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# *Development of Green Nanocomposites based on Natural Resources*

Report of the Project: **SR/S5/GC-13/2008 Dated: 06/02/2009**
for the Period from 1st April 2009 to 31st March 2012

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Dean R&D

Project completion report & UC are attached (DORD/Chem.Sc/TKM/20-17)

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## Introduction:

The growing consciousness for greener and more sustainable technologies has focused attention on use of ecofriendly and cost effective material with high performance. Another aspect as the conventional polymers are obtained from petrochemicals which are non renewable and cause a detrimental effect on the environment. Biopolymers, which exist abundantly worldwide, are one of such promising material. They offer many fundamental and practical advantages of relevance to the chemist as well as to the chemical industries, which are constantly searching for high performing, cost effective and environmentally friendly materials. Besides these, natural fibres with their characteristics properties such as low cost, easy availability, low density, high specific strength, renewability and less abrasive with respect to processing tools, can be added to such class of materials. Among various natural fibres, jute fibre is cheap and widely available. Jute, mainly comprising of cellulose and lignin, is an extensively demanding materials in cloth and other such industries. Therefore, with the use of greener methodologies and environmentally benign materials (such as biopolymers), jute can be modified to a cost–effective and environment friendly 'green' products with improved physical properties.

Various bio-degradable polymers such as starch, soy protein, whey protein, wheat gluten, zein, polyhydroxy butyrate-co-valerate (PHBV), etc., have been used with bio-fibres (like jute, hemp, flax, ramie, etc.) as matrix and reinforcing materials to form eco-friendly product, with minimum impact on the environment. Therefore, the use of natural fibres to reinforce biopolymers as an alternative to synthetic or glass fibres has been and continues to be the subject of research and development. However, biopolymers based films have limited applications due to their two main disadvantages such as high hydrophilicity and inherently low moduli of elasticity.

Polymer – layered silicate nanocomposites, containing small amounts of inorganic nano phase, have exhibited superior properties like modulus, strength, thermal stability, toughness, gas permeability barrier, and flammability resistance compared to those of the pure polymers. These unique properties shown by nanocomposites are due to the nanometric size effect, compared to conventional composite even at low nanofiller content. Therefore, the use of such material can play a vital role in improving the properties of composites based on biopolymers.

## Experimental:

### *Materials*

Soy flour (SF) and Jute fabrics are purchased from Raja Soya, Tezpur and local market, Tezpur, Assam, India. Starch soluble extra pure, glutaraldehyde 25 % , benzene and NaOH pellets used for this study are obtained from Merck Private Limited (Mumbai, India). Glycerol is obtained from Qualigens Fine Chemicals (Mumbai). Montmorillonite K-10 clay, ZnO and $TiO_2$ are obtained from and Sigma Aldrich (USA) respectively. All other chemicals received as such are used without any further treatment.

### *Processing*

#### *Surface Modification of Jute:*

The jute fabrics are initially washed with 2% detergent solution at 70 □C for 1 h followed by washing with distilled water and finally dried in a vacuum oven at 50 □C. The detergent washed fabrics are dewaxed with a 1:2 mixture of alcohol and benzene for 72 h at 50 □C, washed with distilled water and dried. The fabrics are treated with 5% NaOH solution for 30 min at 30 □C, and then washed with several times to leach out the absorbed alkali. The fabrics are kept immersed in distilled water overnight and are again washed repeatedly to avoid the presence of any trace amount of alkali. The alkali treated fabrics are dried in a vacuum oven at 50 □C then stored at ambient temperature in a desiccator.

#### *Preparation of the Slurry:*

To process SF or starch powder into a suitable resin it is mixed with distilled water in a beaker in 1:10 ratio (by weight) and the desired amount of glycerol is added as a plasticizer. The SF or starch mixer is mixed with a magnetic stirrer for 30 min. Then the slurry is transferred to a 500 ml round bottom flask and stirred with a mechanical stirrer maintaining temperature at $60^0$-$70^0$c for 5-6 h. To study the effect of crosslinker, different amount of crosslinking agent (glutaraldehyde) is added to the slurry. This slurry is used for fabrication of composite. To improve various properties like mechanical, thermal etc, different nanofillers are used alone or in combination with one or more.

