

Effect of Alkaline Treatment on the Thermal Stability of Pineapple Leaf Fibers

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<https://doi.org/10.35121/ijapie201904231>

Abstract : Recently, most of the industries are looking towards to incorporate sustainable, renewable, eco-friendly and affordable raw materials and production process. To achieve this goal, engineers and technologists are working on biocomposite material. The primary reason behind the selection of natural fiber based material in the automobile, construction, and aerospace industry is its low cost, lightweight, high specific strength and modulus, biodegradability, and friendly processing. In spite of all beneficial features, one of the main barriers to their utilization in all mentioned sectors is thermal degradability. Natural fibers can be subjected to thermal degradation during composite processing and their application in the high-temperature field. So it is practically significant to understand the thermal decomposition of lignocellulosic fibers and to modify it for the purpose of high-temperature stability. In this work, alkaline treatment of varying concentrations (2%, 4%, 6%, 8%, and 10 wt %) was used to study the effect of alkaline treatment on thermal stability of pineapple leaf fibers. The thermal behavior of untreated and alkali treated pineapple leaf fiber was examined by using a thermal gravimetric analysis instrument (TGA). The results show that 4 wt% NaOH treated pineapple leaf fiber have maximum thermal stability. The decomposition of untreated and treated PALF was a two-stage process attributed to the thermal decomposition of hemicellulose, cellulose, and lignin. The results also showed that the temperature of initial degradation 251 °C increased to 285 °C after 4% alkaline treatment due to partial removal of hemicellulose and lignin.

Keywords: Pineapple Leaf Fiber (PALF), Alkaline Treatment, Thermal Stability, Thermogravimetric Analysis (TGA).

1. INTRODUCTION

Scientists and engineers are looking for a material which is based on renewable and sustainable resources, environment-friendly, economical and of low cost, high strength and light in weight, ease of recycling etc. The lignocellulosic fiber based material is the best solution due to its varieties of attractive properties over synthetic materials. In recent years, natural fiber-reinforced composites have received attention by automotive and construction industries for making structural parts and building materials. Despite a number of advantageous properties, natural fibers like sisal, banana, coconut coir, sugarcane bagasse, pineapple leaf fiber etc have some limitations like hydrophilic nature, poor wettability with synthetic polymer, low thermal stability, and poor interfacial bonding strength with resin. Most of the researchers have already worked for effective solutions to these problems and find out that physical and chemical treatment of natural fiber surface leads to better compatibility with the polymeric resin. But very few works have been done towards the area of surface treatment effect on thermal stability of natural fibers. Na Lu *et al.* (2013) investigated the effect of surface treatment of hemp fibers on the thermal stability of Hemp-PLA biocomposite. They concluded that

the thermal degradation temperature was increased from 330 °C to 340 °C after the treatment of hemp fiber with 5 wt% NaOH solution [1]. Arifuzzaman Khan G M *et al.* (2012) studied the effect of sodium hydroxide on the thermal behavior of coconut husk (coir) fiber. They found that the main degradation temperature peak is shifted to a higher temperature region of about 19 °C [2]. As natural lignocellulosic fibers, they can be subjected to thermo-chemical decomposition during industrial processing and biocomposite production. It is of practical significance to study for understanding, predicting, and evaluating the thermal decomposition mechanism of lignocellulosic fibers. The knowledge of the thermal decomposition process would help to better design final product by estimating the influence on product properties.

Thermogravimetric analysis (TGA) is one of the most popular and widely used technique to analyze the decomposition process of solid material, kinetic analysis of de-volatilisation process, and it provides possibilities to study the effects of heating rate, temperature, pressure, atmosphere gas, gas flow rate, biomass composition, and particles size on mass loss of a sample. Kinetic analysis of thermo-chemical reactions for the solid mass sample can be done either by a

