

The Thermal Decomposition of the Liquid Hot Water & Alkali Pretreated Cotton Fiber

Sevim Özgül^{1,*}, Günnur Koçar²

¹Solar Energy Institute, Ege University, Izmir, Turkey

²Ege University Biomass Energy Systems and Technologies Application and Research Center, Ege University, Izmir, Turkey

Received: 12.04.2021; Accepted: 09.07.2021; Published: 15.07.2021

Turk. J. Mater. Vol: 6 No: 1 Page: 1-8 (2021) ISSN: 2636-8668

SLOI: <http://www.sloi.org/sloi-name-of-this-article>

*Correspondence E-mail: sevimozgl88@gmail.com

ABSTRACT Besides green energy production, exploiting renewable sources in materials production has recently gained interest in being eco-friendly and sustainable. Due to the abundance of agricultural wastes, easy accessibility, eco-friendly and lightweight, the interest in using agricultural wastes for the production of plant fiber has increased. Plant fibers can be used as a reinforcement material for biocomposite. Thermal degradation of the natural fibers has a high significance on the extrusion temperature of thermoplastic composites and the curing temperature of thermosets. Pretreatments of plant fiber improve the thermal degradation of fiber. These research aims are to investigate the thermal analysis of liquid hot water (LHW) and alkali pretreated cotton fibers. Experiments of liquid hot water are carried out by varying temperature (140, 160, and 180 °C), reaction time (30 and 60 min). Cotton fibers are pretreated with NaOH solution (5% in weight) for one h, two h, three h, and four h at room temperature. According to the result of thermogravimetric analysis of LHW and alkali pretreatments, alkali pretreatment (5% w/v, three h) was applied to LHW (180 °C, 60 min) pretreated fibers. The results of liquid hot water and alkali pretreatments, and co-pretreatment were compared with the thermal behavior.

Keywords: Plant fiber; Liquid Hot Water pretreatment; Alkali pretreatment; Thermogravimetric analysis.

Cite this article: S. Özgül, G. Koçar. The Thermal Decomposition of the Liquid Hot Water & Alkali Pretreated Cotton Fiber. Turk. J. Mater. 6(1) (2021) 1-8.

1. INTRODUCTION

Besides green energy production, exploiting renewable sources in materials production has recently gained interest in being eco-friendly and sustainable. The interest in using agricultural wastes for production of fiber has increased due to abundance, easy accessibility, eco-friendly and lightweight of agricultural wastes. The use of lignocellulosic biomass-based materials over petro-materials has received increased attention due to growing environmental awareness, environmental sustainability concerns, increasing global waste problems, and depletion of fossil fuels [1]. The abundant availability and accessibility of plant fibers are the primary reasons for an emerging new interest in sustainable technology. Research shows that the energy used in the production of plant fibers is less than half of the energy required to produce synthetic fibers. Besides, plant fibers are non-abrasive, non-irritant, non-flammable, and non-toxic materials. They are biodegradable materials, as well [2]. Plant fibers can be used as an alternative to glass, carbon, and other human-made fibers [3,4]. Besides, it is estimated that by 2020, fibers from biomass sources will account for 28% of the support material market [5]. Manufacture of currently used materials is quite tricky regarding the consumption of energy, raw materials, and cost. The readily available renewable material resources are significant also from the point of sustainability of material resources. Plant fibers are renewable resources, so they are suitable alternative material resources for the reinforcement of composite.

Therefore, using these “sustainable” natural fibers will reduce structural cost and weight, improve structural performance and increase energy efficiency [6].

