Effects of Reinforcement of Sugarcane Fiber and Wheat Straw Fiber on Flexural and Dynamic Mechanical Properties of Corn Starch Biocomposites

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***Abstract**: The aim of this research work is to investigate the effect of reinforcement of sugarcane fiber and wheat straw fiber on the properties of corn starch biocomposite. The test outcome of flexural and dynamic mechanical properties conducted on seven samples of corn starch matrix with the different amount (0 gm, 5 gm, 10 gm, and 15 gm) of sugarcane fibers and wheat straw fibers. Flexural properties increased with fiber addition up to 10 gm then decreased with the further addition of fibers in both types of biocomposite systems. Storage modulus or degree of stiffness decreased with increasing temperature. Value of storage modulus dropped less in reinforced biocomposite as compared to pure matrix biocomposite. The value of loss modulus initially increased with temperature and reached highest point then decrease with increasing temperature. The loss modulus of pure corn starch matrix biocomposite has maximum value 97.87 MPa as compared to sugarcane fiber biocomposites 62.6 MPa and wheat straw fiber biocomposites 51.32 MPa. The value of tanδ or loss factor or damping factor increase with increasing temperature. The peak value of tanδ gives glass transition temperature. The T_g shifted from 55.3^{0}C to 108.7^{0}C, 120.1^{0}C and 134.2^{0}C for 5 gm, 10 gm, and 15 gm sugarcane fiber reinforced biocomposites respectively and from 55.3^{0}C to 116.9^{0}C, 119.8^{0}C and 135.9^{0}C for 5 gm, 10 gm and 15 gm wheat straw fiber reinforced biocomposites respectively.*

Keywords: Starch based biocomposite, flexural strength, tanδ, glass transition temperature, loss modulus, storage modulus, sugarcane fiber, wheat straw fiber, flexural modulus.

1. Introduction

Growing environmental concern and present depletion of conventional energy sources are forcing towards the development of new biodegradable materials which pollute the environment less at low cost [1].

Bio-composite is a composite material which can be achieved by adding two or more constituents at a nanoscopic or microscopic level and insoluble in each other. One constituent is called matrix (natural polymer) and other is called reinforcement (natural fiber). Some other additives also used like pigments, plasticizers, heat and light stabilizer to obtain certain properties. Biocomposite divided into two parts non-wood fiber biocomposite and wood fiber biocomposite. Non- wood fiber biocomposites are more applicable in industries due to its physical and mechanical properties and relatively long fiber present as compared to wood fiber biocomposites. The biocomposite has low density, high modulus, high tensile strength and stiffness [2]. The thermoplastic starch based biocomposite has more storage modulus, high glass transition temperature, and less water uptake capacity.

1.1 Components of bio-composite material

Biocomposite is the element which consists of two or more than two elements in the form of continuous and discontinuous phase that are mixed together to produce a different material which shows increase properties that are different and better to the properties of individual elements. Generally, biocomposites embodied of matrix and reinforcement, unified to increase the strength and the stiffness of the matrix. Matrix exists in the continuous phase and reinforcement or filler exist in the discontinuous phase. Matrix based biocomposites are softer than reinforcement based biocomposites. Particulars such as bagasse, bamboo, cotton, hemp, jute, wheat straw, garlic stalk, cassava bagasse, rice straw etc are used as filler or reinforcement. Properties and characteristics of biocomposite increased after addition of particulars [1-3]. The bond between the fiber and matrix play important role in structure design.

1.1.1 Matrix

It is the constituent of biocomposite exist in the continuous phase in which reinforcing phase materials embedded is called the matrix. Matrix or continuous phase formed by the biodegradable polymer which is derived from renewable or nonrenewable sources.
The main objectives of the matrix in composites:

- Locate the fiber in proper place
- Protect the fiber from mechanical damage
- Hold the fiber together transfer the load on it
- Protect the fiber from environmental degradation damage

1.1.1.1 Starch

Starch is a low cost biodegradable polymeric carbohydrate. It contains a number of glucose units joined by the glycosidic bond. The chemical formula of starch is $(C_6H_{10}O_5)_n$ and it is responsible for the development of seeds and leaf tissue. This is produced from green plant and act as energy storage. It is easily available in human food and exists in a large amount of maize, wheat, potatoes, rice, and cassava. Starch is actually composed of two types of molecules Amylopectin molecule and Amylose molecule. Both molecules contain α-D glucose units. Amylopectin molecule exists with the branch molecular arrangement while Amylose exists with the helical and linear molecular arrangement. Starch contains approximately 25 wt% Amylose molecules and 75 wt% Amylopectin molecule (F. Xie et al., [4]).
The selection of matrix depends on required properties of composites. There are:-

- Moisture uptake should be low which prevent swelling, dissolve and crack.
- Glass transition should be more which give better dimensional stability.
- Tensile modulus should be more which affect the compressive strength.
- Tensile strength should be more which resist cracking.
- Fracture toughness should be more which control crack growth.

