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Morphological and Thermal Properties of Maize Fiber Composites

Saravana Bavan D.* and Mohan Kumar G.C.

Department of Mechanical Engineering, National Institute of Technology Karnataka, Surathkal, Mangalore-575025, India

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Abstract: Maize stalk has become one of the major sources of fibers from the agricultural residues. Use of these fibers as a reinforcement in the polymer is described in this paper. The present work is focused on establishing the properties such as physical, chemical, morphological structure and thermal properties of maize stalk fiber using different characterization techniques. Simple hand layup method was followed for processing the composite material. Chemical treatments of fibers were carried out to study the interaction of fibers with the matrix. The results revealed that maize fibers can also be used as a traditional fiber as reinforcement in a natural fiber reinforced composite materials.

Keywords: Maize fiber, Thermal properties, Characterization, Composites, Processing

Introduction

Agricultural residue is becoming a major source of fibers in the development of composites in building and packaging industries. Nature has given an immense source of natural fibers to human kind, among them plant fibers or cellulosic or vegetable fibers are dominating in building and packaging. Natural fibers possess a lot of favorable advantages over synthetic fibers in terms of cost, density, bio-degradability, good acoustic and mechanical properties. Natural fibers are classified as plant fibers, animal fibers and mineral fibers. Plant fibers are further divided on the basis of part such as leaf fibers, bast fibers, and seed fibers [1,2]. As petroleum resources are depleting away, there is a need of suitable material alternate to the present man-made fibers and also other fibers such as glass, aramid and carbon fibers [3]. Use of natural fibers in low cost composites will minimize the energy and limited resources of petroleum and also result in biodegradable material.

Maize is a well known crop, in most countries in the world. It had its origin from Mesoamerica and southern Mexico and later spread over America and rest of the world [4]. It is a well known food crop cultivated throughout the world and very well familiar use in Unites States of America, China, Mexico, India, Brazil, France and South Africa [5]. In Indian context, food crops such as maize, sorghum, millet, barley are the chief coarse grain and are grown in any seasons such as in Kharif season or Rabi season, also well grown in variety of soils. But it can perform better on well drained, aerated deep- loams and silt loams containing organic matter and nutrients. Harvesting can be done when the grain moisture reaches 20-25 % and when the cobs-sheath dries up completely. Corn stalks and cobs can also be made into reasonably good fiberboard and particleboard and have applications in ceiling panels, bulletin boards and core materials [6-8].

To have good adhesion between fibers and matrix, the surface of the fibers should be improved. Chemical treatments are used to strengthen the interface between fiber and matrix and to achieve a good bond between natural fibers and the polymeric resin. Various chemical surface treatments can be followed such as alkaline treatment, silane treatment, benzoylation treatment, coupling agents, graft polymerization, permanganate treatment and peroxide treatment [9]. Researcher [10] coated the fibers with novel treatment by using conductive polymers. Polypyrrole composite covered with cellulosic fibers were treated with conductive polymers such as pyrrole and aniline by vapor and liquid phase method and these composites had application in electrically conductive organic polymers. Surface modification of natural fibers by oxygen plasma treatment was studied [11]. The treatment was used to improve the compatibility between jute fibers and polyester. Plasma treatment improves fiber matrix adhesion either by introducing polar or excited groups that form strong covalent bonds between the fiber and the matrix. The natural fiber jute were treated with different plasma reactors and reported that the mechanical properties of the composites improved with increasing plasma power for both radio and low frequency systems. Each method of treatment has its own pros and cons, hence suitability of treatment should be used depending upon the available facility.

The present work is focused on preparing a maize stalk fiber in a polymer based composite material processed by simple hand layup technique and also studying the characterization of maize fibers. Morphological, physical and thermal properties of the fiber were analyzed. Techniques such as Scanning electron microscope (SEM), Differential scanning calorimeter (DSC), Thermo gravimetric analysis (TGA) and X-ray diffraction (XRD) were used to characterize the stalk based maize fibers. The results showed that the maize fiber as a very promising reinforcement material for natural fiber composites. Applications of natural fiber composites can be well suited for bioengineering and environmental engineering applications [12].

