J. Innovative Eng. Nat. Sci., vol. 5, no. 1, pp. 187-195, 2025.
http://doi.org/10.61112/jiens.1540102

Journal of Innovative Engineering and Natural Science
(Yenilikçi Mühendislik ve Doğa Bilimleri Dergisi)
https://dergipark.org.tr/en/pub/jiens

Original Paper

Removal of non-cellulosic materials from hemp fiber under ultrasonication conditions and cetyl trimethyl ammonium chloride (CTAC) catalyst

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ARTICLE INFO

Article history:
Received 28 August 2024
Received in revised form 17 November 2024
Accepted 6 January 2025

Available online

Keywords:
Hemp fiber
Ultrasonication
Pretreatment
Lignocelluloses
Cetyl trimethyl ammonium chloride (CTAC)

ABSTRACT

Recently, due to rising worries about global warming, pollution, and the sustainability of fossil resources, there has been a heightened interest in renewable and sustainable natural materials across different industries. Consequently, the use of renewable and sustainable natural fibers such as hemp instead of synthetic ones, such as glass and carbon has become more popular in certain composite material applications. A drawback of natural fibers including hemp is that their polar nature often leads to incompatibility at the fiber/matrix interface with nonpolar and hydrophobic matrices. This leads to weak adhesion between the fiber and matrix, resulting in reduced mechanical properties of the final composites. To enhance the performance of natural fiber composites, it is essential to modify the fibers. Non-cellulosic substances such as lignin, waxes, hemicelluloses and pectin present in the hemp fiber structure also affect the mechanical performance of composites due to poor fiber/matrix adhesion. In this study quaternary ammonium hydroxide was used in an ultrasonic-assisted pretreatment to increase the degradation rate of non-cellulosic substances in hemp fiber. Cetyl trimethyl ammonium chloride (CTAC) concentrations ranging between 1 and 8% w/w were used with a constant (10% w/w) NaOH concentration. Hemp fiber surfaces were analyzed using a scanning electron microscope (SEM). The findings revealed that ultrasonication-assisted alkali treatment effectively removed non-cellulosic substances from the fiber surface. This removal was further validated by TGA and FT-IR analysis.

I. INTRODUCTION

In recent years, alongside environmental challenges like global warming and pollution, growing concerns about the sustainability of fossil resources have led to a heightened interest in renewable and sustainable natural materials across various sectors. As a result, the use of natural fibers instead of synthetic ones like glass and carbon in composite materials has gained popularity [1]. Specifically, natural bast fibers such as jute, hemp, and flax have become increasingly favored for composite reinforcement due to high specific strength (strength/density) and specific modulus of elasticity (modulus/density) of their composites. In addition to the advantages mentioned above, certain disadvantages of natural fibers, including hemp, hinder their widespread use. The properties of natural fibers, such as length, thickness, and strength, vary depending on the fiber's chemical composition and morphology, plant species, growing region, cultivation conditions, and other factors. This variation leads to difficulties in producing raw materials with consistent properties from these fibers. Additionally, due to the hydrophilic nature of hemp fibers, composites made from these fibers tend to absorb water and moisture. Another disadvantage of natural fibers is that, because these fibers are polar, they often exhibit fiber/matrix interface incompatibility with nonpolar and hydrophobic matrices, resulting in poor adherence between the fiber and matrix and consequently lower composite mechanical strength. Therefore, to enhance the performance of natural fiber composites, modification of the fibers is often necessary [2].