1.1.2 Reinforcement

In biocomposite, the purpose of reinforcement is to increase the properties of pure polymer structure. The properties of the biocomposite depend on the fiber used because all fibers have different properties.

1.1.2.1 Natural fiber

Natural fiber is a very thin hair like material that is obtainable from plants, animals, and mineral sources. It can be used as filler in composite materials where properties depend on the amount of fiber. Properties of fiber depending on the length of the fiber, an age of the fiber, and relative location of the fiber. Natural fiber shows excellent mechanical properties like stiffness, flexibility, and modulus as compared to artificial fiber. In natural fibers, cellulose is an important structural component and it found in large amount on the earth in form of an organic polymer. The quantity of cellulose depends on fiber to fiber. Hemicellulose is a mixture of polysaccharides and found in the cell wall of the plant. The quantity of hemicellulose also depends on fiber to fiber. Lignin is a very complex organic polymer that creates a structure inside a support tissue. It also plays important role in the formation of cell walls.

1.1.3 Additive

A substance used in small quantity to something else to enhance strength or alter it. It is used as pigments, plasticizers, heat and light stabilizer to obtain certain properties.

1.1.3.1 Glycerol

Glycerol also called glycerin or. It is a trihydric alcohol, odorless, colorless, and sweet in taste liquid. It found in nature in the form of ester in all vegetable fats and oils and animals. It can be produced in by-product form by hydrolysis of oils and fats. Due to the strong polar interaction between –OH groups of glycerol and starch it is widely used as a plasticizer for making biocomposites. Generally smaller size of plasticizer is used due to easy penetration and stronger interaction with nano clay [4-6].

2. Experimental

2.1 Materials

The corn starch and glycerol used for this research work ware purchased from the market of Jaipur. The sugarcane bagasse collected from juice seller and wheat straw fiber collected from the farmer.

2.2 Methods

2.2.1 Preparation of biocomposites

First sugarcane bagasse and wheat straw received were washed from the water to remove the impurities and kept in direct sunlight for 10-15 days. When sugarcane bagasse and wheat straw ware dried then grind it to obtain the desired length of the fiber. The sugarcane fiber and wheat straw fiber biocomposites samples were prepared by hand lay method. Make seven compositions as S0 (100 gm corn starch and 0 gm fiber), SS1 (95 gm corn and 5 gm sugarcane fiber), SS2 (90 gm corn starch and 10 gm sugarcane fiber), SS3 (85 gm corn starch and 15 gm sugarcane fiber), SW1 (95 gm corn starch and 5 gm wheat straw fiber), SW2 (90 gm corn starch and 10 gm wheat straw fiber), and SW3 (85 gm corn starch and 15 gm wheat straw fiber). Each composition mixed with 10 gm glycerol in a vessel until to obtain the homogeneous mixture. 500ml water mixed in the homogeneous mixture and kept on the heater at low temperature for 15-20 minutes. When the mixture was viscous in nature then add a fixed amount of fiber and continue to heat for next 15-20 minutes. The amounts of sugarcane fiber and wheat straw fibers used to prepare the biocomposites were 5, 10, 15 wt% of corn starch for each. These hot composites mixtures were transferred to glass mould of 220 mm x 200 mm x 5 mm size to obtain biocomposites plates.

2.2.2 Flexural Test

Flexural test performed on corn starch biocomposites with filler (sugarcane fiber and wheat straw fiber) and without filler with help of computerized Instron 5967 UTM by three point bending fixture with a load cell of 30 kN at room temperature. The dimensions of the samples were cut as per ASTM D 790 into strips of 100 mm x 15 mm and thickness measured along its length with the digital micrometer. The span length taken as 60 mm and the crosshead speed of the tensile load was 1 mm/min [6]. The value of flexural strength, flexural modulus of samples were calculated and recorded as the average value of three measurements of each type [7-11,].