## ***(I) Jute-Reinforced-Soy Flour-Composites***

#### *Effect of Crosslinker and Nanoclay*

We have prepared the samples as coded in Table 1. The wt (%) of the components viz. SF, glycerol and Jute are kept constant in all the samples where as the wt (%) of GA and nanoclay are varied. The wt (%) of the various components used for the synthesis of the composite are provided in Table 1.

**Table 1** Composition of plasticized soy flour based composite.

| Sample | Soy Flour[a] | Glycerol | GA (Wt. %) | Jute | Nanoclay |
|---|---|---|---|---|---|
| S/J | 100 | 5 | - | 75 | - |
| S/J/G30 | 100 | 5 | 30 | 75 | - |
| S/J/G40 | 100 | 5 | 40 | 75 | - |
| S/J/G50 | 100 | 5 | 50 | 75 | - |
| S/J/G60 | 100 | 5 | 60 | 75 | - |
| S/J/G70 | 100 | 5 | 70 | 75 | - |
| S/J/G50/M1 | 100 | 5 | 50 | 75 | 1 |
| S/J/G50/M3 | 100 | 5 | 50 | 75 | 3 |
| S/J/G50/M5 | 100 | 5 | 50 | 75 | 5 |

[a] 20 g of soy flour is assumed to be 100.

## *Results & Discussion:*

### *1. X-ray diffractometry (XRD) study*

Fig [1(a), 1(b) and 1(c)] represents the XRD pattern of pure clay, jute and SF, respectively. A broader peak at $2\theta = 19$ □ is found to appear in SF diffractograms. Fig 1(d) and 1(e) represents the XRD pattern of mixture of S/J and S/J/G50, respectively. It could be seen from the XRD pattern that the mixing of the polymer components along with the crosslinker do not modify the crystallinity of either of the components. However, on incorporation of nanoclay in the synthesized composite (prepared by SF, Jute, GA and nanoclay), a change in the XRD pattern is observed.

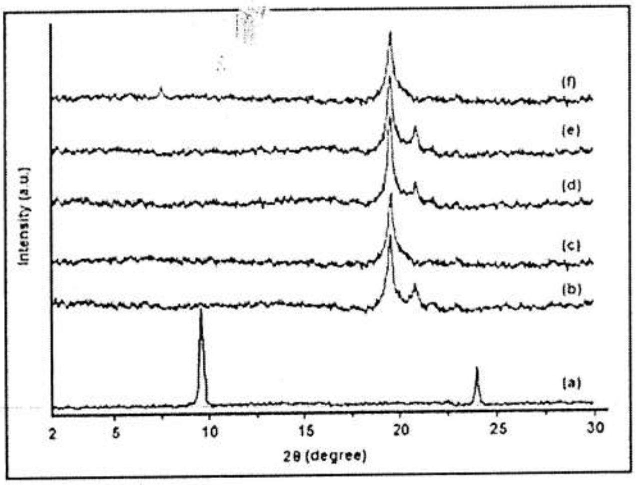

**Fig 1** XRD patterns of (a) clay, (b) Jute, (c) soy flour, (d) S/J, (e) S/J/G50 and (f) S/J/G50/M5.

### *2. Transmission Electron Microscopy (TEM) study*

TEM analysis is carried out to verify the extent of exfoliation of nanoclay particles in the prepared composites and is presented in Fig 2. Fig 2 (a) represents the TEM micrographs without clay composite whereas Fig 2 (b) &2 (c) are the micrographs of clay filled composite. The dispersion of clay layers as dark lines (shown by arrow mark) is observed in both the images. Moreover, it is evident from Fig 2 (b) and (c) that the clay layers are delaminated into thin lamellas by soy protein with a dimension of about 10~15 nm in thickness.