Many lignocellulosic fibers, such as jute fiber, hemp fiber, sisal fiber, abaca fiber, and cotton, are used as reinforcement materials for biomaterials with their excellent mechanical properties and low specific mass. [7]. Furthermore, cotton fiber has high specific strength and modulus in lignocellulosic fiber, which is especially meaningful to enhance composites. However, cotton fiber also has disadvantages as a reinforcing material: the high moisture absorption and the low processing temperature permissible. Processing temperatures must be maintained below 200 °C to avoid the properties' deterioration due to the cotton degradation. Surface modification is often used for decreasing moisture absorption and improving the interfacial properties in composites [8]. Pretreatment methods can improve the interfacial bonding quality between fiber and matrix. Liquid hot water (LHW) is one of the physical treatments [9]. LHW pretreatment uses hot water, which is an environmentally friendly approach due to chemical-free. Also, it has low operational costs and high potential for hemicelluloses dissolution [10]. During the treatment, water itself acts as a hydrolytic catalyst, especially at a higher temperature. The LHW pretreatment of biomass provides not only degrades most of the hemicellulose and part of the cellulose, but also eliminates the sugar, starch, and protein on the surface of plant fiber. Thus, plant fiber has lower molecule polarity and it has better interfacial compatibility with the polymer matrix. There are many types of research on lignocellulosic fibers reinforced polymer matrix composites after surface pretreatment of fibers. Results showed improved strength and a better thermal property of the composites [11, 12, 13, 14]. Alkali pretreatment or mercerization is one of the most used chemical pretreatments for natural fibers. The necessary modification done by alkaline treatment is the disruption of hydrogen bonding in the network structure, thereby increasing surface roughness. This treatment removes a certain amount of lignin, wax, and oils, depolymerizes cellulose, and exposes the short-length crystallites [15]. It is reported that alkali treatment has two effects on the fiber: (1) it increases surface roughness resulting in better mechanical interlocking; and (2) it increases the amount of cellulose exposed on the fiber surface, thus increasing the number of possible reaction sites [16]. Several researchers employed different percentages of an alkali solution (5%, 7%, 10%, and 15% in weight) and immersion times (1, 3, and 24 h) to treated natural fibers [17-21].

Materials are subject to thermal decomposition and combustion depending on conditions exposed to fire or any other high-intensity heat source. The combustibility of a natural fiber reinforced polymer composite depends on many factors. These factors are type of raw materials (fibers, polymer, and additives), composite density, structure, thermal conductivity, and humidity [22, 23]. Several methods can help to analyze the thermal properties of a material. The mass change, thermal degradation temperature, and thermal stability of composite materials can be measured by thermogravimetric analysis (TGA). In general, the thermal degradation process of natural fiber-polymer composites can be roughly divided into five parts [24-27]. The evaporation of water on the fiber surfaces starts at 100°C, thermal decomposition of hemicelluloses, celluloses, and lignin starts at 200°C, 250°C, and 280°C, respectively. Also, polymer matrix macromolecular degradation or depolymerization starts at 200°C. The thermal degradation of natural fibers has a high significance on the extrusion temperature for thermoplastic composites and the curing temperature of thermosets, as well [24]. Natural fiber polymer composites are typically manufactured below 200 °C to avoid the thermal degradation of natural fibers [28]. Hemicellulose and lignin are removed from the fibers through pretreatments. Thus, thermal decomposition of pretreated fibers is started at high temperatures. Also, untreated fibers have higher content of hemicellulose and lignin compared to pretreated fibers, and so they begin to degrade at a lower temperature.

2. EXPERIMENTAL

The detailed experiment should be given with mark (brand) of using materials and measurement devices. The experiment should be understandable and can be repeated easily.

2.1 Material

The cotton stalk was obtained from a field in İzmir, which is in the west of Turkey. The particle size of the cotton stalk was minimized for storing at dry and room temperature by using a cutting mill. Cotton stalks were separated in 2 mm particle size by the sieve. Sieved samples were used for the liquid hot water and alkali pretreatment processes.

2.2 Method

2.2.1 Proximate analysis

Moisture content and an ash content of the cotton fibers were determined according to TS 1562 standard for each experiment. All samples were dried at 105 °C for 24 h, and then moisture content was determined by the loss of mass. For ash content, 1 g of the oven-dried sample was kept in a muffle furnace at 575 °C for three h. The ash content was determined as the residue.

2.2.2 Ultimate analysis

The ultimate analysis of the cotton fibers was carried out using a Leco TruSpec® CHN-S Analyzer in order to determine the carbon (C), hydrogen (H), nitrogen (N), and sulfur (S) contents of the samples.

2.2. Calorific value

The higher heating value (HHV) of raw cotton fiber was measured using a bomb calorimeter (Parr 6300, Parr Instrument Co., Illinois, USA) according to ASTM D 5865 [29]. For each test, a sample pellet of 1.0 g was taken into the crucible and then combusted under a pressurized oxygen atmosphere (3000 kPa). All of the samples were tested in three replicates.

2.2.1 Liquid Hot Water Pretreatment

Before treatment, untreated fibers were washed with distilled water to remove dirt. Afterward, fibers were dried in an oven at 80 °C for 48 h [30]. LHW was carried out on the dried cotton stalk in 1 dm³ Erlenmeyer flasks (100 water and 10 g cotton stalk in each flask) at three different temperatures (140 °C, 160 °C, and 180 °C) for 30 and 60 min in an oven. After the pretreatment, the hydrolysates were collected, and the product was put on filter paper and washed with deionized water three times. Afterward, the fibers were dried at 80 °C for 12 h and stored in plastic containers until thermogravimetric analysis.