*Corresponding author: saranbav@gmail.com

Equivalence of Natural Fiber Composite with Manmade Fiber Composite

Natural fibers have appreciable mechanical and other properties compared to synthetic fibers. The below studies confirms that, natural fibers can be a good competitive material to manmade fibers. Researcher [13] developed a hybrid composite of nano scaled silica with natural rubber and short nylon fiber. The composite material showed good mechanical properties in presence of nano silica and this nano silica had improved thermal stability than that of commercial and nylon fiber and also improved the thermal properties of rubber fiber composite. Researcher [14] carried work in manmade fibers of polypropylene with hydrophobic silica composite fibers and concluded that the thermal stability of polypropylene fibers could be improved with hydrophobic silica in comparison with hydrophilic silica. Natural zeolite as filler in polypropylene composite and optimizing them was studied [15] and addition of coupling agents resulted in increasing the mechanical properties of the composite material. Several mechanical tests were carried out for treated and untreated composite material and the results were correlated to the theoretical basis. Natural fiber composite material of polypropylene matrix reinforced with natural fibers and short glass fibers were studied [16] and the results were related to the theoretical predictions. Statistical approach to evaluate and predicting the properties of natural fiber reinforced composites were formulated and the model was applied to different composites and the results showed that the theoretical values were closed to the experimental values. Study of natural cellulosic materials as nano composites were carried out by several researchers [17,18] and proved that have great potential in nano composites field [19]. Researcher [20] worked on using clay and silica particles in glass epoxy composite material and the mechanical properties of the fiber reinforced composite indicated advancement with the inclusion of nano particles. Polymer nano composites with organo clay and orientation with polymer matrix were studied [21] and these nano composites have several advantages over traditional polymer composites and they are of great interest in all fields because of their favorable properties.

Experimental

Materials

Maize stalk residues were obtained from a local farm; they were thoroughly cleaned with running water and sun-dried in an open atmosphere for a few days. The raw fibers were chemically treated, initially with alkaline and later with the acetylated method. Chemical treatments were carried in order to increase the affinity between fibers and the matrix, and also to reduce the water absorptivity. Further, these fibers were cleaned thoroughly in distilled water and the fibers were kept in an oven to remove the moisture and then used for the work. Commercially available general purpose unsaturated polymeric resin (thermo set polymer), Methyl Ketone Peroxide (MEKP) as a catalyst and Cobalt Octoate as a promoter was used.

Processing of Natural Fiber Composite Material

Simple hand layup method with the natural fibers arranged in a unidirectional manner was practiced for processing the composite material and suitable release agent was applied to the open mold. Chemically treated maize stalk fibers are kept in an oven at 60 ^{o}C for 12 hours and then used for the work. Thermoset polymer of general purpose unsaturated polymeric resin with Methyl ketone peroxide (MEKP) as a catalyst and cobalt octoate as a promoter were used with a ratio of 1:0.5. Stalk fibers of length 60 mm, width of 4 mm and thickness of 1.0 mm were used to prepare the composite material. Finally the properties of raw fibers and chemically treated fibers were analyzed using different techniques as described above.

Properties of Maize Stalk Fiber

Physical Properties of Maize Stalk Fiber

All maize stalk fiber samples were selected at the bottom and mid portion of the plant. The fibers extracted by removing soft pith manually and checked that they are not rotted by any bacterial/fungal diseases. Healthy stalk fibers of sufficient length, width and thickness were selected and examined for morphological and thermal properties. Maize stalks, like other agricultural fiber sources, consist of a pithy core with an outer layer of long fibers. The physical property of maize natural fiber is shown in Table 1. From various research studies [22] shows that the fiber has the characteristics of smaller crystal size, lower percent crystallinity, and lower orientation. Maize fibers are expected to have less strength but are anticipated to be superior in other properties like durability, pliability, and elongation [23].