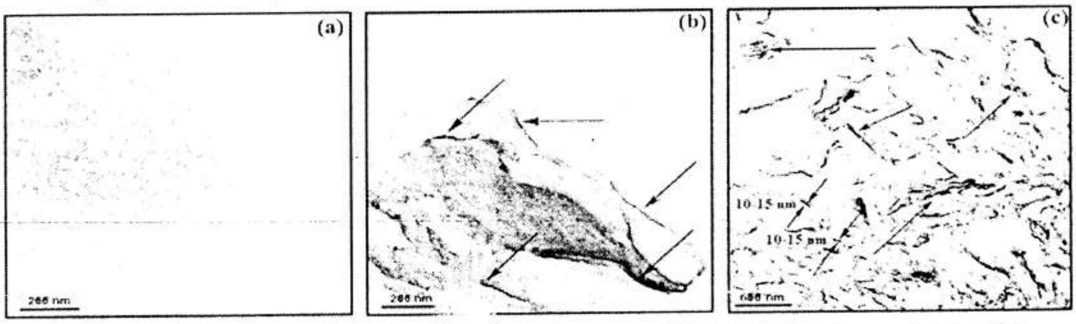

**Fig 2** TEM micrographs of Soy flour/jute composite (a) without clay taken within 200 nm range and (b) and (c) with clay composite at 200 nm and 600 nm scales.

### *3. Scanning Electron Microscopy (SEM) study*

The SEM micrograph of SF as shown in Fig 3 (a) indicated that the particles are irregular compact disc shape, whereas the SEM micrographs of the jute fibers are smooth and regular as observed from Fig 3 (b). Fig 3 (c & d) showed micrographs of composites without and with GA. From the micrographs, it is observed that composites with GA crosslinks showed better adhesion of the SF matrix onto the jute surface compared to the composites without GA. However, on addition of the clay nano particles, the brittleness along with the roughness of the composites is increased [Fig (3f-3i)]. This might be due to the fact that the clay particles enhanced the interaction between resin and jute surface through its hydroxyl groups. This resulted in enhancement of adhesion and consequently less pull out of fibres from the fracture surface.

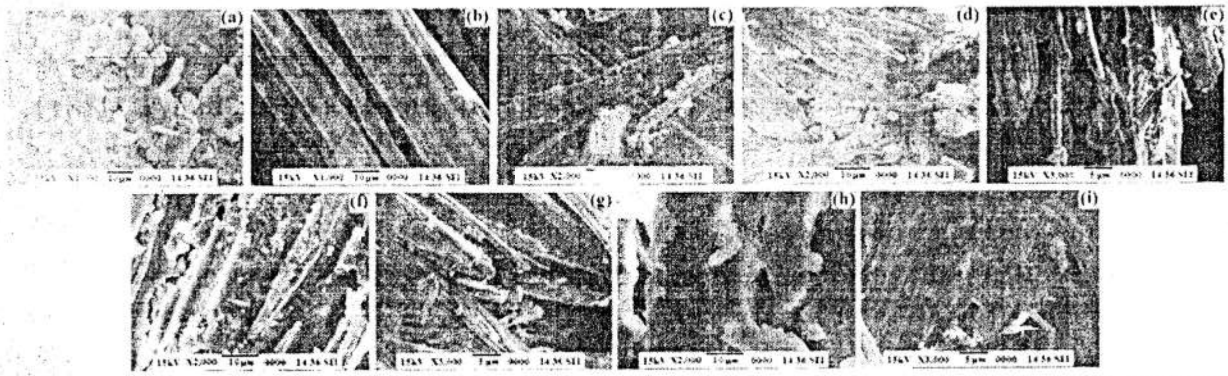

**Fig 3** SEM micrographs of (a) soy flour, (b) jute, (c) S/J surface, (d) S/J/G50 surface, (e) S/J/G50 fracture surface, (f) S/J/G50/M1 surface, (g) S/J/G50/M1 fracture surface, (h) S/J/G50/M5 surface and (i) S/J/G50/M5 fracture surface.

### *4. Fourier transform infrared spectroscopy (FT-IR) study*

FTIR spectra for soy flour, jute, clay, S/J, S/J/G50 and S/J/G50/M are presented in Fig 4. The