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Hemp fibers are exceptionally stiff and strong compared to other natural fibers, making them particularly suitable for composite applications. Similar to other natural fibers, hemp fibers are hydrophilic owing to hydroxyl (-OH) groups [3]. These fibers contain 20-35% non-cellulosic materials, mainly pectin, lignin, and hemicellulose [4]. The presence of pectin and waxy substances on the fiber surfaces hinders the interaction of hydroxyl groups with polymer matrices, leading to poor bonding and potential issues like weak interfaces and voids in composites. Chemical pretreatments, such as alkalization, are effective in removing non-cellulosic components from cellulose fibers, improving bonding and introducing functional groups into polymer composites. Alkaline treatment can also modify the crystal structure of cellulose and enhance the tensile properties of the fibers [5-7]. Alkali (NaOH) treatments reduce the hydrophilic nature of the fibers by reacting with the hydroxyl groups, as described in the following reaction mechanism:

$$\text{NaOH} + \text{Fibre-cell-OH} \longrightarrow \text{H}_2\text{O} + \text{Fibre-cell-O}^{-}\text{Na}^{+} + \text{impurities} \quad (1)$$

This pretreatment also removes a portion of the hemicellulose and lignin from the fiber surface, resulting in an increased number of potential reaction regions for cellulose to bond with the matrix [8-9]. Numerous studies have investigated the effects of alkalization on the properties and performance of both fibers and composites. Oushabi et al. examined the impact of alkali treatment on palm fibers using different NaOH concentrations for one hour at 25 °C. Their findings revealed an increase in the tensile strength of alkali-treated palm fibers compared to untreated fibers [10]. Mishra et al. reported that a one-hour alkali treatment (30°C, 5 wt% NaOH) led to an improved strength for sisal/glass fiber composites [11]. Sunny et al. conducted high-temperature alkaline treatment of hemp fibers (120°C, 5 wt% NaOH and 2 wt% Na_2SO_3). They observed that this process enhanced the tensile strength and Young's modulus of the treated fibers up to 51% and 62%, respectively, in comparison to untreated hemp fibers [12]. Alao et al. investigated the effect of alkali and silane treatment on hemp/PLA composites. FT-IR, TGA, and SEM investigations highlighted structural alterations in the fibers and removal of noncellulosic substances [13]. Wang et al. explored the influence of alkali and acetylation fiber treatments on hemp composites. They found that the treatments remove the impurities and lignin, increasing the cellulose content of the hemp fibers [14].

Surfactants are surface-active agents that feature both hydrophobic (tail) and hydrophilic (head) groups. Consequently, a surfactant molecule has components that are both water-insoluble and water-soluble. Most surfactants have hydrocarbon chains as their hydrophobic tails [15]. When surfactant concentration exceeds the critical micelle concentration (CMC), these molecules aggregate to form micelles [16]. These micelles, which self-organize, can alter the rate of chemical reactions. This effect is attributed to the electrostatic and hydrophobic interactions between the micelles and the reactants [17].

In this study, ultrasonication-assisted alkali treatment method was applied to hemp fibers with increasing CTAC concentration as an effective method in removing non-cellulosic materials from hemp fiber. To test this hypothesis, different concentrations of CTAC ranging from 1 to 8 wt% were used along with a constant (10% w/w) NaOH concentration. The ultrasonication process was also used as a means to ensure effective removal of non-cellulosic substances during the alkali treatment of hemp fibers. A series of analysis methods, including FT-IR, SEM, and TGA, were performed to determine the effect of CTAC addition on hemp fiber properties.

II. EXPERIMENTAL METHOD

2.1 Materials

Water-retted hemp fibers from the Samsun region of Turkey were used in this study. After harvesting, the hemp stalks were soaked in the pool for seven days. The fibers were then stripped from the stem by hand and carefully combed using nailed boards. After carding, the fiber bundles were cut into 1 m lengths. These bundles were then used in sonication-assisted alkaline pretreatments. NaOH and cetyl trimethyl ammonium chloride (CTAC) were purchased from Sigma Aldrich and Fluorochem, respectively.

2.2 Method

2.2.1. Fiber Treatment

Hemp fiber material was subjected to alkali treatment in an ultrasonic bath using 10 wt% NaOH solution. The alkali concentration was selected based on our previous study [18]. A liquid/fiber ratio of 45 ml/g was used for the treatments. Ultrasonication and CTAC catalysis were used to ensure effective removal of non-cellulosic fiber components during the NaOH process. Ultrasonication-assisted alkali treatment was carried out at 50 Hz frequency and 330 W power at 40 °C for 2 hours. CTAC was used as a surfactant in the range of 1–8 wt%. A hemp fiber sample sonicated using only distilled water without the use of alkali was prepared as a control sample. Following treatment, the fibers were washed using distilled water until all NaOH and CTAC catalysis were removed and the pH was equaled to 7. The hemp fibers were then dried and conditioned at 70 °C for 12 h. The samples were coded such that HFU represents the sample treated without alkalization and catalyst. HFA-S1, HFA-S2, HFA-S4, HFA-S8 denote hemp fibers treated with ultrasonication and alkali in the presence of 1, 2, 4 and 8% surfactant respectively.