2.2.3 Dynamic mechanical analysis (DMA)

The dynamic mechanical analysis or viscoelastic measurements of the composites were measured in Perkin Elmer 8000, Dynamic Mechanical Analyzer instrument in the tensile mode where samples were clamped at both ends. The sinusoidal deformation was applied at a fixed frequency of 1 Hz, heating rate of 2^0C/min, temperature range from room temperature to 140^0C on rectangular samples with approximate dimensions of 25 mm x 9 mm and thickness varied from 1 mm to 2 mm which were measured before each experiment. The Dynamic mechanical analyzer is a function of stress, frequency, time, atmosphere temperature, or combination of these parameters. The value of loss modulus, storage modulus and tan delta as a function of temperature were obtained. The temperature where the maximum value of tanδ obtained gives the value of relaxation temperature and this relaxation temperature gives the value of glass transition temperature [12].

3. Result

3.1 Flexural test

Fig. 3.1 and Fig. 3.2 show that effect of fiber addition on flexural properties of sugarcane fiber and wheat straw fiber reinforced biocomposites. It is observed that flexural strength and flexural modulus increased with fiber addition into pure corn starch matrix [6,7,13]. The flexural strength and modulus showed increasing trend with fiber loading up to 10 gm then decreased with 15 gm fiber loading. Flexural strength decreases at 15 gm fiber addition probably due to the weak interfacial attraction between fiber and matrix, agglomeration of fiber and small aspect ratio leading to ineffective stress transfer between matrix and fiber [10,11,14].

Regarding sugarcane fiber biocomposites, the flexural strength and flexural modulus of SS1, SS2 and SS3 are approximately 3, 5 and 4.5 times more than flexural strength of S0. Similarly, for wheat straw fiber, the flexural strengths of SW1, SW2 and SW3 are 2.5, 4.3 and 2.6 times more than flexural strength of S0 and the flexural modulus are 2, 4 and 1.5 times more than flexural modulus of S0.

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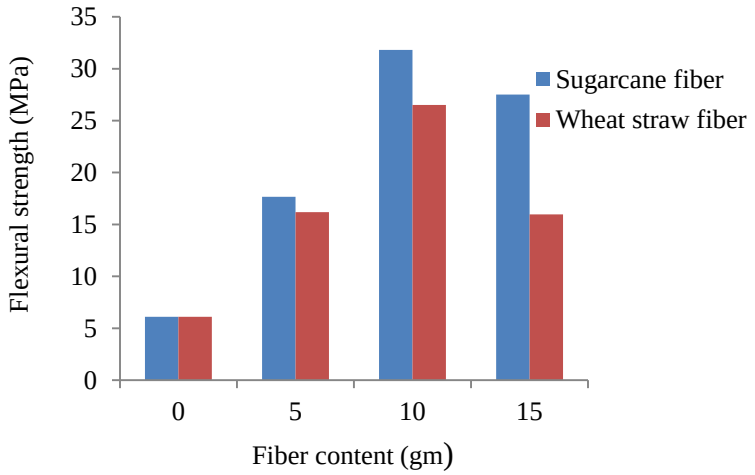

Fig. 3.1: Flexural strength of sugarcane fiber and wheat straw fiber biocomposites

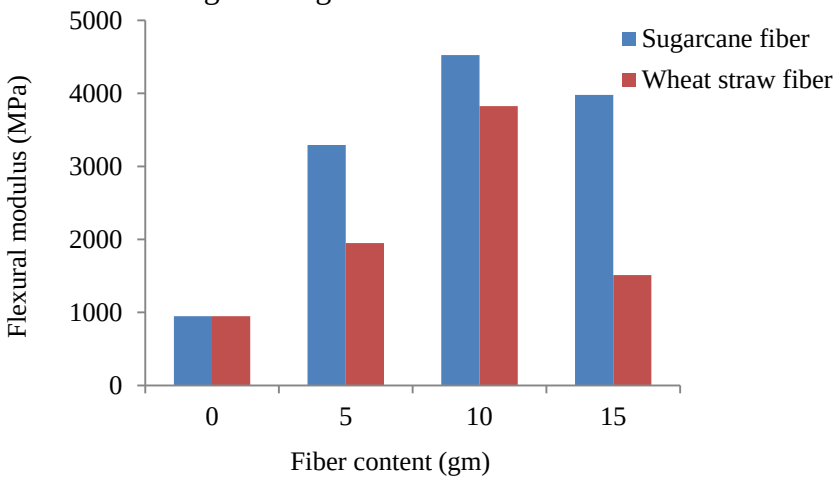

Fig. 3.2: Flexural modulus of sugarcane fiber and wheat straw fiber biocomposites

The crack during flexural test always occurs on the tension side of biocomposites and slowly moves in the upward direction. Flexural modulus depends on matrix properties and fiber matrix interaction, so surface modification has more effect on flexural modulus than strength. The flexural strength depends on water content, fiber content and lignin content. The fraction of the specimen caused by separation between resin and fibers.