2.2.2 Alkali Pretreatment

Untreated fibers were immersed in sodium hydroxide solution (5% w/v) for one h, two h, three h and, four h at room temperature. The suspension was further filtered. The residue was washed with distilled water until the filtrate pH was 7. Afterward, the filtered fibers were dried at 80 °C for 12 h.

2.2.3 Co-Pretreatment of Liquid Hot Water and Alkali

According to the thermogravimetric analysis of LHW and alkali pretreatments, alkali pretreatment was applied to LHW pretreated fibers. LHW pretreated fibers (180 °C, 60 min) were immersed in sodium hydroxide solution (5% w/v) for three h. The suspension was further filtered. The residue was washed with distilled water until the filtrate pH was 7. Afterward, the filtered fibers were dried at 80 °C for 12 h.

2.2.3 Thermogravimetric analysis

Thermogravimetric analysis (TGA) of untreated and pretreated cotton fibers was measured using Setaram TG-DTA / DSC instrument. About 15 mg of samples were heated from 30 °C to 600 °C at a rate of 10 °C/min under argon flow.

3. RESULTS

3.1 Properties of untreated cotton fiber

The proximate and ultimate analyses of cotton fiber samples are listed in Table 1. The moisture value of raw cotton fiber was high. The moisture content of the fibers has a critical effect on the quality of the final product. That is due to the high temperatures used during the processing, which causes water to evaporate from the composite melt. The evaporation of water leads the formation of bubbles, which increase the porosity of the composite and consequently deteriorates the properties of the composite. For this reason, before pretreatments, fibers were dried in an oven at 80 °C for 48 h to remove the moisture.

Table 1. Properties of raw cotton fiber

Cotton fiber	% C	% H	% N	% S	% Moisture	% Ash	HHV (MJ/kg)
	41,52	5,91	0,09	0,47	12,90	8,55	4043,93

3.2 Thermogravimetric analysis

TGA analysis was carried out to observe the distinct process of weight loss of fibers at different pretreatment conditions. The thermogravimetric analysis of raw cotton fiber is shown in Figure 1 and it shows three stages of the weight loss process with a long temperature range. From the curve, the first stage of weight loss, which started from 30 °C to 200 °C, is due to removing of the moisture content of the fiber. Significant degradation occurred at the second stage with the temperature range of 200–350 °C, which is related to the degradations of lignin and hemicelluloses of the fiber. The last stage of weight loss ranging from 350 °C to 500 °C, indicates the degradation of cellulosic and other non-cellulosic materials in the fiber. Also, the temperature at which the most mass loss occurs was 385,68 °C. The thermal decomposition of untreated cotton fiber is similar to the study of Dobircau et al.[31].