2.3. Characterization of materials

2.3.1 FT-IR Analysis

FT-IR analysis was performed to identify the types of bonds and chemical groups present on the fiber surface both before and after chemical treatments. This analysis was conducted on untreated and surface-treated hemp fibers using a Perkin Elmer Spectrum 400 FT-IR Spectrometer in ATR mode. The spectral range was 400-4000 cm^{-1} with a resolution of 4 cm^{-1} at room temperature. Each spectrum was averaged from 40 scans.

2.3.2 TGA

TGA was conducted to ascertain the thermal properties of the hemp fibers. The analyses were conducted using Hitachi STA 7300 Thermal Analysis System. Samples having a weight of 5 mg were used for the tests. The temperature range for TGA was kept at 20–600 ˚C with 10 ˚C/min heating rate in nitrogen atmosphere.

2.3.3 SEM Analysis

SEM images of the chemically treated and untreated fibers were taken using a FEI Quanta FEG 450 electron microscope. The sample surfaces were gold- sputtered before being observed. The accelerating voltage was 10 kV.

III. RESULTS AND DISCUSSIONS

3.1. FTIR Results

Figure 1 shows the FTIR results of the untreated and alkali treated hemp fibers. After the treatments, the peak intensities at 1000 and 3300 cm^{-1} increased indicating that the number of hydroxyl groups on the fiber surface increased with the treatment. The removal of the peak at 1241 cm^{-1} (C-O and C = O stretching of G ring in lignin) indicate that the treatment removed a good amount of lignin and hemicellulose. The peak at 1728 cm^{-1} originating from the carboxylic ester (C = O) in waxes, pectin and hemicellulose partly disappeared after the treatments suggesting that the treatment removed these substituents. The peak intensity at 2919 cm^{-1}, representative of the C-H bond stretching in hemicellulose reduced after the alkali treatment suggesting the removal of hemicelluloses. FT-IR analysis demonstrated the removal of non-cellulosic substances. Islam et al. reported similar FT-IR results regarding noncellulosic material removal from hemp fibers. They found that alkali treatment led to a reduction in size of sharp peak at 1735 cm^{-1} (C = O stretching vibration of carboxylic acid and ester groups in hemicellulose) which indicates the removal of hemicellulose for alkali treated fibers They also demonstrated that peak intensity at 2921 cm^{-1} (C-H stretching vibration in hemicellulose) reduced after alkali treatment which is another sign of hemicellulose removal with the treatment [19]. Sepe et al. also showed that alkali treatments results in a reduction of the weak at 1734 cm^{-1} which was ascribed to the removal of hemicellulose after alkali treatment [20]. Karaduman et al. reported that FT-IR results of ultrasonication-assisted alkali treated hemp fibers indicated the removal of noncellulosic materials after the treatments. [18].