model fitting method or model-free method. Model fitting methods of kinetic analysis require fitting of different models to the kinetic data for obtaining the best statistical fit. The disadvantage of this strategy is the possibility of wrong model selection which results in an error in kinetic parameters. The model-free methods consist of several kinetic curves with the multi-heating rate for estimating the activation energy (E_a). Kissinger, Flynn-Wall-Ozawa (FWO), and Friedman are the common and effective methods based on multiple heating rates, increasingly adopted by researchers to analyze the thermo-chemical conversion of natural fiber, kinetic analysis of de-volatilization, and estimation of activation energy. All these model-free methods are summarized in Table 1 [3-5]. Alwani M. Sitiet al. (2014) examined the kinetic analysis of SCB, COIR, PALF, and BPS fibers by Kissinger, Friedman, and F.W.O methods. They concluded that COIR was the most thermally stable fiber followed by PALF, BPS, and SCB. The activation energy of COIR, PALF, SCB, and BPS fibers were 100.84, 96.28, 92.87, and 80.79 (kJ/mol) respectively when calculated by Friedman's method [6]. Yao Fei et al. (2007) studied the thermal decomposition kinetics of 10 types of fibers by Kissinger. They found the activation energy of Bagasse, Bamboo, Cotton Silk, Hemp, Jute, Kenaf, Rice husk, Rice straw, Wood maple, and Wood pine were 161.1, 161.6, 146, 171.1, 165.6, 157.7, 167.4, 176.2, 153.7, 159.3 respectively [7].

Table 1: Kinetic methods used for calculating the activation energy

Methods	Equation	Reference
Kissinger	$\ln \frac{\beta}{T^2} = \ln \frac{AR}{E} - \frac{E}{RT}$	Kissinger, 1957 [2]
Friedman	$\ln \frac{d\alpha}{dt} = \ln[Af(\alpha)] - \frac{E}{RT}$	Friedman, 1964 [3]
F.W.O	$\ln \beta = \log \frac{AE}{Rg(x)} - 5.331 - 1.052 \frac{E}{RT}$	Flynn and Wall, 1966 [4]

The decomposition of natural fibers occurs in two to three stages depends on the type of fiber and its chemical composition. Alwani M. Sitiet al. (2014) reported that SCB and COIR fiber was decomposed in two steps but BPS fiber decomposes in three steps. It was due to the presence of high amount of lignin and cellulose in BPS fiber compared to SCB and COIR [6]. Na Lu et al. (2013) concluded that hemp fiber was decomposed in two steps, starting with the loss of moisture around 100 °C and followed by successive decomposition of hemicellulose, cellulose, and lignin in the range of 150-400 °C [1]. According to JayamaniElammaranetal. (2014), thermal decomposition of both untreated and treated betel nut fiber polyester composites had two mass loss steps, where 10 wt% mass losses shifted from 110 °C to (120-140) °C after 5 wt% of alkaline treatment [8]. The purpose of this work was to study and analyze the effect of alkaline treatment with different

concentrated solutions (2%, 4%, 6%, 8%, and 10 wt %) on thermal stability of pineapple leaf fiber (PALF). The pyrolysis process was performed by TGA machine under the condition of constant heating rate and constant mass flow rate of the gas.

2. EXPERIMENTAL

A. Materials

Raw pineapple leaf fiber (R-PALF) was purchased from Go Green Products, Chennai, India. The average density and moisture content in PALF was equal to 0.98 g/cm³ and 10-11% respectively. Table 2 shows the chemical composition of the materials [9]. Sodium hydroxide (NaOH) grade for alkalinetreatment was of laboratory reagent (LR) used and obtained from the local supplier.

Table 2: Chemical composition of pineapple leaf fiber

Fiber	Cellulose %	Hemicellulose %	Lignin %	Pectin %
PALF	70-82	18.8	5-12.7	1.1

B. Fiber Treatment

Pineapple leaf fibers were treated by immersing in (2%, 4%, 6%, 8%, and 10 wt %) of alkaline (NaOH) solutions for 24 hrs at 25 °C, followed by washing with deionized water (until the pH was reached 7), and drying in oven at 60 °C for 24 hrs (until the constant weight was maintained). The untreated raw pineapple leaf fibers (R-PALF) were also washed in deionized water and dried at 60 °C for 24 hrs.

C. Method

1) *Fourier-Transform Infrared Spectroscopy (FTIR)*: Fourier-transform infrared spectroscopy, model Perkin Elmer 2000 was used to analyze the effect of alkali treatment of different concentrations (2%, 4%, 6%, 8% and 10 wt %) on chemical bonding exist in untreated pineapple leaf fiber. FTIR spectra were analyzed with an infrared spectrophotometer in the range 4000 cm⁻¹ to 400 cm⁻¹. FTIR of untreated and alkali treated pineapple leaf fiber had done in CSIR-CSIO analytical instrumentation laboratory.