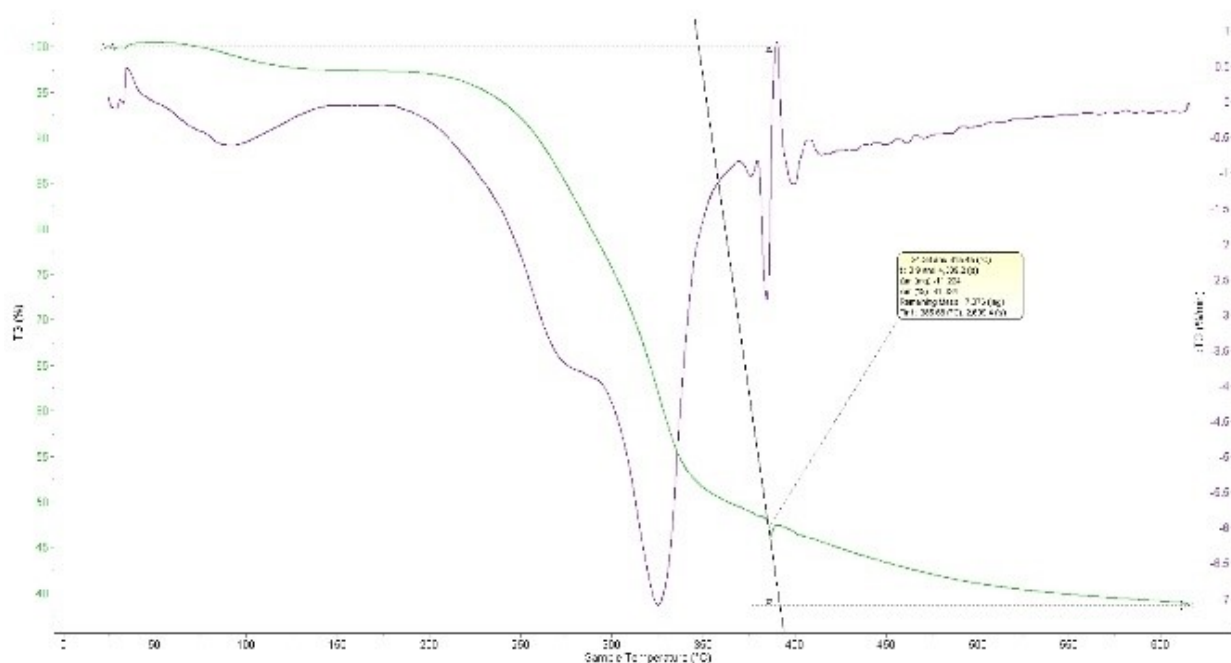


Fig. 1. Thermal decomposition of untreated cotton fiber

It was examined that untreated cotton fiber started degrading at 200 °C. When TGA analysis of biomass is interpreted, in the first stage, mass loss at temperatures below 100 °C, loss of volatile substances quickly, loss of moisture in the range of 100-130 °C, loss of volatile matter at 130-250 °C. In the next stage, volatile matter, hemicellulose, cellulose, and lignin are removed due to structural deterioration in the range of 150-600 °C, and a significant mass loss occurs [32]. Hemicellulose degrades in a wide range of 160-900 °C, starting from 220-300 °C, cellulose 275-350 °C and 400 °C by weight [33, 34, 35]. However, the start temperature of degradation for the LHW pretreated fibers increased, and also, the fibers showed higher thermal stability. Thermal degradation of raw material begins at lower temperatures compared to the pretreated one. Since pretreated fibers have a lower percentage of moisture and hemicellulose, they begin to degrade at higher temperatures. The highest mass loss occurred at LHW-180 °C-60 min condition. As the temperature and residence time was increased, mass loss was increased too. The mass loss was % 61,33 for untreated cotton fiber while it was % 73,39 at LHW-180 °C-60 min. Figure 2 presents TGA analysis of the LHW treated fiber samples.

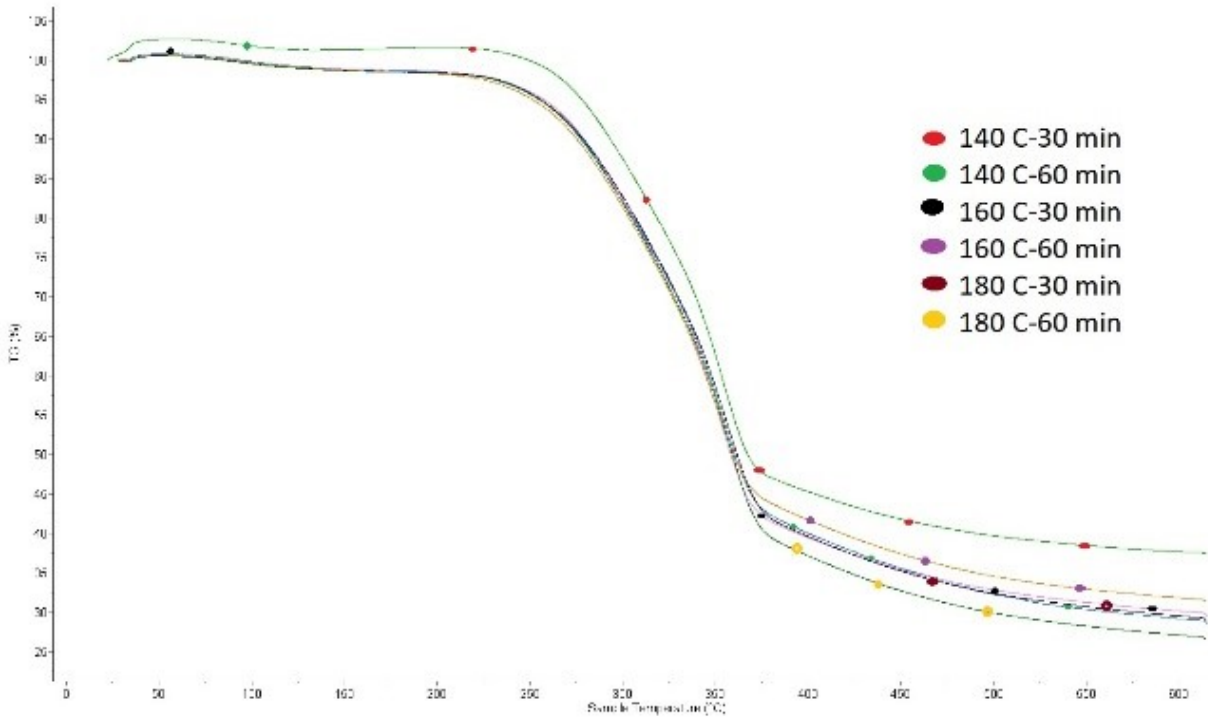


Fig. 2. TGA analysis of the LHW treated fiber samples.