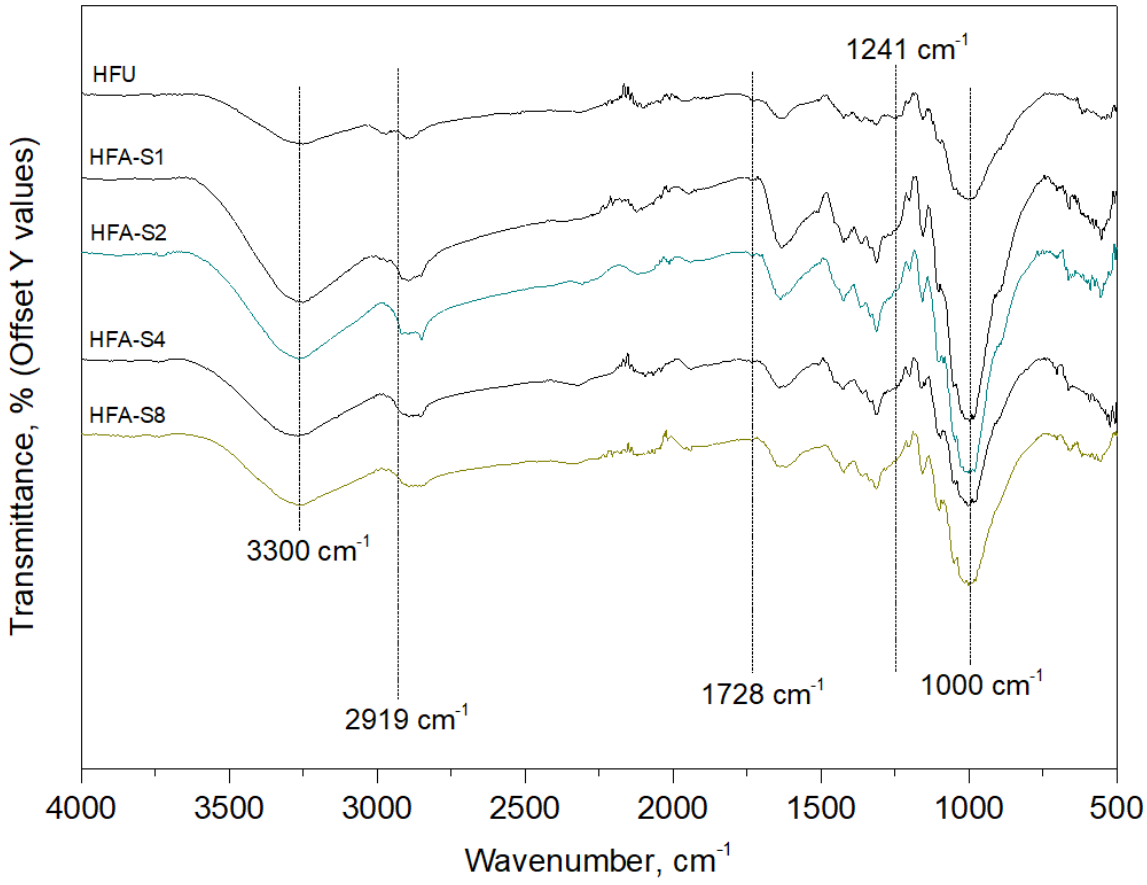

Figure 1. FTIR results of the untreated and alkali treated fibers

3.2. SEM Study

Figure 2 shows the SEM photomicrographs of the untreated and alkali treated hemp fibers. The SEM pictures highlighted that untreated fibers (HFU) are mostly in bundle form without fiber separation. Pectin and waxy substances are visible on fiber surfaces. Alkali treatment with 1 % surfactant (HFA-S1) partly removed the waxy substances and pectin but there are still impurities on fiber surfaces. The parenchyma cells were mostly broken down but cell residues are still visible. Surfactant addition resulted in cleaner fiber surfaces when compared to untreated fibers. Surfactant concentrations of 2 and 4 removed most of the noncellulosic substances but still there are impurities visible on the fiber surface. A surfactant concentration of 8 % w/w completely removed the surface wax and pectin layer and yielded to fiber separation. Treatment with higher surfactant concentrations resulted in clean and well-separated fibers with almost no impurities. SEM micrographs clearly demonstrate that surfactant addition has a positive impact on treatment of fibers. Surfactant is thought to reduce the interfacial tension (IFT) between alkali solution and waxy layer on fiber surfaces, thus enhancing the wettability of the fibers and facilitating the access of hydroxide ions into the fiber structure. This most probably resulted in more effective elimination of hemicelluloses, pectin and lignin from fiber structure. Several studies in the literature [18-22] have reported similar findings where alkali treatment removes noncellulosic substances from hemp fibers and results in a cleaner, rougher and more separated fiber surfaces.