Pyrolysis oil, produced by fast pyrolysis of maize stalk was investigated by researcher [24] and determined the elemental analysis of pyrolysis oil using standard ASTM methods, the results of various element compositions in terms of weight percentage are determined as shown in the Table 2. Proximate analysis of maize stalk was also investigated by the same researcher using standard ASTM

Table 1. Physical properties of maize natural fibers

Fiber	Fiber length (mm)	Fiber width (μm)	Lumen width (μm)	Cell wall thickness (μm)	References
Maize stalk	1.32	24.3	10.7	6.8	[22]

Table 2. Elemental analysis of maize stalk

Fiber	Carbon (wt. %)	Hydrogen (wt. %)	Oxygen (wt. %)	Nitrogen (wt. %)	Sulphur (wt. %)	References
Maize stalk	49.1	6.1	43.7	0.7	0.11	[24]
	44.2	5.8	43.5	1.3	<0.01	[25]

Table 3. Proximate analysis of maize stalk

Material	Moisture (wt. %)	Ash (wt. %)	Volatile Matter (wt. %)	Fixed Carbon (wt. %)	Lower Heating Value (MJ/kg)	Higher heating Value	References
Maize stalk	7.67	8.33	71.95	12.05	15.07	-	[24]
	8.42	5.25	70.31	16.03	12,905 (kJ/kg)	14,357 (kJ/kg)	[25]

method, in which the weight fractions of moisture, ash, and volatile content, fixed carbon contents and heat value are determined as shown in Table 3 [24,25]. The elemental composition and oxygen-carbon atomic ratio of maize stalk fiber was characterized [26] and expressed that maize stalk can be a good reinforcement material for composites.

Chemical Properties of Maize Stalk Fiber

The most familiar, economically and the older method is the alkaline treatment leading to surface cleaning by partially removing secondary and tertiary constituents such as hemicelluloses and lignin [27]. First the raw fibers were treated with alkaline method using 5 % of NaOH for 6-8 hours, washed with distilled water. Later the alkaline treated fiber were soaked in glacial acetic acid, poured out and later soaked in acetic anhydride with few drops of concentrated sulphuric acid (H_2SO_4).

First treatment: Alkali treatment (Mercerization) improves the fiber-matrix adhesion and also causes to break down the fiber bundles in to smaller fibers. It removes some of the constituents such as hemicelluloses, lignins and wax. Modification leads to disruption of hydrogen bonding in the polymer structure and increasing the roughness of the surface leading to better mechanical properties [28,29]. Second treatment: Acetylation identifies having an acetyl functional group in to an organic compound involving the generation of acetic acid as by product and must be removed from the lingo cellulosic material before using the fiber. Alkaline treated fibers were soaked in glacial acetic acid for one hour at room temperature, decanted and again soaked in acetic anhydride containing 1-2 drops of concentrated sulphuric acid (H_2SO_4) for 4-6 minutes, later washed in distilled water and dried in an oven for 40 ^oC for 24 hours [9,28]. Chemical composition of the maize fibers shows that the cellulose content in the fiber are rich when compared to other constituents as shown in Table 4 and Table 5 shows the chemical analysis of corn stalk based on dry matter basis.

Thermal Properties of Maize Stalk Fiber

It is useful to determine the thermal stability and thermal degradation of the materials. Additionally, it permits to quantify the amount of possibly damaging, deteriorating volatiles, such as the moisture uptake during a hydrothermal treatment, which can cause deterioration in the composites. The thermal stability of the natural fibres can be influenced by some fibre surface treatments [34,35]. The thermal properties of maize stalk fiber were studied by using Differential Scanning Calorimeter (DSC) and Thermal Gravimetric Analysis (TGA).

Differential Scanning Calorimeter (DSC)

Differential Scanning Calorimeter measures the temperature and heat flow associated with phase transitions in substances as a function of time and temperature and such measurements provide important information about physical and chemical changes that involve endothermic or exothermic effects, or heat capacity changes. DSC is primarily used to characterize polymers and other organic materials, but it is also applicable for testing some inorganic materials.