Similar results were observed in pretreated alkali fibers. The amount of degradation of pretreated fibers increased compared with the untreated fiber with increasing residence time. It might be cause by the alkali treatment, which reduced the hemicelluloses and lignin content of the fiber. As a result, fibers became more hydrophobic and enhanced the better possibility to adhere with the matrix. Fig. 3 presents TGA analysis of the alkali-treated fiber samples. The characteristics of thermal degradation of the treated fibers show similarity, and the best result was observed for 5%-NaOH-3h pretreated fiber sample.

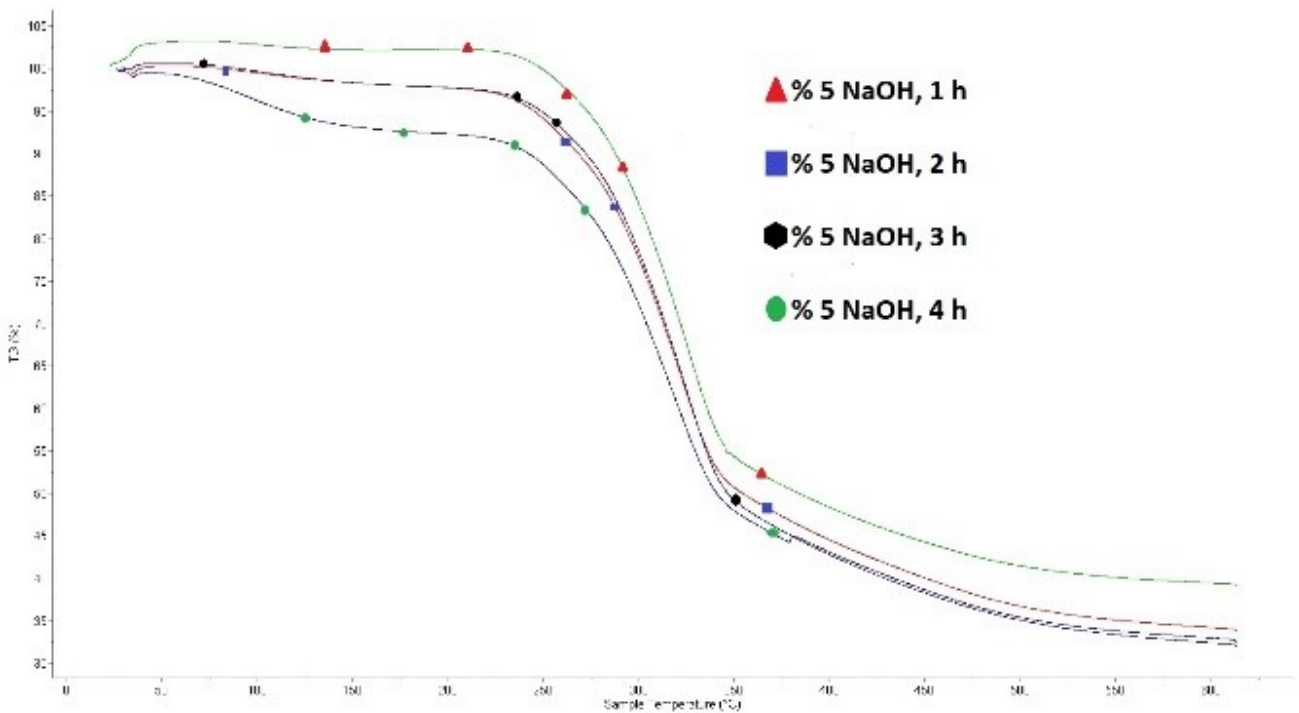


Fig. 3. TGA analysis of the alkali-treated fiber samples

It was observed that the co-pretreatment of LHW and alkali causes lower mass loss than individual pretreatment. Fig. 4 presents TGA analysis of the co- pretreatment fiber.

