

A details study of the relationship between the behaviors of jute fiber when they are heated at different temperature with varying duration by using regression analysis: a textile case from Bangladesh perspective.

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Abstract

The thermal behavior of jute fiber under various temperatures range with varying time, degree of crystallinity and tenacity was studied in detail. When this fiber was exposed in various temperatures with varying time it showed various changes in different properties such as physical and chemical. This paper had analyzed the effects of thermal exposure on degree of crystallinity and tensile property such as tenacity. Finally It was found that increasing temperature after certain range affects fiber properties a lot causes significantly dropped in tenacity and because of chain scissions a slight increase in degree of crystallinity was observed.

Keywords: Chain scissions, tenacity, crosslinked polymers, degree of crystallinity, depolymerization, recrystallization, Differential Scanning Calorimetry, cellulose & activation energy.

Introduction

Natural fibers are gaining progressive account as renewable, environmentally acceptable, and biodegradable starting material for industrial applications, technical textiles, composites pulp and paper as well [1]. Now a day the governments of almost all the countries are conscious about environmental damages, ecological risks and increasing global energy crisis. So the researchers give more interest in using least damage sources of raw material such as usages of natural fibers in various interests in fiber reinforced composites [2]. The most attractiveness side of a plant-based fiber comes from its high specific strength and stiffness [3]. In recent years, wide range of research has been carried out on natural fiber reinforced polymer composites [4]. Another issue is that cellulose based natural fibers combine good mechanical properties with low density and can be used in general successfully as reinforcements for different kinds of thermosets and thermoplastics polymers [5]. The major advantages of plant fibers are low cost, less tool wear during processing and

recycling properties as well as environmental friendly behavior [6]. One of the known natural fibers is hemp, which has been used as a composite material and increasingly in the construction of building envelopes [7]. As regards hemp in buildings, it is increasingly used with a lime base binder for wall constructions [8]. Another study, been conducted to evaluate the flexural and impact performances of glass/sisal hybrid composites with different fiber loadings and different volume ratios of sisal and glass fibers [9]. Evan and Woolley's study has identified a wide range of benefits including: exceptionally high levels of air tightness achieved through the monolithic wall construction, improved air quality due to the hygroscopic properties of the wall, and lower energy consumption attributed to the heat transfer process involving the sensible and latent thermal capacities of hemp-lime walls. It is usually used as material for insulating walls or insulation layers for floors and roofs. To sum up it can be said that the biodegradable, recyclable, nonabrasive, environmentally friendly makes them suited for various end usages [10]. But the thermal degradation is

major problem for these fibers. As a result of overheating the polymers thermal degradation has occurred due to molecular deterioration. The long backbone chain of the polymer starts to be broken (chain scission) and react with one another to change the properties of the polymer at high temperatures. With indication of possible mechanical loss, thermal degradation also represents tolerable limit for service temperature of plastics [11].

Polymers can be differentiated into several types depending on the nature of thermal degradation:

- (1) Polymers whose chain scissions occur from the backbone chain tend to vaporize completely at sufficiently high temperatures.
- (2) Polymers whose chain scissions occur between the carbons of the backbone and the side groups form double bonds in the channel and also crosslinkages between the chains. When they are exposed to prolonged heating they become more or less stabilized in the form of a partially carbonized residue.
- (3) Polymers which contain excessive crosslinked are converted into a combed structure of carbonized residue at the time of heating.

The major disadvantages of these fibers are limited thermal stability as degradation occurs at above 180°C. As a result the typically used thermoplastics as matrix are polyvinylchloride, polypropylene, and polyethylene have melting temperatures below or equal to the temperature of degradation. The later issue is that they have poor resistance to moisture often reduce the potential of natural fibers [12]. Furthermore the reason of disadvantages is that the presence of surface impurities and the large amount of hydroxyl groups make plant fibers less attractive for reinforcement of polymeric materials. Plant fiber modified with alkali promotes the development of fiber resin adhesion, which then will result in increased interfacial energy and, hence, improvement in the mechanical and thermal stability of the composites. Natural fibers from agricultural residues and forest product's processing mainly consist of natural lingo cellulosic polymers. As a result, they are subjected to thermal degradation during composite processing [13]. Cellulose is the most abundant polymer on the earth among other natural textile polymers. Understanding the cellulose thermal degradation is of great importance in a vast array of areas such as generation of energy from biomass and the improvement of thermal resistance of cellulosic fibers. Thermal decomposition of cellulose has been widely studied for the past several years. Both source of cellulose and its composition greatly affect its pyrolysis. Thermogravimetric (TG) analysis is a method, based on continuous measurement of weight on a sensitive balance as sample temperature was increased in an inert atmosphere. This is referred to as non isothermal TGA.