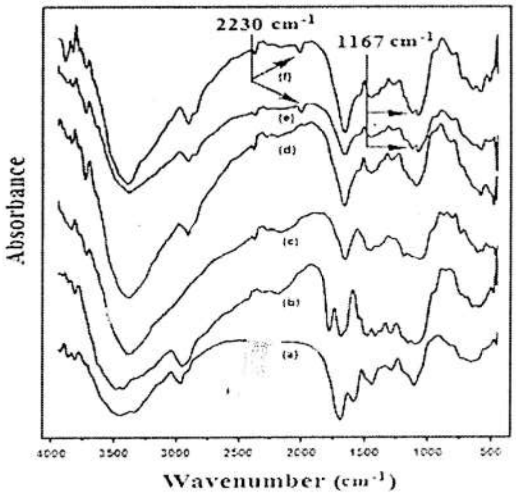

**Fig 4** FTIR spectra of (a) soy flour, (b) Jute, (c) clay, (d) S/J, (e) S/J/G and (f) S/J/G/M.

FTIR spectra for all the samples except clay and jute showed the peaks in the region 3400 - 3000cm$^{-1}$ which could be attributed to the – OH and – NH stretching vibrations respectively. Characteristics peaks of soy flour and jute are apparent in all the spectra of the prepared composite [Fig 4 (d-f)]. However, on addition of GA into the S/J composite (Fig 4e), the peak intensities in the region 3400-3000 cm$^{-1}$ assigned for – OH and – NH stretching vibrations are found to decrease. Further, two peaks corresponding to 2230 and 1167 cm$^{-1}$ assigned for –N–C=O and C–N stretching vibration are appeared [Fig 4 (e-f)]. This might be attributed to the interaction of – OH and – $NH_2$ groups present in jute and SF with the GA.

### *5. Mechanical property study*

The flexural properties of composites with varying percentage of glutaraldehyde and clay are shown in Fig 5. It is observed that both the flexural modulus and strength increased with the increase in the concentration of glutaraldehyde. Although the mechanical properties of composites are found to increase with the concentration of GA, however, the increase in strength is significant up to 50%. Hence, considering the 50% concentration of the crosslinker as optimum, we modified the composite (S/J/G50/M1, S/J/G50/M3 and S/J/G50/M5) with different percentage of nanoclay ranging from 1-5%. The flexural properties of the samples viz. (S/J/G50/M1, S/J/G50/M3 and S/J/G50/M5 are found better compared to the clay untreated samples. The higher the percentage of clay the higher is the flexural properties. The increase in flexural values is due to the restriction in the mobility of the intercalated polymer chains present inside the silicate layers of clay

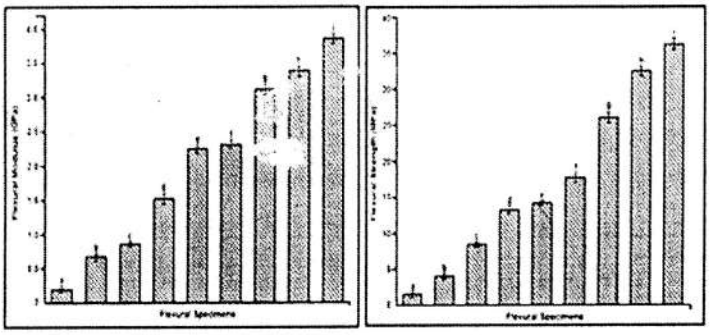

**Fig 5** Mechanical properties of (a) S/J, (b) S/J/G30, (c) S/J/G40, (d) S/J/G50, (e) S/J/G60, (f) S/J/G70, (g) S/J/G50/M1, (h) S/J/G50/M3 and (i) S/J/G50/M5.

### *6. Thermal property study*

The initial decomposition temperature ($T_i$), maximum pyrolysis temperature ($T_m$), decomposition temperature ($T_D$) at different weight loss (%) and residual weight (RW) for soy flour, jute, S/J composites with or without crosslinker and nanoclay treated S/J composite are shown in Table 2. $T_i$ values of S/J composites are found to enhance with the increase in the percentage of crosslinker. $T_i$ values increased further due to incorporation of clay. $T_m$ value for jute apparent at 368 °C, is due to the decomposition of cellulose. In the case of soy flour, $T_m$ values for the first and second stages of pyrolysis are due to the dissociation of the quaternary structure of proteins and degradation of peptide bonds in the amino acid residues. Nanoclay incorporation further increased the values.