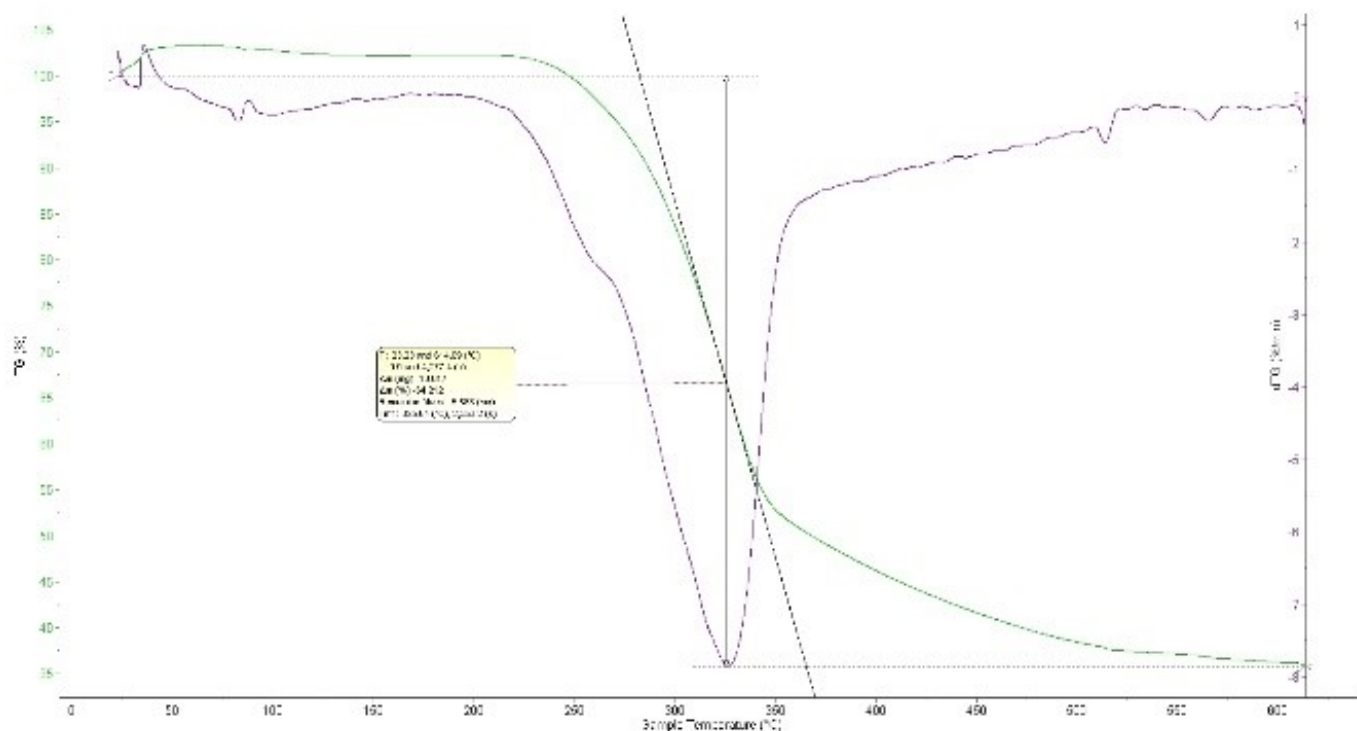


Fig. 4. TGA analysis of the co- pretreatment fiber

The residual mass for all samples at 600 °C is shown in Table 2.

Table 2. Values of residual mass for samples

Type of material	Residual mass at 600 °C (%)
Untreated cotton fiber	38,666
LHW-140 °C-30 min	37,155
LHW-140 °C-60 min	28,544
LHW-160 °C-30 min	29,567
LHW-160 °C-60 min	31,266
LHW-180 °C-30 min	28,906
LHW-180 °C-60 min	26,602
%5 NaOH-1 h	38,655
%5 NaOH-2 h	33,649
%5 NaOH-3 h	32,015
%5 NaOH-4 h	32,443
LHW-180 °C-60 min -%5 NaOH-3 h	35,788

Based on the literature, after pretreatment of LHW and alkali, the content of hemicellulose decreases is observed. The high crystalline nature of cellulose has been reported to improve the mechanical properties of fiber-reinforced plastics. Lignins and hemicelluloses have no free hydroxyl groups to react with the PP chains, leads to lower interfacial adhesion between fibers and matrices when the contents of lignin and hemicellulose are higher. Therefore, low hemicellulose contents are desirable. It is because high contents can degrade thermal stability and increase moisture absorption. Lignin is advantageous in that it inhibits water absorption and enhances thermal stability. Lignin also increases the resistance of the biomass to chemical and biological degradation [36].