Data were recorded as a thermogram of weight versus temperature [14] is a widely used technique in this area. It is useful for the thermal characterization of both inorganic and organic materials, including polymers (such as cellulose). It provides quantitative results regarding the loss of mass of a sample as a function of increasing temperature or time [15]. This thermal degradation of cellulose-based fibers is greatly influenced by their structure and chemical composition [16]. Due to the complexity of thermal decomposition reactions of natural fibers, extensive researches have been done in determining individual behaviors of the main components (or pseudo-components) of natural fibers (e.g., pure cellulose, lignin, and hemicelluloses). In this case, improvement of classic "Broidoe Shafizadeh" model and calculation of decomposition activation energy of pure cellulose is the primary focus. Antal and Varhegyi and Antal et al [17] reviewed the pyrolysis of pure, ash-free cellulose and described it with a single step, irreversible, first-order rate law containing high activation energies (238 or 228 kJ/mol). Milosavljevic and Suuberg reviewed global cellulose pyrolysis kinetics and found that low activation energies (140-155 kJ/mol) were obtained when cellulose was rapidly heated above 600 K. Capart et al. calculated kinetics parameters of microgranular cellulose using dynamic and isothermal methods in nitrogen atmosphere and described it with two reactions with activation energies of 202 and 255 kJ/mol respectively. Besides pure cellulose, the pyrolysis of lignin and hemicelluloses (i.e., xylan) has also been studied. In developing fiber decomposition kinetics, different reaction schemes have also been considered for a better interpretation for fiber decomposition process. Koufopoulos et al. established multi-step reaction mechanisms for wood and wood components. Diebold later developed an elaborate seven-step global kinetics scheme for cellulose pyrolysis. Orfao et al. represented a model named three independent reactions to pyrolysis kinetics of some lignocellulosic materials but Di Blasi [18] used three parallel reactions showing the fast pyrolysis process of wood. More recently, Chen et al. [19] employed a two-step consecutive reaction model for some forest fuels. For practical engineering applications, however, it may be sufficient to consider only the basic characteristics of the thermal decomposition process with some simple mechanisms. For natural fiber reinforced polymer composite processing, it is of more practical relevance to understand and predict the thermal decomposition of the reinforcing fibers based on the simplified kinetic scheme and parameters under specific process temperature of polymer/natural fiber composite. However, there have been few fundamental studies in this field. Another study shows that degradation is followed by the orders in thermal stability (in absence of oxygen): lignin, alpha-cellulose, hemi cellulose as published by