3.2 Dynamic mechanical analysis (DMA)

The effect of the addition of sugarcane fiber and wheat straw fiber on the thermo-mechanical property of pure corn starch and its reinforced biocomposites were determined by using dynamic mechanical analysis with frequency 1 Hz from room temperature to 140^0C. This analysis gives visco-elastic response of thermo plastic starch composite and its reinforced biocomposites in a wide range of temperature [15,16]. It provides information at the molecular level [16]. The dynamic mechanical analysis also gives a relation of relaxation mechanism with the composition and microstructure of the composites.

Table 3.1 shows the relation between storage modulus (E') as a function of temperature for pure corn starch biocomposite and its reinforced biocomposites with different amount of sugarcane fiber and wheat straw fiber biocomposites. Storage modulus or degree of stiffness decreased with increasing temperature [15-19]. Storage modulus drop occurs less in reinforced biocomposites

when compared to pure starch biocomposite, which shows improvement in thermo mechanical properties. The addition of 10 gm sugarcane fiber biocomposite has the highest storage modulus (679.9 MPa) at room temperature while 15 gm wheat straw fiber biocomposite has the maximum storage modulus (719.04 MPa) at room temperature and highest storage modulus over an entire temperature range. At low temperature the biocomposite is in glassy state and its storage modulus increased with increasing fiber content as compared to pure corn starch biocomposite [16,17,19-21] probably due to interaction probability between starch and fibers, high stiffness behavior if fiber and density of biocomposites. At room temperature the storage modulus decreased speedily which reveals the main relaxation transition when relaxation transition completed the storage modulus tends to be stable.

Table 3.1 shows that storage modulus increase with increasing fiber content. At 5 gm and 15 gm fiber addition, the storage modulus of wheat straw fiber composite is maximum while at 10 gm fiber addition the storage modulus of sugarcane fiber composite shows maximum value probably due to the homogeneous distribution of fiber and better interaction between fiber and matrix.

Table 3.1 also shows a relation between loss modulus (E") and temperature of sugarcane fiber and wheat straw fiber biocomposites. Loss modulus increased with increasing temperature and reached at the highest point where maximum mechanical energy dissipation takes place then decreased with increasing temperature. According to J. O. Akindoyo et al., [22] loss modulus decreased with increasing temperature because of the mobility of polymer chain increase as temperature increase. The loss modulus of pure corn starch matrix biocomposite has maximum value 97.87MPa as compared to sugarcane fiber biocomposites 62.6 MPa and wheat straw fiber biocomposites 51.32 MPa. Loss modulus peak shift towards high temperature region with fiber addition. The peak of the loss modulus shows maximum energy dissipation so lower energy dissipation is an indication of the strong interface. There is a close relationship between loss modulus and interfacial adhesion [22]. Loss modulus is an indication of energy dissipation in the form of heat (the measure of vibrational energy that has been converted during vibration) [23] by the system during deformation cycle due to viscous motion inside the biocomposites itself. The rise in loss modulus in the biocomposites system indicates an increase in polymer chain movement due to relaxation process that allows movement along the chain (A. Jabbar et al., [24]).

Fig. 3.3 and fig. 3.4 shows a relation between tanδ (loss factor or damping modulus) and temperature range (from room temperature to 140^0C) of sugarcane fiber system and wheat straw fiber system respectively. Both figures represent that value of tanδ increase with increasing temperature [16,18]. For the determination of tanδ, two relaxation transition region exists for starch/fiber system [12,17,18]. The upper transition region is called the main α-relaxation associated with the glass transition of starch rich region whereas lower transition region is called the second transition of glycerol rich region [12,21,25]. Lower transition temperature exists below ambient temperature. Main α-transition temperature is very important because it is associated with thermo-mechanical properties of biocomposites and the height of the glass transition temperature shows the degree of crystallinity. The glass transition temperature (T_g) can be measured from the peak value of tanδ [15-17] and T_g is the temperature where chain mobility prevented due to molecular cohesion [17].

Figures shows that the addition of fibers (sugarcane fiber and wheat straw fiber) in starch matrix resulted upper relaxation temperature shifted towards high temperature and magnitude decreased of the main α-relaxation process of the starch rich region[12,16,18,19] probably due to decrease of the molecular mobility at glass transition temperature (T_g) and mechanical coupling effect.