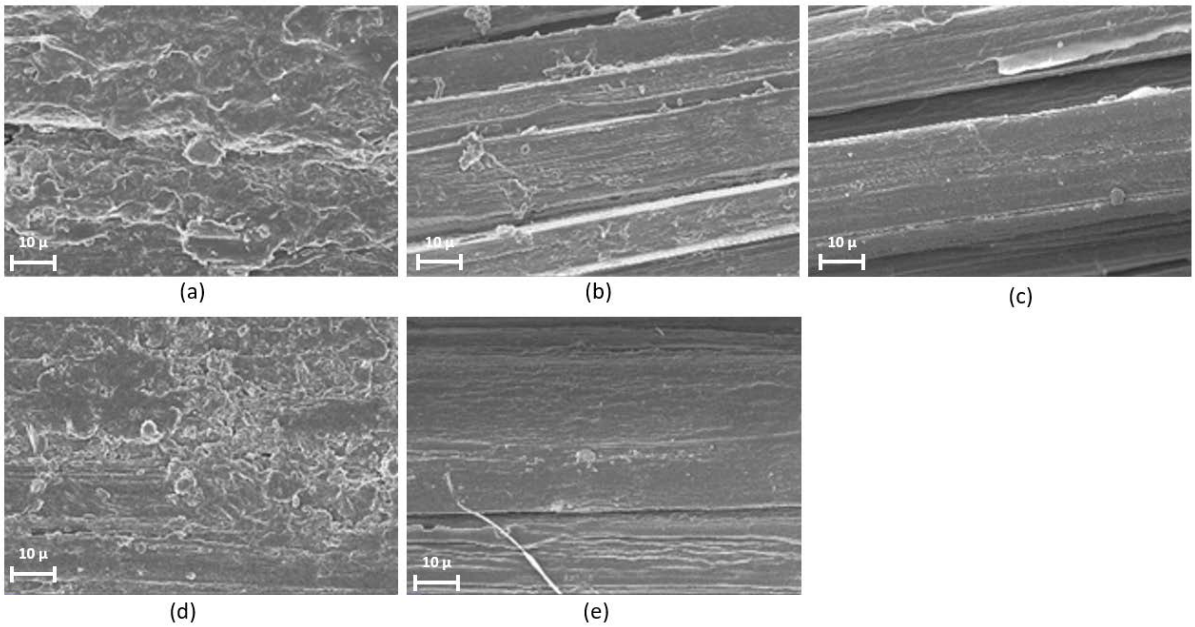

Figure 2. SEM pictures of the untreated and alkali treated fibers at a magnification of 1500 x. (a) HFU (b) HFA-S1 (c) HFA-S2 (d) HFA-S4 (e) HFA-S8

Mechanical treatment was used together with catalysis to remove lignocellulosic materials. In this way, a more effective method was created by combining mechanical-chemical pretreatment with both destruction of the outer surface and internal fragmentation of lignocelluloses. A proposed mechanism of action for CTAC-catalyzed alkali treatment of hemp fibers is shown in Figure 3. In the first step of the mechanism, CTAC catalysis and NaOH dissolve ionically in water. Damage occurs on hemp fiber surfaces through hydroxide ions in the alkaline

environment. As hydroxyl ions begin to perform external damage on the hemp fiber surface, the speed of access to the inner regions will begin to increase. Ultrasonic waves produce microbubble cavitation that transfers energy to the hemp fiber surface, causing mechanical breakdown of its outer structure and allowing ions to penetrate deeper. Concurrently, the improved mixing and ion transport driven by acoustic flow enhance interactions between ions (e.g., CTA+ and OH−) and the internal cellulosic tissues. The ions disrupt intermolecular hydrogen bonds within the cellulose chains and alter the interaction between cellulose and hemicelluloses, thereby aiding in the removal of non-cellulosic substances from the hemp fiber surface.