4. CONCLUSION

Recently, the increase of environmental awareness has impacted materials design and manufacturing; many products and structures made by non-renewable resources and required a substantial amount of energy for productions that would excessively generate carbon dioxide, which is put into scrutiny. The introduction of natural fibers to composites may cause environmentally beneficial consequences such as bio-degradability and natural availability. The low fire resistance of plant fibers is a significant disadvantage of these materials. The thermal degradation of the fibers begins at 200 °C approximately, and it has high significant effect on the extrusion temperature of thermoplastic composites and the curing temperature of thermosets. Pretreatments of plant fiber improve the thermal degradation of fiber; also, it increases surface roughness

resulting in better mechanical interlocking and increases the amount of cellulose exposed on the fiber surface, thus increasing the number of possible reaction sites. In this study, different pretreatments were conducted, and the thermal behaviors of pretreated fibers were observed.

References

- [1] Rinaldi, R., Jastrzebski, R., Clough, M.T., Ralph, J., Kennema, M., Bruijninx, P.C., Weckhuysen, B.M., Paving the way for lignin valorisation: recent advances in bioengineering, biorefining and catalysis, *Angewandte Chemie International Edition*, 55 (29): 8164-8215, 2016.
- [2] Shekar, H.S. and Ramachandra, M., Green Composites: A Review, *Materials Today: Proceedings*, 5: 2518–2526, 2018.
- [3] Vimal, R., Subramanian, K.H.H, Aswin, C., Logeswaran, V. and Ramesh, M., Comparisional study of succinylation and phthalicylation of jute fibres: Study of mechanical properties of modified fibre reinforced epoxy composites, *Materials Today: Proceedings*, 2:2918–27, 2015.
- [4] Ramesh, M., Palanikumar, K. and Reddy, K.H., Plant fibre based bio-composites: sustainable and renewable green materials, *Renewable and Sustainable Energy Reviews*, 79: 558–584, 2017.
- [5] Shah, D., Developing plant fibre composites for structural applications by optimising composite parameters: a critical review, *Journal of Materials Science*, 48(18):6083–107, 2013.
- [6] Yan, L., Chouw, N., Huang, L., Kasal, B., Effect of alkali treatment on microstructure and mechanical properties of coir fibres, coir fibre reinforced-polymer composites and reinforced-cementitious composites, *Construction and Building Materials*, 112:168–182, 2016.
- [7] Liu, L., Yu, J., Cheng, L., Yang, X., Biodegradability of poly(butylene succinate) (PBS) composite reinforced with jute fibre, *Polymer Degradation and Stability*, 94, 90–94, 2009.
- [8] Väisänen, T., Das, O., Tomppo, L., A review on new bio-based constituents for natural fiber-polymer composites, *Journal of Cleaner Production*, 149, 582-596, 2017.
- [9] Wang, L., Li, A., Chang, Y., Relationship between enhanced dewaterability and structural properties of hydrothermal sludge after hydrothermal treatment of excess sludge, *Water Res.*, 112, 72-82. DOI:10.1016/i.watres.2017.01.034
- [10] Wang, N., Cai, C.J., Cai, D.Q., Cheng, J.J., Li, S.L., Wu, Z.Y., Hydrothermal fabrication of hydroxyapatite on the PEG-grafted surface of wood from Chinese glossy Privet, *Appl Surf Sci*, 259:643-649, 2012.
- [11] Hamzeh, Y., Ashori, A., Marvast, E.H., Rashedi, K., Olfat, A.M., A comparative study on the effects of coriolus versicolor on properties of HDPE/wood flour/paper sludge composites, *Compos B Eng*, 43(5):2409-14, 2012.
- [12] Gregorova, A., Hrabalova, M., Kovalcik, R., Wimmer, R., Surface modification of spruce wood flour and effects on the dynamic fragility of PLA/wood composites, *Polym Eng Sci*, 51(1):143-50, 2011.
- [13] Bledzki, A. and Gassan, J., Composites reinforced with cellulose based fibres, *Prog Polym Sci*, 24(2):221-74, 1999.
- [14] Doan, T.T.L., Brodowsky, H., Mäder, E., Jute fibre/polypropylene composites II. Thermal, hydrothermal and dynamic mechanical behaviour. *Compos Sci Technol*, 67(13):2707-14, 2007.
- [15] Mohanty, A.K., Misra, M., Drzal, L.T., *Compos Interfaces* 8:313, 2001.
- [16] Valadez-Gonzalez, A., Cervantes-Uc, J.M., Olayo, R., Herrera-Franco, P.J., *Compos B: Eng*, 30:309, 1999.
- [17] Alawar, A., Hamed, A.M., Al-Kaabi, K., Characterization of treated date palm tree fiber as composite reinforcement, *Compos B*, 40:601–6, 2009.
- [18] Mishra, S., Mohanty, A.K., Drzal, L.T., Misra, M., Parija, S., Nayak, S.K., Studies on mechanical performance of biofibre/glass reinforced polyester hybrid composites, *Compos Sci Technol*, 63:1377–85, 2003.