The increment in tanδ with temperature indicated that the biocomposites were becoming more viscous in nature [17,20].

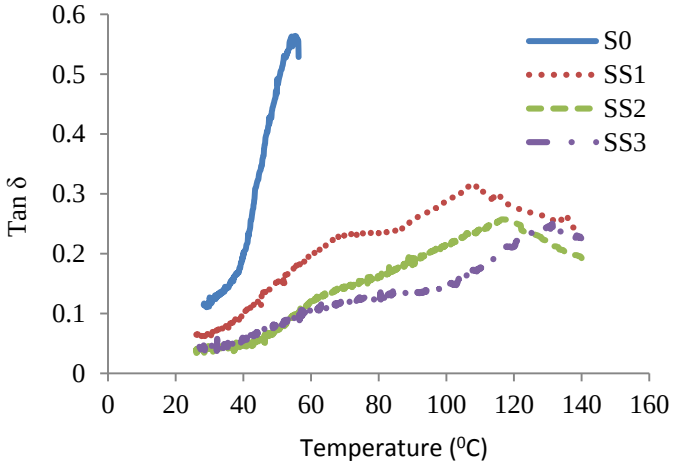

Fig. 3.3: Graphical representation of Tanδ as a function of temperature for sugarcane fiber biocomposites

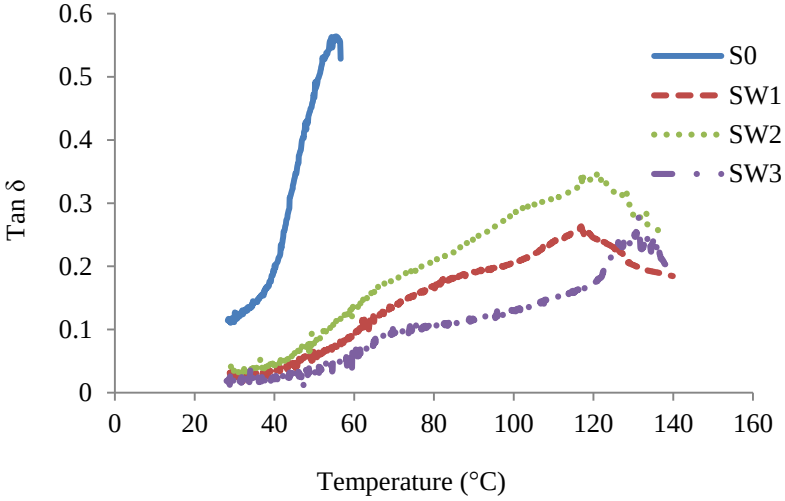

Fig. 3.4: Graphical representation of Tanδ as a function of temperature for sugarcane fiber biocomposites

Table 3.1 also shows that the main α-relaxation temperature was shifted from 55.3^{0}C to 108.7^{0}C, 120.1^{0}C and 134.2^{0}C for 5 gm, 10 gm, and 15 gm sugarcane fiber reinforced biocomposite respectively and from 55.3^{0}C to 116.9^{0}C, 119.8^{0}C and 135.9^{0}C for 5 gm, 10 gm, and 15 gm wheat straw fiber reinforced biocomposites respectively. The movement of T_g indicates the fibers were able to affect the segmental motion or flexibility of the biocomposites [16,17,19]. The temperature shift also indicated the improvement in thermal stability and strong interfacial interaction between matrix and fibers. The maximum value of T_g shown by 15 gm fiber reinforced system while 5 gm sugarcane fiber reinforced biocomposite and 10 gm wheat straw fiber reinforced biocomposite shows the maximum value of tanδ.

The semicrystaline composite material shows more complicated DMA graphs because of additional melting transition and a considerable broadening of glass transition. For pure matrix biocomposite, there is a peak at 55.3^{0}C, which is the relaxation in the glassy state [26]. T_g of

starch biocomposites depends on humidity, plasticizer content, and composition of starch and test condition [15-17,19].

Table 3.1: Dynamic mechanical properties of sugarcane fiber and wheat straw fiber reinforced corn starch biocomposites

Sample	Dynamic mechanical properties			
	Storage modulus at 45^0C (MPa)	Loss modulus (MPa)	Tanδ	Glass transition temperature (T_g)
S0	285.22	97.87	0.56	55.3
SS1	464.58	62.6	0.32	108.7
SS2	606.08	48.3	0.26	120.1
SS3	523.18	42.14	0.25	134.2
SW1	635.94	51.3	0.26	116.9
SW2	505.87	44.52	0.34	119.8
SW3	681.34	40.9	0.26	135.9

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