2) *Thermogravimetric Analysis (TGA)*: Thermogravimetric analysis (TGA) of Pineapple leaf fiber (both untreated and treated) was carried out using a thermogravimetric analyzer (Perkin Elmer, TGA 4000). The samples of mass 5 mg were evenly and uniformly distributed in the alumina crucible which was supported by a precision balance. This small amount of natural fiber was taken for uniformity of temperature throughout the sample. The variation in mass of sample with respect to temperature and time was controlled, monitored and recorded using Perkin Elmer thermal software (Pyris). The temperature change of PALF was controlled from 25 °C to 700 °C at a heating rate of 10°C/min under the high purity nitrogen (inert) atmosphere at a flow rate of 20 ml/min. The heating rate of 10°C/min was selected for better resolution of transition. TGA of COIR and PALF fibers had done in Central Instrumentation Laboratory, DTU (Delhi).

4. RESULT AND DISCUSSION

Fourier-Transform Infrared Spectroscopy (FTIR)

Fig. 1 shows the IR spectra for untreated and alkali treated pineapple leaf fiber (PALF) that was obtained by using the FTIR spectrometer.

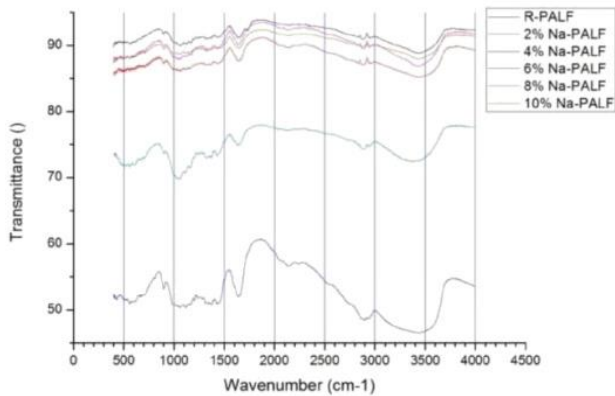


Fig. 1: IR spectra of untreated and alkali treated pineapple leaf fibers

The broad peak between 3200 cm^{-1} to 3500 cm^{-1} is linked to OH stretching vibration present in amorphous and crystalline cellulose. The carbonyl stretching ($\text{C}=\text{O}$) peak (1730 cm^{-1}) related to hemicellulose can be seen in untreated PALF but not present in alkali treated pineapple leaf fibers. This may be due to the removal of hemicellulose component. CH_2 bending peaks at 1432 cm^{-1} are present in both untreated and alkali treated fiber. The increase in peak intensity at around ($1600\text{--}1650\text{ cm}^{-1}$) after alkaline treatment corresponds to the removal of wax, adhesives, pectin, and gummy substance from the fiber surface. The small peak at 1525 cm^{-1} is related to lignin component. This peak is not present in the alkali treated sample. It could be due to partial removal of lignin after alkali treatment. The peak at 1244 cm^{-1} is much smaller in alkali treated PALF than untreated sample. This peak corresponds to $\text{C}=\text{O}$ stretch of the acetyl group of lignin and is reduced because lignin is partially removed from the fiber surface.

Thermal Decomposition of Untreated and Treated Pineapple Leaf Fiber

TGA and DTG curves of untreated and alkali treated pineapple leaf fiber (2%, 4%, 6%, 8%, and 10 %) were shown in Fig. 2 and 3. Tests were performed from $25\text{ }^{\circ}\text{C}$ to $700\text{ }^{\circ}\text{C}$ in the nitrogen atmosphere at $10\text{ }^{\circ}\text{C}/\text{min}$ heating rate.

