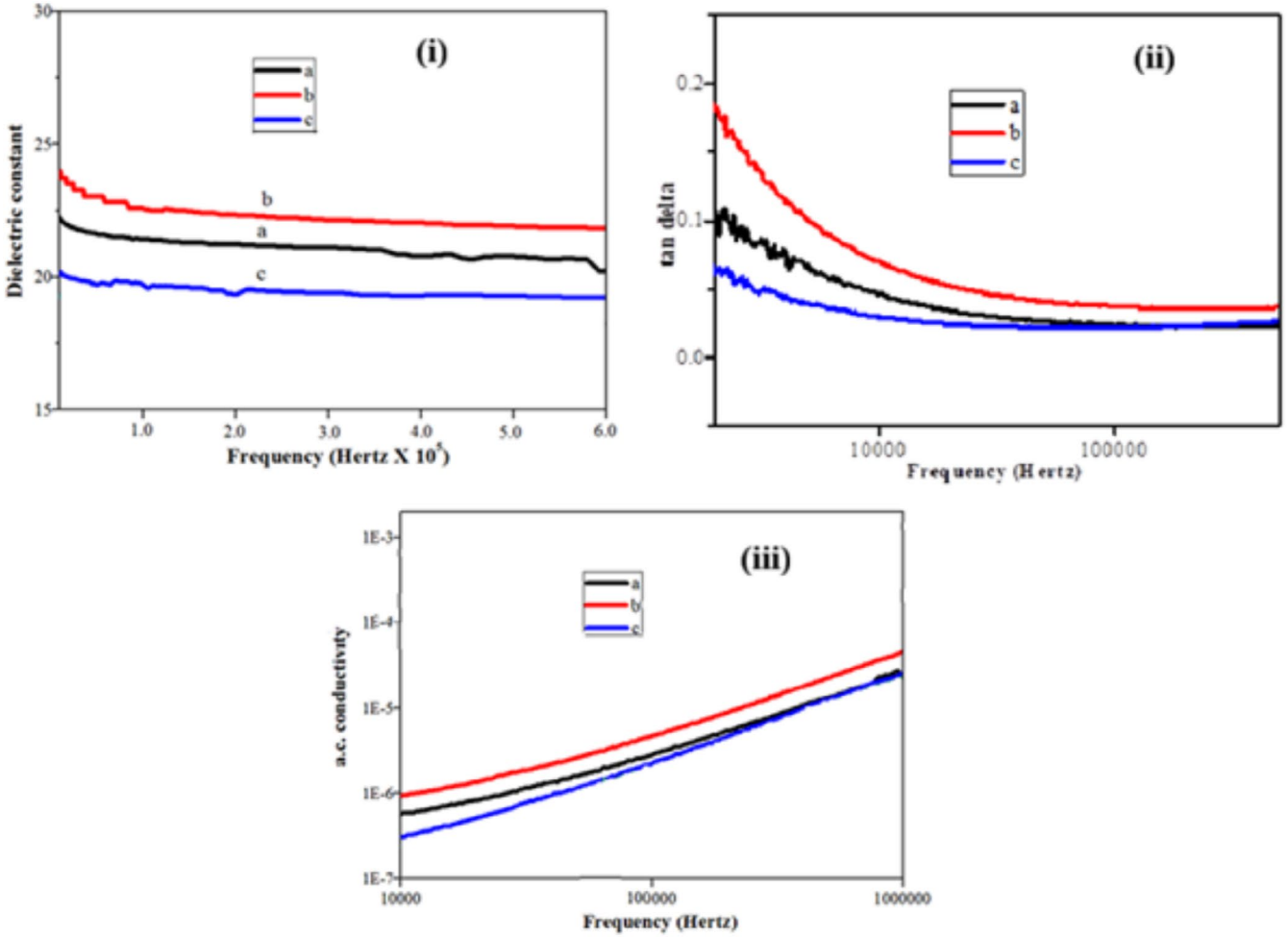


FIGURE 8 | (i) Dielectric constant vs. Frequency, (ii) tan delta vs. Frequency (iii) a. c. conductivity versus Frequency of (a) starch matrix, (b) raw HE fiber reinforced biocomposite, and (c) modified HE fiber reinforced biocomposites.

of frequency is presented in Figure 8. The figure shows that the conducting nature of composites increases with frequency. Raw fiber reinforced composites exhibit the highest conductivity compared to poly (AN) grafted fiber reinforced composites. This is attributed to the increased presence of polar groups in the raw HE fibers. However, the random orientation of these fibers does not significantly promote current flow.