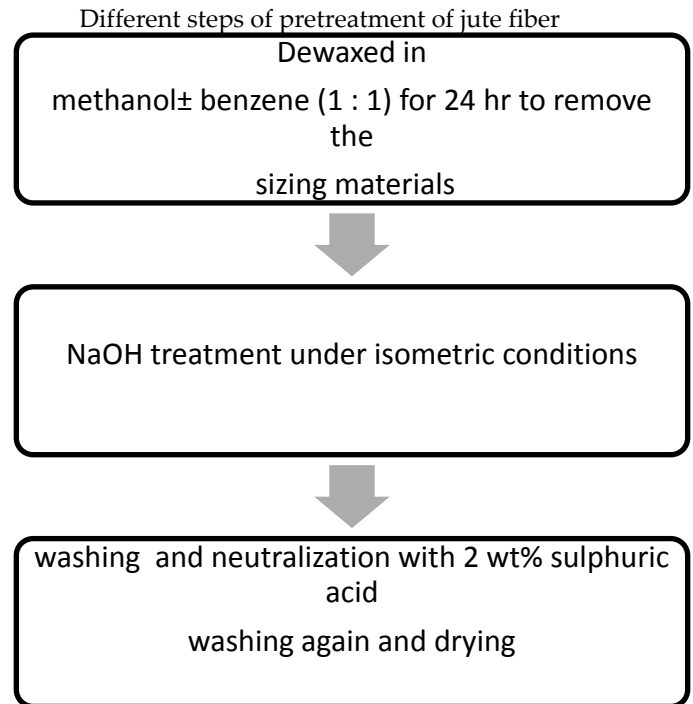
Nasser [20]. Opposite data were published by Ramiah with decomposition temperatures in the order: hemicellulose, lignin, alpha cellulose by using the dilatometric method [21]. When cellulose-based materials are heated in the range of 100 to 250°C some of the changes in physical properties of the fibers due to the alterations in either physical or chemical structures such as depolymerization (Depolymerization is the conversion of a polymer into its component monomers [22]), hydrolysis (Hydrolysis is a process of breaking the bond of a molecule by using water. The reaction mainly occurs between an ion and water molecules and often changes the pH of a solution [23]), oxidation (Oxidation is defined as the loss of electrons during a reaction by a molecule, atom or ion [24]), dehydration (Dehydration is occurred when someone loses more fluids than it takes in [25]), decarboxylation (Decarboxylation is a chemical reaction that removes a carboxyl group and releases carbon dioxide [26]) and recrystallization [27]. For instance, a thermal heating of cotton fibers for 6 hr at temperatures from 165°C upto 240°C leads to chain scission and decrease in the degree of polymerization (DP) from 5360 to 320, determined with viscosity measurements. The ability to crystallize could be increased by chain scission because this would permit the cellulose chain store align themselves more easily and then crystallize (degree of crystallinity was calculated from Valentine's relation). Zeronian stated that heating increased the crystallinity of the fiber. For example, the amorphous part of the cellulose, F_{am} decreased from 0.38 to 0.30 by being heated at 240°C for 6h. A similar behavior of DP was found in 1971 by Ruzna Āk et al. for untreated and alkali-treated cotton fibers at different initial moisture contents. He further found that an increasing moisture content of the cellulose generally reduces the decrease of degree of polymerization.

As far as I know there is no work done on thermal degradation property with strength property of different jute fiber when higher temperature is applied with stepwise degradation of cellulose [28].

Experimental Part

Materials and Methods

For this study jute fiber both with untreated and alkali-treated was taken. At first fiber was alkali treated like below procedure-



NaOH Treatment

It was carried out by immersing the fibers in 1 N sodium hydroxide (NaOH) solution for 1 hr at room temperature. Then the fibers were washed with distilled water containing few drops acetic acid, followed by washing under continuous stream of water until the complete removal of NaOH residue. Subsequently, the mercerized fibers were dried at room temperature for 24 hrs and then in a vacuum oven at 80°C for 12 hrs.

Conditions of Exposure

In a laboratory oven the fibers were thermally treated at temperatures at 23, 180, 200, and 220°C for a maximum of 120 min at standard humidity. Thereafter, the fibers were cooled down to 23°C in a discreet followed by storage of 24 h at ambient temperature. About 8 wt % initial moisture was present on both types of fibers measured by Carl Fischer titration.

Degree of Crystallinity (DC)

The degree of crystallinity is defined as the fractional amount of polymer that is crystalline and it is either expressed in terms of the mass fraction, w_c or the volume fraction, j_c . The degree of crystallinity is one of its most influential physical parameters for semi-crystalline polymers as it reflects the sample's morphology with determination of various mechanical properties, such as the Young modulus, yield stress and impact strength. The fractional amount of crystallinity in a polymer sample can

be obtained widely by Differential Scanning Calorimetry. Other commonly used methods are X-ray diffraction, density measurements, and infrared spectroscopy [29].

DC was measured by using the iodine absorption method with the below formula

$$DC = 100 - \frac{37.925}{m} \left[1 - \frac{V_{sample}}{V_{control}} \right]$$

Here m [g] as mass of the sample,

V_{sample} [mL] and $V_{control}$ [mL] are the values obtain by titration with and without fibers with $Na_2S_2O_3$. Three samples were investigated in each case; the standard deviation was at maximum 1%.