**Table 2** Thermal properties of soy flour, jute and S/J glutaraldehyde and nanoclay composite.

| Sample Particulars | $T_i$ | $T_m^I$ | $T_m^{II}$ | Temperature of Decomposition at different weight loss (%) | | | | | | RW % at 600 $^0$C |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | 20 | 30 | 40 | 50 | 60 | 70 | |
| Soy Flour | 182 | 235 | 308 | 255 | 285 | 315 | 337 | 394 | | 29 |
| Jute | 195 | | 368 | 326 | 347 | 360 | 364 | 368 | | 7 |
| S/J | 168 | 221 | 309 | 250 | 280 | 302 | 325 | 378 | | 26 |
| S/J/G30 | 187 | 230 | 313 | 254 | 282 | 310 | 326 | 363 | | 27 |
| S/J/G50 | 191 | 234 | 317 | 261 | 285 | 312 | 329 | 356 | | 28 |
| S/J/G70 | 230 | 326 | 378 | 286 | [illegible] | 321 | 332 | 344 | | 30 |
| S/J/G50/M1 | 200 | 250 | 322 | 250 | [illegible] | 322 | 330 | 382 | | 30 |
| S/J/G50/M5 | 214 | 252 | 325 | 268 | 300 | 327 | 364 | 427 | | 31 |

$^I T_m$ value for 1st step.

$^{II} T_m$ value for 2nd step.

### 7. *Limiting Oxygen Index study*

The LOI values of the S/J composites with different percentage of crosslinker and clay are shown in the Table 3. From that table, it is observed that LOI value increased with the increase in crosslinker percentage. LOI values are further improved with increasing concentration of nanoclay and are found more than the nanoclay untreated composite.

**Table 3** Limiting Oxygen Indices (LOI) and Flaming Characteristics of the prepared composites.

| Samples | LOI (%) | Flame description | Smoke & Fumes | Char |
|---|---|---|---|---|
| S/J | 29 (±1.0) | Candle like Flame | Small and black smoke | Little |
| S/J/G30 | 29 (±2.0) | Small localised flame | Small and black smoke | Little |
| S/J/G40 | 38 (±1.0) | Small localised flame | Small and black smoke | Little |
| S/J/G50 | 38 (±3.0) | Small localised flame | Small and black smoke | Little |
| S/J/G60 | 44 (±1.0) | Small localised flame | Small and black smoke | Little |
| S/J/G70 | 47 (±2.0) | Small localised flame | Small and black smoke | Little |
| S/J/G50/M1 | 50 (±2.0) | Small localised flame | Small and black smoke | Higher |
| S/J/G50/M3 | 56 (±1.0) | Small localised flame | Small and black smoke | Higher |
| S/J/G50/M5 | 56 (±1.0) | Small localised flame | Small and black smoke | Higher |

### 8. *Dimensional stability test*

The effect of swelling in water vapour at room temperature and 65% relative humidity for the composite samples for different time periods is shown in Fig 6. From the Fig, it is found that the composites having higher percentage of GA showed less swelling than the composites containing lower percentage of glutaraldehyde. Clay treated composites swelled less than those of clay untreated samples. The higher the amount of clay, the lower is the swelling. The silicate layer of clay provided a tortuous path which hindered the diffusivity of water through the composites.

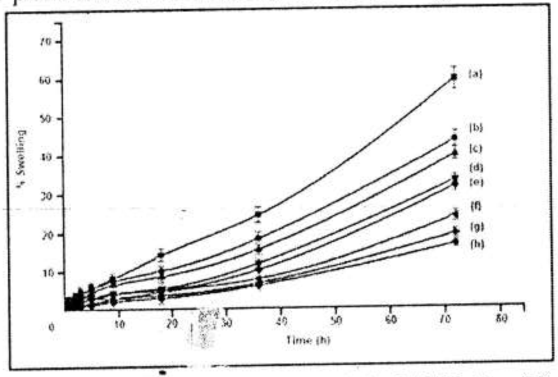

**Fig 6** Swelling behaviour of (a) S/J, (b) S/J/G30, (c) S/J/G40, (d) S/J/G50, (e) S/J/G70, (f) S/J/G50/M1, (g) S/J/G50/M3 and (h) S/J/G50/M5.

## *(II) Jute-Reinforced-Starch-Composites*

### *Effect of Crosslinker and Nanoclay*

We have prepared the samples as coded in Table 1. The wt (%) of the components viz. Starch, glycerol and Jute are kept constant in all the samples where as the wt (%) of GA and nanoclay are varied. The wt (%) of the various components used for the synthesis of the composite are provided in Table 1.