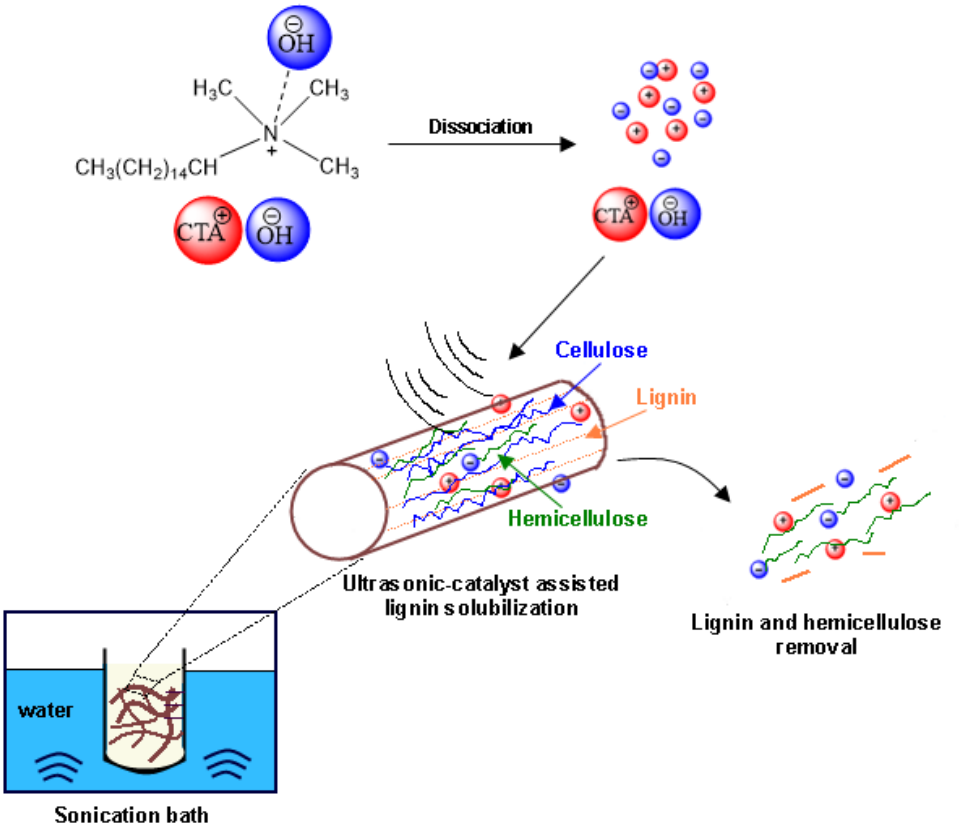

Figure 3. Mechanism of the CTAC-catalyzed alkali treatment of hemp fibers

3.3. TGA Results

TGA curves presented in Figure 4 show three distinct stages of weight loss of hemp fibers as a function of temperature. The first stage can be spotted between 30 and 140 °C corresponding to moisture removal from fibers. The second stage that took place at 220-320 °C temperature range is related to hemicelluloses degradation. The last stage of weight loss between 320-380 °C corresponds mainly to degradation of cellulose and lignin. It can be noticed from TG curves that untreated fibers experienced an abrupt decrease in the range of cellulose and lignin degradation. This can be ascribed to the elimination of lignin constituents since lignin degrades in a slow and steadier manner. Islam et al. reported similar results with alkali treated hemp fibers where the temperature at which percentage weight losses have occurred was higher for alkali treated fibers compared to untreated fibers [19]. Kabir et al. showed that the degradation temperature of hemp increases after alkali treatment suggesting a higher thermal stability of the fiber. They attributed this to the reduced lignin and hemicelluloses content by the alkali treatment

[21]. Thermal degradation of alkali treated samples did not show any other noticeable fashion in terms of thermal behavior.