Table 4. Chemical composition of maize stalk fibers

Fiber	Cellulose (%)	Lignin (%)	Hemicellulose (%)	Pentosans (%)	Ash (%)	References
Maize stalk	38-42	10-13	21-23	-	-	[8]
	38-40	7-21	28	-	3.6-7.0	[30-32]
	40.28	19.35	-	35.06	-	[33]

Table 5. Chemical anlaysis of corn stalk (dry matter basis)

Fiber	C:N Ratio	Carbon (%)	Nitrogen (%)	P_2O_5 (%)	K_2O (%)	CaO (%)	MgO (%)	References
Maize stalk	68	55	0.81	0.37	1.61	0.35	0.48	[24]

Thermal Gravimetric Analysis (TGA)

Thermo gravimetric analysis was conducted to know the degradation characteristics of raw maize fiber and composites. It was determined using TGA series thermo gravimetric analyzer (TA Instrument, USA) and studied as a function of % weight loss with the increase in temperature. Thermo Gravimetric (TG) curves and Derivative Thermo Gravimetric (DTG) curves of the fibers were obtained by heating the samples under a Nitrogen atmosphere at a heating rate of 10 ºC/min. Results indicate that the presence of cellulose fibers affects the degradation process of the composites.

SEM Analysis of Maize Stalk Fiber Composite

Morphological analysis of raw maize stalk fiber and alkali treated maize fiber with unsaturated polymeric resin was carried out by studying Scanning Electron Microscope (SEM) micrographs. Natural Fiber samples were coated with gold using a vacuum sputter coater and placed in for analyzing. The morphology changes were analyzed and observed using Jeol JSM-5600 LV electron microscopy with an accelerating voltage of 15 kV. The changes are important to predict fibre interaction with the polymer matrix in composites. The SEM micrographs of the resin and composites show a clear cut difference in the morphology of the resin and the composite.

XRD Analysis of Maize Stalk Fiber Composite

Maize stalk fibers and its crystalline structural characteristics were observed by X-ray diffraction. X-ray diffractogram studies were carried out using JEOL JSM-2550PC diffractometer using Beryllium-filtered Cu-Kα radiation of wavelength 0.1542 nm. The X-ray unit was operated at 40 kV and 20 Ma. Angular scanning was conducted from 5° to 50° at 1°/min and data were collected using 2 step scan mode with angular intervals of 0.05°. Crystallinity Index measures the orientation of the cellulose crystals with respect to the fiber axis. Crystalline and amorphous region was observed at closely at 30° and 23° respectively. Percent Crystallinity and Crystallinity Index (C.I) can be calculated as follows [36] and are tabulated as shown in Table 6.

$$Cr(\%) = \frac{I_C}{I_C + I_A} \times 100$$

Table 6. Percent crystallinity and crystallinity index for maize stalk fibers

Maize stalk fiber	2θ(degree)		Crystallinity (%)	C.I
	I_C	I_A		
Raw	29.46°	22.58°	56.71	0.044
Alkali treated	29.28°	22.44°	56.61	0.233
Chemically treated with unsaturated polymer	28.12°	20.36°	58.00	0.275

$$\text{C.I} = \frac{I_C - I_A}{I_c}$$

Where I_C represents the Intensity diffraction of crystalline region and I_A represents the Intensity diffraction of amorphous region.

Results and Discussions

Fiber-Matrix Interface

The required and important factor is the fiber matrix interface as a good bonding essential if the stresses are to be adequately transferred to the reinforcement and providing a true reinforcing functions. If the interfacial adhesion breaks down, it allows various toughening mechanisms to become operative. These mechanisms include crack blunting, frictional sliding and debonding fibre fragments within the matrix and fibre fracture. As natural fibers are hydrophilic, they are