4.9 | Acid and Base Resistance Properties

The acid and base resistance behavior of matrix and biocomposites was performed in terms of percent weight loss and results have been represented in Figure 9 respectively. In the case of the acid resistance study, natural starch totally degraded after 24 h and in the case of the base resistance study, the natural starch completely degraded after 4 h. Figure 9a,b illustrate that both crosslinked starch matrix and biocomposites reinforced with modified fibers show greater resistance to acids and bases compared to natural starch. This enhanced resistance is due to condensation reaction of starch's active hydroxy and hydroxymethyl groups with urea–formaldehyde during crosslinking, which forms a robust 3D-network linked by covalent bonds. Because the active sites that were vulnerable to acid or base attack were blocked, both the matrix and its biocomposites showed increased resistance. Furthermore, composites fabricated with modified HE fibers had even better acid and base resistance than the starch matrix. Modified fiber reinforced biocomposites display superior chemical resistance when compared to the crosslinked matrix and native starch. This improvement is likely due to the presence of poly (AN) chains onto chemically modified fibers which resist acid and base attack.

4.10 | Water Absorption Properties

Water absorption studies were performed on optimized UF matrix and biocomposites, which show highest mechanical strength, as shown in Figure 10a. Native starch showed 85% water uptake after 24 h, and crosslinking significantly improved the starch matrix resistance to water uptake. This improved resistance is likely due to the condensation reaction of hydroxy group of starch and formation of a three-dimensional network during pre-curing and curing processes. Further, chemically modified HE reinforced starch composites exhibited superior water resistance as compared to the starch matrix. Biocomposites took a great deal of time to reach equilibrium, and their water uptake decreased with the increase in fiber content. For instance, the water uptake decreased from 47% for cross linked starch matrix to 28% for biocomposites

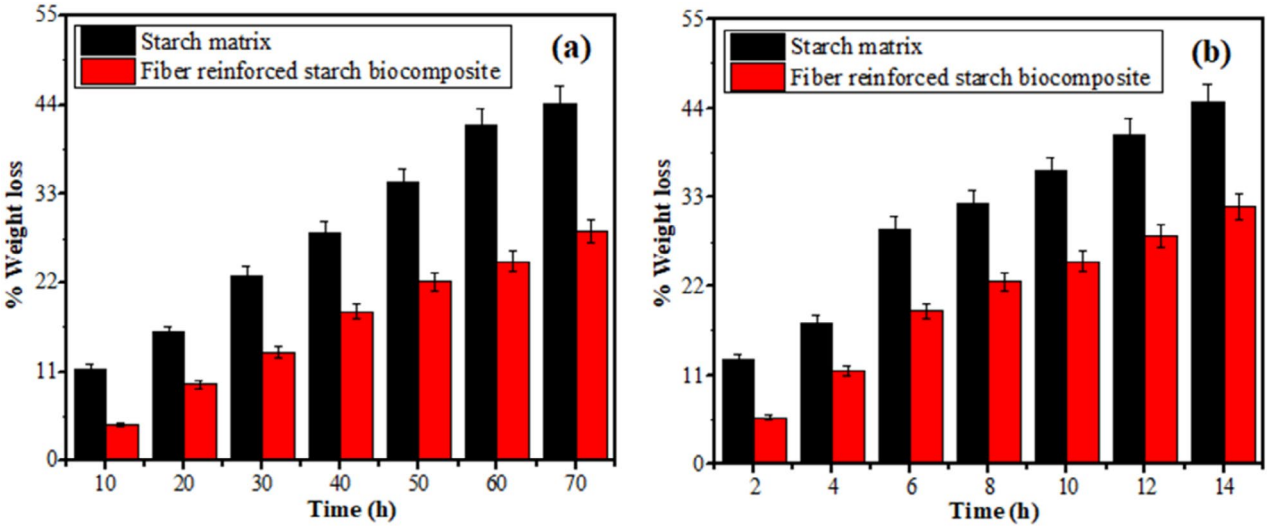


FIGURE 9 | (a) Acid resistance behavior and (b) base resistance behavior of the starch matrix, chemically modified HE fiber reinforced biocomposite.