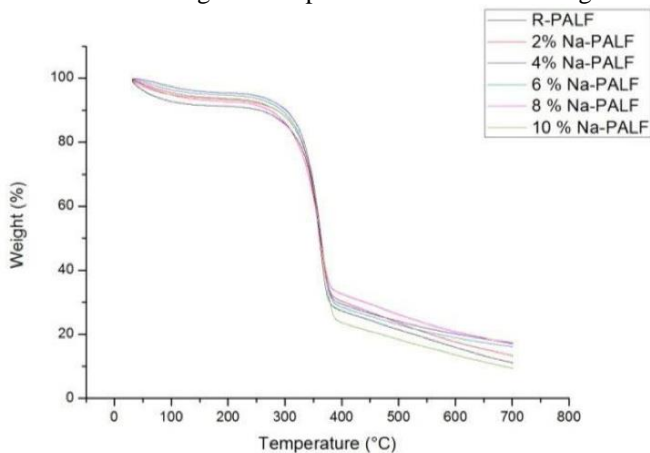


Fig. 2: TGA curve for untreated and alkali pineapple leaf fibers

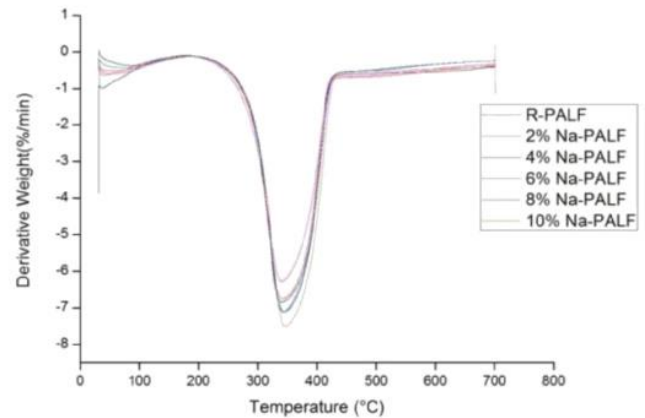


Fig. 3: DTG curve for untreated and alkali pineapple leaf fibers

The thermal decomposition of pineapple leaf fiber (untreated and alkali treated) was two-stage processes, where the first stage was the evaporation of water and extraction of volatile compounds and the second stage was the decomposition of hemicellulose, cellulose, and lignin component. Initial mass loss due to evaporation of water is common for all types of plant fiber but the rate of evaporation depends on the hydrophilicity of natural fiber [8]. The weight percentage of water extraction was reduced from 9% to 3% after 4 wt% NaOH treatment of PALF. This was because of the removal of a hydroxyl group and free water after alkaline treatment. Brigida *et al.* (2010) reported that structurally bound water is resistant to evaporation during drying [11]. Mortari Daniela A *et al.* (2014) found the mass loss of sugar cane bagasse around 8.7 wt% under the atmosphere of CO_2 [12]. As the natural fibers were heated, the weight of the material was reduced.

Thermal degradation data of untreated and treated PALF is tabulated in Table 3 where T_{onset} is the temperature at which degradation starts, $T_{d,1}$ & $T_{d,2}$ are the first and second stage of decomposition temperature and T_p is the peak temperature of maximum rate of degradation. Table 3 shows that the initial decomposition temperature of PALF was increased from $251.23\text{ }^{\circ}\text{C}$ to $285.31\text{ }^{\circ}\text{C}$ after 4 wt% NaOH treatment of fiber. This might be because of the removal of hemicellulose component. The presence of the carbonyl group ($\text{C}=\text{O}$) in hemicellulose may be responsible for lower thermal stability.

Table 3: Onset and degradation temperatures of raw pineapple leaf fiber obtaining from TGA thermogram

Sample	T_{onset} ($^{\circ}\text{C}$)	$T_{d,1}$ ($^{\circ}\text{C}$)	$T_{d,2}$ ($^{\circ}\text{C}$)	T_p ($^{\circ}\text{C}$)	Max. ROD ¹	R_m
R-PALF	251.23	360.6	526.09	341.58	6.85	10.89
2% Na-PALF	272.71	361.87	556.79	341.52	6.75	13.17
4% Na-PALF	285.31	363.37	603.97	343.43	7.13	17.24
6% Na-PALF	275.08	363.48	569.82	343.12	7.091	16.01
8% Na-PALF	263.36	362.07	619.18	339.72	6.28	16.83
10% Na-PALF	271.59	364.17	468.7	346.85	7.51	9.19

¹ROD: Rate of decomposition, R_m : Residual mass at $700\text{ }^{\circ}\text{C}$