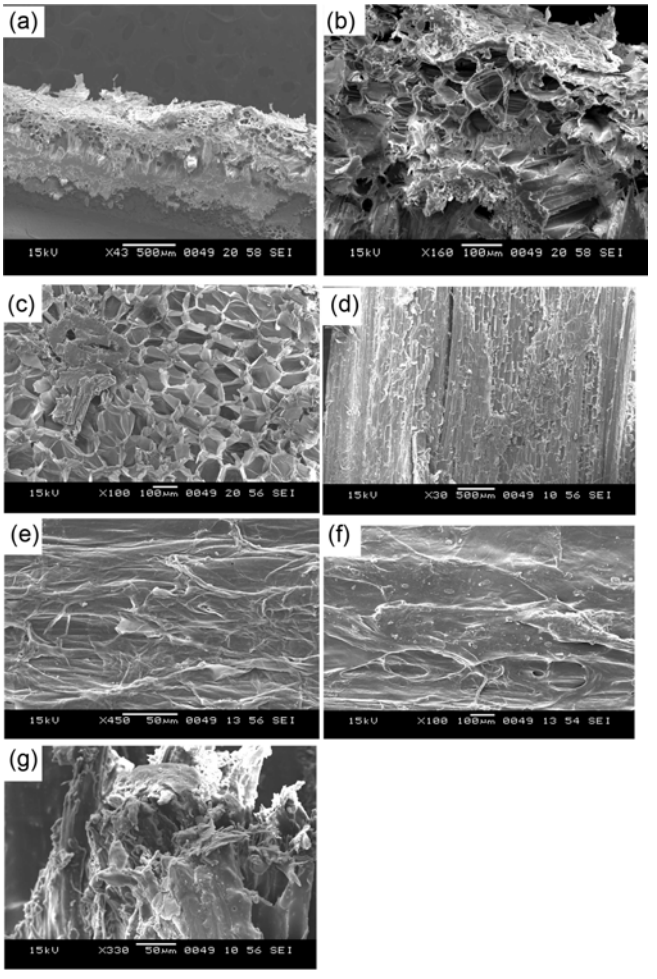

Figure 1. SEM micrographs of maize stalk fiber; (a) cross section of raw maize fiber with cortex, (b) cross section of raw maize fiber, (c) cross section of maize stalk pith fiber, (d) surface of raw straw fiber, (e) alkaline treated fiber, (f) acetylene treated fiber, and (g) chemically treated fiber with polymeric resin.

allowed to go for some chemical treatment analysis such as alkali treatment or acetylation treatment and make the composite fiber material to become hydrophobic material.

Morphology of Maize Fiber Composites

The SEM micrographs of the samples reveal the information about the morphology of the fiber and its respective polymeric resin. These micrographs clearly show the difference between reinforced matrix and one which is not reinforced. Figure 1(a), (b) reveals the cross section of raw maize fiber. It has a thick layer of protective material and cellular deposits and also presence of other constituents such as lumen (inner most part of the fiber) in increasing the absorbency of the fibers. During fiber extraction, most of the non-cellulosic substances are removed but the vascular fiber bundles are retained. An interesting feature of the fiber cells in cornstalk is the presence of a large lumen as shown in Figure 1(c), larger than the width of the cell wall in most cells, reducing the density of the fibers. Surface of raw straw fiber is shown in Figure 1(d). Chemical treatment of alkali and acetylation treatment are shown in Figure 1(e), (f) it shows that the surface morphology of the natural fiber changes with respect to the chemicals and also the crystalline structure of cellulose. The changes that expected in the chemical treatment were the diameter of the natural fibers that were reduced and the hemicellulose and lignin constituents were partly removed resulting in good surface area and better adhesion between fibers and the matrix. Figure 1(g) shows the natural fiber and matrix are well blended thus producing good interfacial adhesion in the composites.