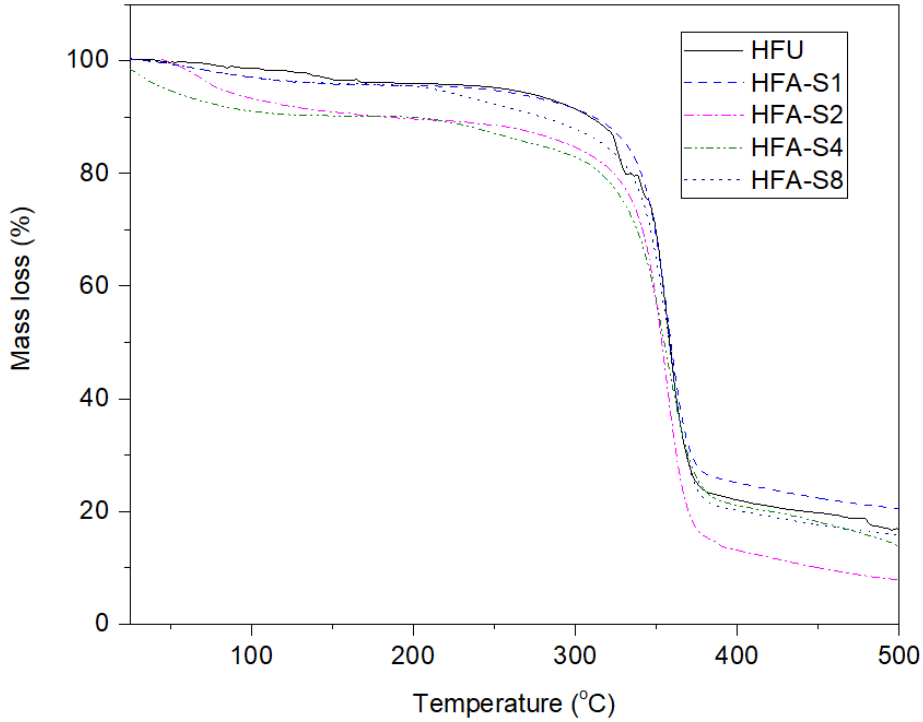

Figure 4. TGA results of the untreated and alkali treated fibers

IV. CONCLUSIONS

This study investigated the effect of ultrasonication assisted alkali treatment of hemp fibers in the presence of cetyl trimethyl ammonium chloride (CTAC) surfactant with values ranging between 1 and 8% w/w. The following conclusions can be drawn from this study:

- FT-IR studies on untreated and alkali-treated hemp fibers indicated that the number of hydroxyl groups on the fiber surface increased following treatment. The results also showed that the treatment effectively removed significant amounts of lignin, hemicellulose, waxes, and pectin. Overall, FT-IR analysis confirmed the removal of non-cellulosic substances from the fiber structure.
- SEM results indicated that untreated fibers are mostly in bundle form without fiber separation with pectin and waxy substances on fiber surfaces. Alkali treatment with a surfactant concentration of 8 % w/w completely removed the surface wax and pectin layer and yielded to fiber separation. Treatment with higher surfactant concentrations resulted in clean and well-separated fibers with almost no impurities. SEM micrographs clearly demonstrate that surfactant addition has a positive impact on treatment of fibers. This was attributed to the fact that the surfactant reduces the interfacial tension between alkali solution and waxy layer on fiber surfaces, thus enhancing the wettability of the fibers and facilitating the access of hydroxide ions into the fiber structure, leading to more effective elimination of hemicelluloses, pectin and lignin from fibers.

- The TGA study revealed that untreated fibers exhibited a sharp decline during the cellulose and lignin degradation phase. This was attributed to the removal of lignin components, as lignin tends to degrade more gradually and steadily. In contrast, the thermal degradation of alkali-treated samples did not display any significant pattern in thermal behavior when compared to untreated fibers.

Future studies will focus on the effect of ultrasonication-assisted alkali treatment and the effect of cetyl trimethyl ammonium chloride (CTAC) surfactant on the properties of hemp fiber composites.

ACKNOWLEDGMENT

*This study was presented as an oral presentation at the 14th International Fiber and Polymer Symposium (14th ULPAS) in Bursa/Turkey on 24-25 May 2024.

This work was supported by Yozgat Bozok University Scientific Research Projects Coordination Unit, Turkey (grant number FHD-2023-1294).

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