**Table 1**. Composition of plasticized Starch based composite.

| Sample | Starch | Glycerol | Jute | GA | MMT |
|---|---|---|---|---|---|
| | | | Wt % | | |
| S/J | 100 | 5 | 75 | 0 | 0 |
| S/J/G30 | 100 | 5 | 75 | 30 | 0 |
| S/J/G40 | 100 | 5 | 75 | 40 | 0 |
| S/J/G50 | 100 | 5 | 75 | 50 | 0 |
| S/J/G60 | 100 | 5 | 75 | 60 | 0 |
| S/J/G70 | 100 | 5 | 75 | 70 | 0 |
| S/J/G50/M1 | 100 | 5 | 75 | 50 | 1 |
| S/J/G50/M3 | 100 | 5 | 75 | 50 | 3 |
| S/J/G50/M5 | 100 | 5 | 75 | 50 | 5 |

## *Results & Discussion:*

### *1. Fourier transform infrared spectroscopy (FT-IR) study*

FTIR spectra of starch, jute, clay, S/J, S/J/GA and S/J/GA/M are presented in Fig 1. The spectrum of starch (curve-a) shows the presence of absorption bands at 571, 980, 1160, 1650, 2920 and 3400 cm$^{-1}$ confirming the carbohydrate nature. The typical saccharide bands appeared in the range 1180-950 cm$^{-1}$ is considered the vibration modes of C–C and C–O stretching and the bending of C–H bonds. Jute (curve-b) shows the presence of peaks in the range 3440-3390 cm$^{-1}$ for -OH stretching, 1738 cm$^{-1}$ for the C=O stretching vibration of ester groups of hemicelluloses, 1640 cm$^{-1}$ for C=O stretching, 1254 cm$^{-1}$ for –C–O–C– bond in cellulose chain and 1057-1116 cm$^{-1}$ for C–O stretching. Clay exhibits (curve-c) peaks at 3465 cm$^{-1}$ (-OH stretching), 1619 cm$^{-1}$ (–OH bending), 1030-[illegible]0 cm$^{-1}$ (oxide bonds of metals like Si, Al, Mg etc). Curve-e represents the spectrum of glutaraldehyde crosslinked S/J composite. The intensities of –OH and C=O stretching are found to decrease in the crosslinked composites suggesting the formation of covalent bond between jute and starch.

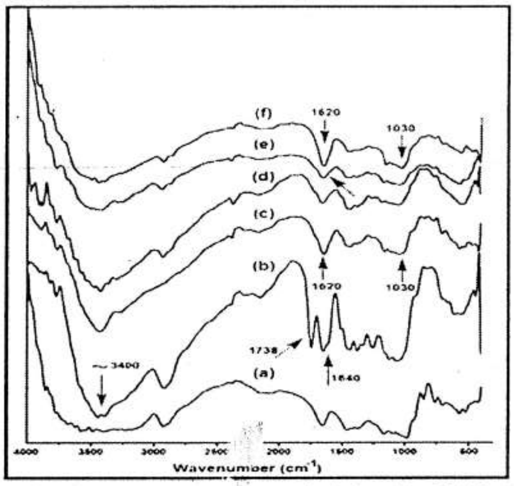

**Fig 1** FTIR spectra of (a) Starch, (b) Jute, (c) clay, (d) S/J, (e) S/J/G50 and (f) S/J/G50/M5.

Clay filled (curve-f) S/J composites, the intensity of peak corresponding to –OH has further decreased. The intensities of peaks at 1620 cm$^{-1}$ and 1030 cm$^{-1}$ assigned for Si–O–Si stretching are more pronounced compared to glutaraldehyde crosslinked S/J composites. All this suggested the participation of hydroxyl group of clay in crosslinking reaction with starch and jute

### *2. X-ray diffractometry (XRD) study*

Fig 2 shows the XRD patterns of Jute, starch, S/J, S/J/G50, clay and the nanocomposites.