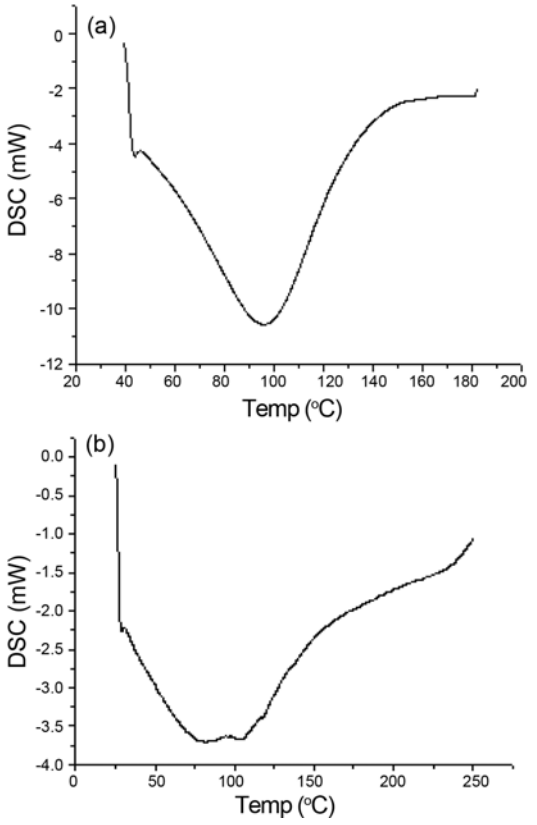

Figure 2. DSC thermographs of maize fiber and with polymeric resin; (a) raw maize stalk fiber and (b) alkali treated fiber with unsaturated polymeric resin.

Thermal Analysis of Maize Fiber Composites

Displayed in the Figure 2(a), (b) are the DSC results obtained by heating the specimen of raw fiber and fiber treated with chemicals at a constant heating rate of 10 °C/min. The plot shows the heat flow as a function of the sample temperature. The Samples having size of 6±3 mg were heated at a constant rate of 10 °C/min between temperature ranges of 20 °C to 270 °C and then cooled with nitrogen to 40 °C at a cooling rate of 10 °C min^{-1} with a flow rate of 30 m*l*/min. For raw fiber, the glass transition event T_g is observed at 43 °C as an endothermic stepwise decrease in the heat flow or heat capacity and a broad endothermic peak at 97 °C. For alkali treated fiber, the glass transition

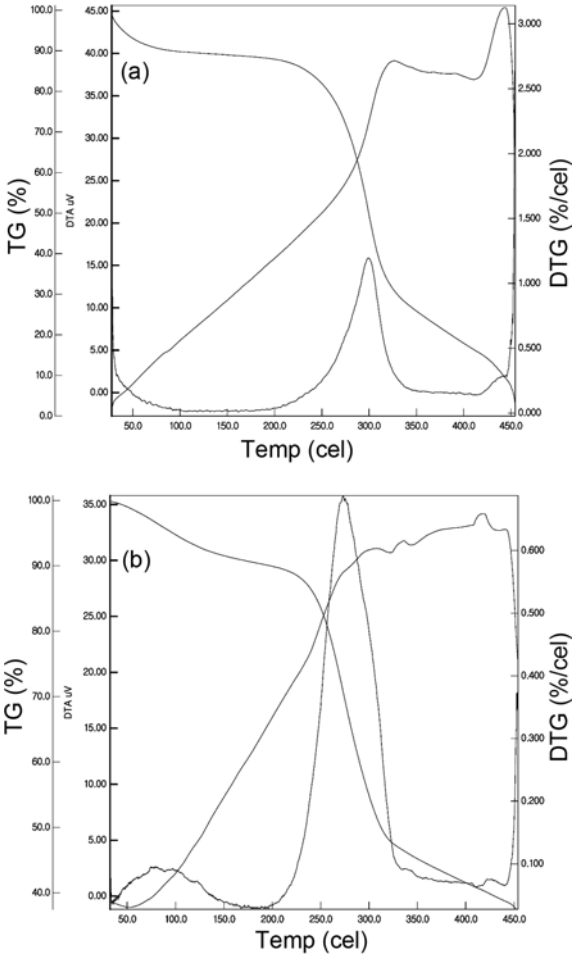

Figure 3. TGA thermographs of maize fiber; (a) raw stalk maize fiber and (b) alkaline treated maize stalk fiber.

Table 7. Weight loss (%) in TGA analysis for maize fibers

Maize fiber	Stages of degradation	Decomposition temperature	Weight loss (%)	Maximum temp (°)
Raw fiber	I-Stage	211-334 °	47.6	278 °
	II-Stage	334-434 °	13.4	
Alkaline treated fiber	I-Stage	221-340 °	41.8	284 °
	II-Stage	340-444 °	11.1	

temperature was observed at 27 °C and a sharp endothermic peak at 104 °C and the fiber is stable up to 240 °C. With a further increase in the sample temperature, the resin eventually undergoes curing and thus it can be observed as exothermic peak.