StevulovaNadezda *et al.* (2016) reported that the primary decomposition of lignocellulosic materials occurs within 200-400 °C [13]. Alwani M. Sitiet *et al.* (2014) found that sugarcane bagasse fiber had higher mass loss compared to coir fiber due to the presence of more hemicellulose content [6]. Table 3 also shows that initial decomposition temperature was reduced beyond 4% alkaline treatment. This was because of excess removal of hemicellulose. NdaziBwire S *et al.* (2007) reported the reduction in temperature of maximum weight loss by at least 26 °C, beyond 4 wt% alkaline treatment of rice husk fiber. This was due to the excess removal of cementing material like hemicellulose and lignin [14]. The second step of thermal degradation was ranging from 400-620 °C. It was observed that $T_{d, 2}$ of untreated and alkali treated fiber at 526.09 °C, and 619.18 °C respectively, is from the decomposition of lignin. PanyasartKloykamolet *et al.* (2014) reported the first step decomposition temperature of alkaline (Na-PALF) treated and silane (Si-PALF) treated fiber higher than raw pineapple leaf fiber composite [10]. Table 4 reveals the percentage weight loss of untreated and treated PALF. It was observed that there is a delay in degradation temperature after alkaline temperature.

Table 4: Degradation temperatures (°c) for untreated and treated PALF

Wt. Loss (%)	R-PALF	2% Na-PALF	4% Na-PALF	6% Na-PALF	8% Na-PALF	10% Na-PALF
10	254.48	285.30	301.68	294.48	272.5	285.02
20	324.22	329.12	333.62	330.43	321.67	329.52
30	343.47	344.62	347.21	345.69	340.93	346.33
40	353.45	354.25	356.3	355.62	353.15	356.6
50	360.6	361.8	363.37	363.48	362.7	364.17

Na Lu *et al.* (2013) investigated the effect of alkaline treatment of 5 wt% at 50 °C on thermal decomposition of hemp fiber. They concluded that untreated hemp fiber degrade earlier than treated fiber [1]. Fig. 2 showed that the major mass loss (30-50%) occur at the temperature greater than 300 °C. This was because of the decomposition of cellulose and lignin. It was investigated that crystalline cellulose was degraded between the temperatures of 302-375 °C. The DTG curves show that at peak temperature, the rate of decomposition was increased from 6.83 %/min to 7.13 %/min due to 4% alkali treatment of pineapple leaf fiber. These results are because of depolymerization of native cellulose structure to short length crystallites.

Lignin was the most difficult component to decompose compared to other components because of its cross-linked highly complex aromatic structure of phenylpropane units. It starts to decompose at a lower temperature (typically 160-175 °C) compared to cellulose but it decomposed slowly under the whole temperature range and extend its temperature as high as 900 °C. The DTG curves for untreated and treated pineapple leaf fibers have reached the equilibrium stage beyond 400 °C where the rate of decomposition is approximately constant and lignin component of natural fiber decomposes slowly.

According to Paiva *et al.* (2006), the decomposition of lignin occurred in a wider temperature compared to cellulose and hemicellulose [15]. After 700 °C, the remaining mass of pineapple leaf fiber was shown in Table 3. It was observed that the residue was increased up to 8% alkali treated fiber compared to the untreated one. This was due to the slow rate of the chemical decomposition reaction. Only ash and char was left after 700 °C. The differences in the amount of char left can be attributed to the change in chemical composition of pineapple leaf fiber after alkali treatment. It was reported by Williams (2004) that a high lignin content in natural fiber results in the production of a higher level of ash and char during pyrolysis [16]. The 10% NaOH treated PALF shows less residue content than untreated PALF. This might be due to excess delignification of pineapple fiber after 10% alkaline treatment.

5. CONCLUSIONS

This study concludes that pineapple leaf fibers (both untreated and treated) decompose in two steps due to hemicellulose, cellulose, and lignin decomposition. The major mass loss (30 to 50%) of pineapple leaf fibers were in the range of 340-365 °C. It was attributed due to major decomposition of cellulose.

The initial decomposition temperature of pineapple leaf fiber was increased from 250 °C to 300 °C after 4 wt% alkaline treatment. It was due to the removal of hemicellulose which results the remaining cellulose occupies a crystalline structure that leads to better thermal stability.

The results depict that 4 wt% alkaline treated pineapple leaf fiber shows maximum thermal stability. The residue content of PALF was increased from 10.89% to 17.24 wt% after 4% alkaline treatment. This elevation was attributable to the change in chemical composition of pineapple leaf fiber.

The maximum rate of decomposition was increased from 6.85 %/min to 7.51 %/min after 10 wt% NaOH treatment. This was because of depolymerization of native cellulose to short length crystallites.

ACKNOWLEDGMENT

The authors gratefully acknowledge all support received from Analytical Instrument Laboratory at CSIR-CSIO, Chandigarh.

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