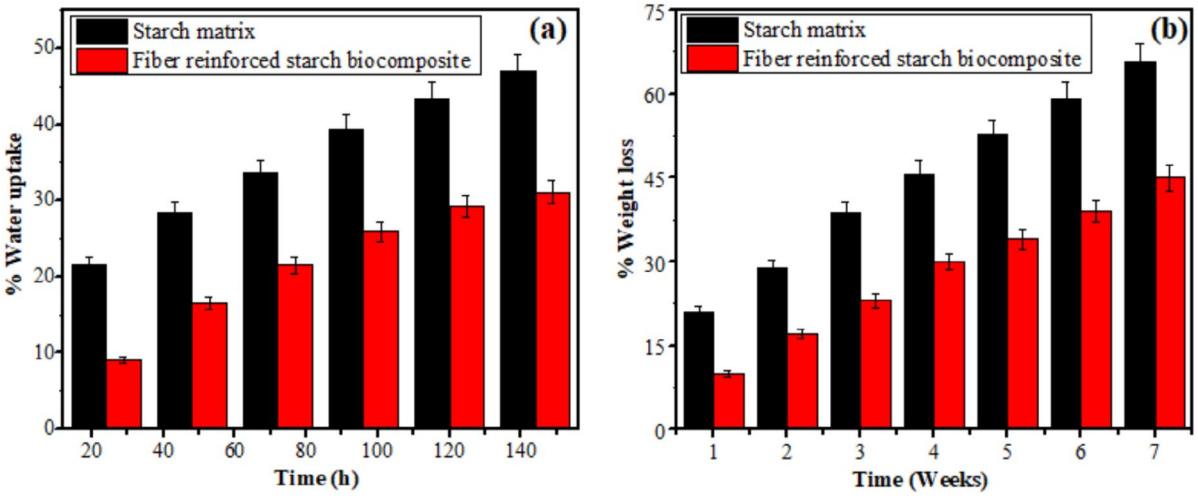


FIGURE 10 | (a) Water uptake behavior and (b) biodegradable behavior of starch matrix and chemically modified HE fiber reinforced biocomposites.

reinforced with modified HE cellulosic fibers. This enhanced water resistance and slower equilibrium are attributed to the less hydrophilic structure of cellulosic fibers compared to the starch matrix [24].

4.11 | Biodegradation Studies

Figure 10b represents the biodegradation studies of UF starch matrix and its chemically modified HE fiber reinforced composites. These studies were evaluated by measuring the weight loss of samples which were buried in soil rich in microorganisms. Biodegradability studies indicate that increasing the percentage of modified HE biofibers in the biocomposites led to a slow degradation rate. This slower degradation in biocomposites was likely due to the grafted chains on cellulosic biofibers, which are inherently more resistant to degradation than the starch matrix. It has been found that the starch matrix lost about 60% weight by the seventh week; however, 15% modified fiber reinforced biocomposites lost 40% weight within the same time interval. Thus, the biodegradability of composites is lower than UF cross-linked starch matrix. This reduction in degradation rate is attributed to the slower degradation of cellulosic biofibers themselves as compared to the matrix [32]. Furthermore, the surface morphology of starch matrix and its modified fiber reinforced composites at various stages of biodegradation was evaluated and SEM images were shown in Figure 6d–f. It can be observed from the surfaces of both the matrix and composites undergoing biodegradation that they became significantly rougher as compared to those that had not been subjected to biodegradation.

5 | Conclusions

This research focused on fabricating advanced biocomposite from starch matrix using modified HE biofibers as reinforcing agent. It was found that increase in fiber loading in matrix exhibited significant improvement in mechanical properties. TS, CS and FS increase as fiber loading increased from 0 to 15 wt% due to enhanced

interactions between the matrix and reinforcing fibers. However, at higher fiber loading mechanical properties decreases due to poor interfacial adhesion between fiber and matrix. The thermal stability of matrix and composites was confirmed through TGA and modified fiber reinforced biocomposite showed maximum thermal stability as compared to starch as well as to matrix. Biocomposites show improved resistance to acid, base and water compared to matrix. Further, chemically modified HE fibers reinforced starch composites were found to have better dielectric properties that is, dielectric constant and dissipation factor as compared to matrix. The fire retardancy of biocomposites was greater than crosslinked starch matrix and it was enhanced by addition of zinc borate as well as magnesium hydroxide flame retardants. These biocomposites offer a viable end of life solution through biodegradation and hence they return valuable organic matter into the biosphere which minimizes the burden associated with landfill. This research aligns directly with the core aspect of circular economy by promoting resource efficiency, minimization of waste generation and eco-design of materials.

Author Contributions

Ashish Kumar Sharma: investigation, methodology, software, formal analysis, writing – review and editing. **Maurice N. Collins:** writing – original draft, writing – review and editing, validation. **Nav Rattan:** conceptualization, methodology, project administration, visualization, writing – review and editing. **Garima Kumari:** visualization, validation, investigation, conceptualization, formal analysis, writing – review and editing, data curation. **Arvind Singh Chauhan:** conceptualization, writing – review and editing, formal analysis, methodology, validation, data curation. **Aakanksha Jain:** investigation, validation, formal analysis, writing – review and editing, data curation. **Ashish Guleria:** conceptualization, investigation, writing – original draft, supervision, data curation.

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Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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