Tensile Test

A DIN 53 834 yarn tensile test with a free span length of 500 mm and a test speed of 2 mm/min was used to measure the strength and tenacity of the yarns at ambient temperature. Fifteen samples were investigated, and in each case with a standard deviation below 15%.

An overview of Correlation and Regression Analysis

Correlation Analysis

Correlation Analysis is a group of statistical techniques to measure the association between two variables known as dependent and independent variable. The Dependent Variable is the variable being predicted or estimated. The Independent Variable provides the basis for estimation. It is the predictor variable [30]. A Scatter Diagram is used to portray the relationship between two variables.

Correlation coefficient is the representation of degree of linear relationship between two variables[31]. It is represented by "r". The value lies between -1 to +1.

Characteristics of the correlation coefficient

- identify by the lowercase letter r and ranges from -1 to +1.
- shows the direction and strength of the linear relationship between two variables.
- near 0 and ±1 indicates little, strong positive and negative relationship between the variables[32].

2.5.2 Regression Analysis

In mid to late 1800's a scientist named Galton was studied largely on observational study on human being and tried to find out the relationship between the heights of fathers and first sons[33]. The concept regression analysis was deprived from the study of Galton. Simple (single) regression analysis simply indicates the value of a dependent variable is estimated on the basis of one independent variable where as Multiple regression analysis is something which indicates the estimation of the value of a dependent variable in terms of two or more independent variables [34]. Here, Y stands for dependent variable and X for independent variable[35]. So it can be said that single regression analysis involves with one for both dependent and independent variable but we have to go for multiple regression analysis we want to estimate a value which depends on more than one independent variable.

2.5.3 Construction of simple Regression equation

Regression Equation is an equation that expresses the linear relationship between two variables.

General form of liner Regression Equation, $Y_i = a + bX_i$ (1)

Where, X_i, Y_i represent the criterion and the predictor variable a, b respectively are regression coefficients [36].

Step-1: Determination of Coefficient of Correlation "r".

$$\text{Here, } r = \frac{\sum (x_i - \bar{x})(y_i - \bar{y})}{(n - 1) s_x s_y} \dots\dots\dots(2)$$

Where

\bar{x} = is the mean of dependent variable X

\bar{y} = is the mean of independent variable Y

S_x = is the Standard deviation of dependent variable X =

$$\sqrt{\frac{\sum (X_i - \bar{X})^2}{n - 1}} \dots\dots\dots(2.a)$$

S_y = is the Standard deviation of independent variable Y =

$$\sqrt{\frac{\sum (Y_i - \bar{y})^2}{n - 1}} \dots\dots\dots(2.b)$$

And n= Number of Samples

Step-2: Determination of Y intercept "a"

Here, a = Y intercept = $\bar{y} - b \bar{x}$ (3)

Step-3: Determination of slope of the regression Line "b"

Here, b= Slope of the Regression Line= $r \frac{S_Y}{S_X}$ (4)

Step-4: Finally formation of regression equation.

Results and Discussion

Amorphous region of the cellulose of natural fibers forms hydrogen bonds at 60°C and recrystallize at 150°C. Another issue is that the differences in the thermal expansion coefficient of a-cellulose, hemicellulose, and lignin can cause nonreversible damages and voids that can affect the physical properties of such fiber. For exposure temperatures up to 180°C, both, recrystallization and the differences in thermal expansion coefficient seem not to be significant enough to have a remarkable influence on the tenacity of the investigated untreated jute fiber and tenacity of jute fiber decreases at maximum 15% after an exposure of 120 min. For higher temperatures (above 180°C), a significant decrease in tenacity was measured. It is well known that the fine structure affects the pyrolysis and other thermal characteristics of cellulose and cellulose-based materials, i.e., the thermal stability increases with an increase in molecular weight and crystallinity.

Table 1- Correlation between different Temperature and Exposure Time (40 min) on the Degree of Crystallinity DC (%) of Untreated Jute Fibers

Temperature (°C), X	DC at 40 min, Y
23	68
180	70
200	75
210	81

By using the excel software we find the value of correlation of determination (r) is 0.73 which indicates there is a strong relationship between them. And the regression equation is $Y = -660.7079 + (11.07)*X$.