- [19] Mylsamy, K., Rajendran, I., Investigation on physio-chemical and mechanical properties of raw and alkali-treated Agave Americana fibre, J Reinforced Plast Compos, 29:2925–35, 2010.
- [20] Ramadevi, P., Sampathkumar, D., Srinivasa, C.V., Bennehalli, B., Effect of alkali on water absorption of single cellulose abaca fiber, Bioresources, 7:3515–24, 2012.
- [21] Edeerozey, A.M.M., Akil, H.M., Azhar, A.B., Ariffin, M.I.Z., Chemical modification of kenaf fibers, Mater Lett 61:2023–5, 2007.
- [22] Horrocks, A., Kandola, B., Flammability and fire resistance of composites. In: Long, A.C. (Ed.), Design and Manufacture of Textile Composites. Woodhead Publishing, Cambridge, UK, pp. 330-363, 2005.
- [23] Kozłowski, R., Władysław-Przybylak, M., Flammability and fire resistance of composites reinforced by natural fibers, Polym. Adv. Technol, 6, 446-453, 2008.
- [24] Saheb, D.N. and Jog, J., Natural fiber polymer composites: a review. Adv. Polym. Technol. 18, 351–363, 1999.
- [25] Monteiro, S.N., Calado, V., Rodriguez, R.J., Margem, F.M., Thermogravimetric stability of polymer composites reinforced with less common lignocellulosic fibers—an Overview. J. Mater. Res. Technol. 1, 117–126, 2012.
- [26] Stokke, D.D., Wu, Q., Han, G., 2014, Introduction to Wood and Natural Fiber Composites. John Wiley & Sons, West Sussex, UK.
- [27] Beyler, C.L., Hirschler, M.M., Thermal decomposition of polymers. In: DiNenno, P. (Ed.), SFPE Handbook of Fire Protection Engineering. National Fire Protection Association, Quincy, Massachusetts, US, pp. 110–131, 2001.
- [28] Yao, F., Wu, Q., Lei, Y., Guo, W., Xu, Y., Thermal decomposition kinetics of natural fibers: activation energy with dynamic thermogravimetric analysis. Polym. Degrad. Stab. 93, 90–98, 2008.
- [29] Singh., Kaushlendra and Zondlo., John, Characterization of fuel properties for coal and torrefied biomass mixtures, Journal of the Energy Institute, 90(4):505-512, 2017, <https://doi.org/10.1016/j.joei.2016.05.012>.
- [30] Sawpan, M.A., Pickering, K.L., Fernyhough, A., Flexural properties of hemp fibre reinforced polylactide and unsaturated polyester composites, Composites: Part A, 43, 519–526, 2012.
- [31] Dobircau, L., Sreekumar, P.A., Saiah, R., Leblanc, N., Terrié, C., Gattin, R., Saiter, J.M., Wheat flour thermoplastic matrix reinforced by waste cotton fibre: Agro-green-composites, Composites: Part A, 40, 329–334, 2009.
- [32] Singh, R., Babu, J.N., Kumar, R., Srivastava, P., Singh, P., Raghubanshi, A.S., 2015. Multifaceted application of crop residue biochar as a tool for sustainable agriculture: an ecological perspective. Ecol. Eng. 77, 324–347.
- [33] Basu, P., 2018. Biomass Gasification, Pyrolysis and Torrefaction: Practical Design and Theory. Academic Press.
- [34] Bridgewater A.V., 2012, Review of fast pyrolysis of biomass and product upgrading, Biomass Bioenergy, 38:68–94.
- [34] Chen, W.-H., Lu, K.-M., Tsai, C.-M., 2012, An experimental analysis on property and structure variations of agricultural wastes undergoing torrefaction. Appl. Energy 100, 318–325.
- [35] Zhao, C., Jiang, E., Chen, A., 2017. Volatile production from pyrolysis of cellulose, hemicellulose and lignin. J. Energy Inst. 90 (6), 902–913.
- [36] Yiga, V.A., Pagel, S., Lubwama, M., Epple, S., Olupot, P.W., Bonten, C., Development of fiberreinforced polypropylene with NaOH pretreated rice and coffee husks as fillers: Mechanical and thermal properties, Journal of Thermoplastic Composite Materials, 1–23, 2019.

***Acknowledgement: 5th International Anatolian Energy Symposium
24-26 March 2021, Karadeniz Technical University, Trabzon/Turkey***