The thermal degradation of natural fiber studies are further supported by Differential Thermal Analysis (DTA) and the results are shown in Figure 3(a), (b). TGA curve shows two stages of decomposition, initial stage can be due to the decomposition of cellulose and hemicellulose segments and the later stage due to the degradation of lignin and other alkali segments on the fiber surface. TGA curve for raw fiber as shown in Figure 3(a), the initial and final decomposition temperatures are 211 °C and 434 °C respectively. TG/DTG curves of maize fiber (alkali treated) is shown in Figure 3(b), confirms the increase of thermal stability of the fibers, initial and final decomposition occurred at 227 °C and 444 °C. The DTGA curves show a single peak at 272 °C may be due to decomposition of some flexible segments. Final thermal degradation has occurred at nearly 400-440 °C and also much of the heat is taken by the matrix (unsaturated polymer resin) and lesser heat to the natural fiber and weight loss (%) is shown in Table 7.

XRD Analysis of Maize Fiber Composites

The X-Ray Diffraction (XRD) analysis determined the crystallinity of the maize fiber and was used to indicate the dramatic change in the crystallinity of the maize fiber. All the fiber samples were scanned in 2θ range varying from 10 ° to 50 °. The observed X-ray diffraction peaks for the above materials can be attributed to crystallinity scattering and the diffuse background to disordered regions. The spectrum corresponding to maize raw fibers shows the diffraction peaks of amorphous region and crystalline region at the following 2θ angles at 22.58 ° and a high peak nearly at 29.46 ° as shown in Figure 4. For alkali treated fibers, same peaks can be observed at 22.44 ° and 29.28 °. Similarly for the chemically treated fiber with unsaturated polymeric resin, the crystalline region peak at 28.12 ° and amorphous region at 20.36 ° was observed. The position of the peak indicates an increase of inter planar distance in relation to fibre treated. This occurs due to generation of disorder when fibre is treated. The patterns for the above materials are similar; however non-treated/raw fiber is more crystalline than the treated fibre.

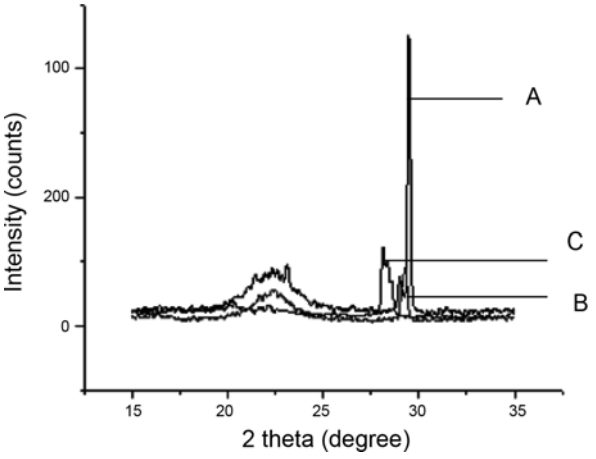

Figure 4. XRD of maize stalk fiber and with polymeric resin; (A) raw maize fiber, (B) alkaline treated fiber, and (C) chemically treated polymeric resin fiber.

Conclusion

Natural fibers can be a worthy substitute material for the existing manmade fibers, in a composite material. It has the potential ability to be used in exterior applications such as in automobiles and structural field. Maize stalk fibers are appreciable fibers because they have good morphological features with favorable excellent thermal degradation properties that can withstand the polymer environment. Thermal stability of the fibers was improved in comparison to raw maize fibers and the fiber size was increased. Characterization studies show that it can be a good reinforcement fiber material to composites and it can be well used if the fibers were treated with enough additional chemical treatments, thereby the adhesion between the fibers and the matrix are improved. Stiffness and glass transition properties of the treated fibers are better compared to untreated raw maize stalk fiber.

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