Table 2- Correlation between different Temperature and Exposure Time (120 min) on the Degree of Crystallinity DC (%) of Untreated Jute Fibers

Temperature (°C)	DC at 120 min
23	68
180	70
200	72
210	71

Again by using the excel software we find the value of correlation of coefficient (r) is 0.91 which indicates there is a strong relationship between them. And the regression equation is $Y = -3144.4857 + (46.94)*X$.

Table 3- Correlation between different Temperature and Exposure Time (40 min) on the Degree of Crystallinity DC (%) of alkali treated Jute Fibers

Temperature (°C)	DC at 40 min
23	65
180	67
200	68
210	70

By the same procedure as before we obtain the value of correlation of coefficient (r) is 0.87 which indicates there is a strong relationship between them. And the regression equation is $Y = -2326.0769 + (36.73)*X$.

Table 4- Correlation between different Temperature and Exposure Time (120 min) on the Degree of Crystallinity DC (%) of alkali treated Jute Fibers

Temperature (°C)	DC at 120 min
23	65
180	64
200	71
210	70

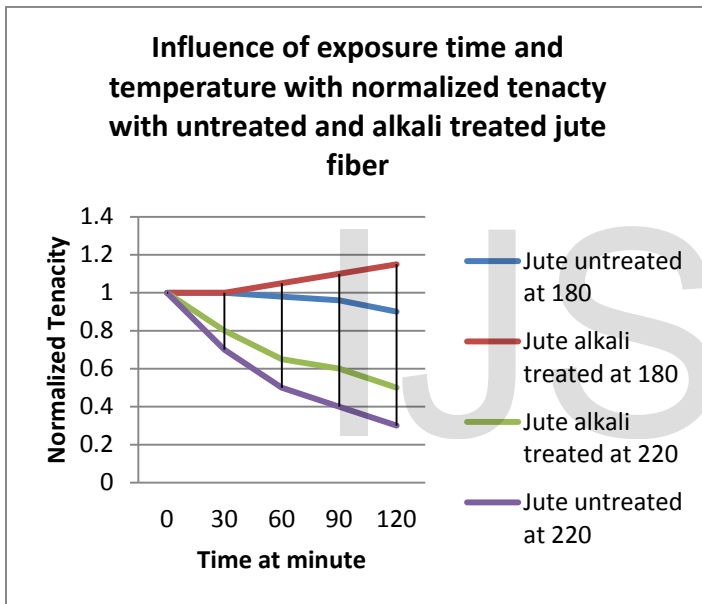
Finally we obtain the value of correlation of coefficient (r) is 0.58 which indicates there is a strong relationship between them. And the regression equation is $Y = -827.32430769 + (14.53)*X$.

A thermal exposure leads to chain scissions and depolymerization, respectively. For higher temperatures (above 180°C), a significant decrease in tenacity was measured. It is well known that the fine structure affects the pyrolysis and other thermal characteristics of cellulose and cellulose-based materials, i.e., the thermal stability increases with an increase in molecular weight and crystallinity.

Starting from a higher tenacity, the drop of the values measured by increasing time or temperature of alkali-treated jute fibers is similar to the results measured for the untreated ones. Confirmed with the published data for linen fibers, a slightly improved thermal stability of jute fibers can be reached due to alkali treatment.

Another reason for decreasing the tenacity is the increase of the number of broken bonds due to chain scissions and depolymerization when exposed to higher temperature. More the temperature and time more the number of broken bonds.

Graphical representation of exposure time and temperature on the normalized tenacity of untreated and alkali-treated jute fibers



Conclusions and recommendation for future research

From the study it can be concluded that below 180°C both fibers shows none or slight decrease in tenacity and increase in degree of crystallinity but significant change occurred over it. Increasing the exposure time also shows same trend. At 220°C and for 120 min, this drop in tenacity was found to be roughly 70%.

In future an extensive research can be done by pairwise comparison among these parameters by using Analytical Hierarchy Process (AHP) and other fuzzy logic and the study can be done by others natural fiber hence understand their thermal and strength related responses.

Disclosure statement

No potential conflict of interest was reported by the authors

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