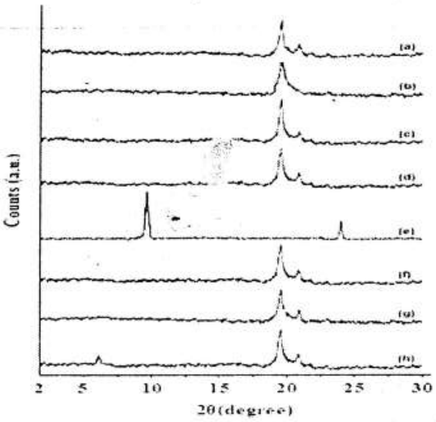

**Fig 2** XRD patterns of (a) Jute, (b) Starch, (c) S/J, (d) S/J/G50, (e) Clay (f) S/J/G50/M1, (g) S/J/G50/M3 and (h) S/J/G50/M5.

Clay shows sharp peaks around $2\theta = 24$ and $9^\circ$. Jute shows peaks at $2\theta = 22^\circ$ (002 plane of cellulose I) and $19^\circ$ (101 plane of cellulose II). Curve – b represents the diffractograms of starch. A little broader peak around $2\theta = 20^\circ$ is found to appear. The diffraction peak of the nanoclay tactoids is absent in the X-ray diffractograms for 1% and 3% clay loaded composites (curves-f & g). It could be said that either the full expansion of the MMT gallery occurred, which is not possible to detect by XRD, or the MMT layers became delaminated and no crystal diffraction peak appeared. In curve -h, the peak observed for pure clay at around $9^\circ$ is shifted towards left with reduction in intensity in the S/J/G50/M5 composites.

### 3. *Transmission Electron Microscopy (TEM) study*

The dispersion of clay layers as dark lines (shown by arrow mark) is observed in both the images. The TEM micrographs of nanoclay incorporated composites are shown in Fig 3.

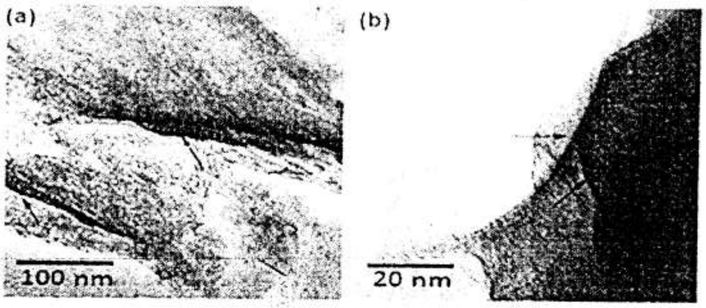

**Fig 3** TEM micrographs of S/Clay composite with 5% clay (a) 100 nm and (b) 20 nm scale.

As indicated by TEM micrographs, the clay layers are delaminated into thin lamellas by starch having a dimension of 2~3 nm in thickness.

### 4. *Scanning Electron Microscopy (SEM) study*

SEM micrographs of jute, starch and the fracture surface of starch/jute composite with and

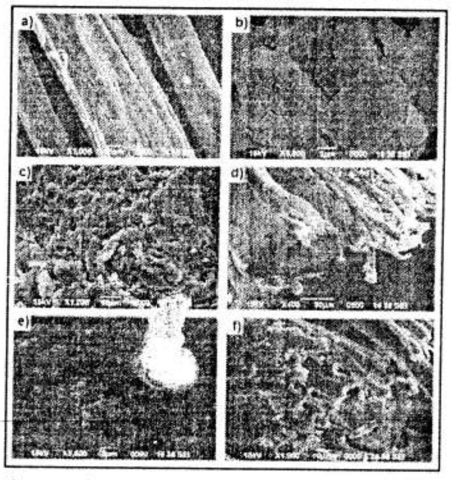

**Fig 4** SEM micrographs of (a) jute, (b) starch, (c) S/J/G50 smooth surface, (d) S/J/G50 fracture surface, (e) S/J/G50/M5 smooth surface (f) S/J/G50/M5 fracture surface.

without clay are presented in Fig. 4. The shape of starch particles are irregular compact disc type as shown in fig. 4b. The surface of jute fibres is smooth and regular (fig. 4a). Fig. 4d shows the micrographs of fracture surface of glutaraldehyde crosslinked Starch/Jute composite. It showed the protruding out of less fibre. This suggested a brittle failure. The resins are found to adhere on some of the fibre surface. Surface of some fibres are smooth as there is no resin. The addition of clay increased the brittleness as judged from the less pull out of fibre from fractured surface (fig. 4f).

Further work is done through energy dispersive X-ray analysis of the nanoparticles observed in the fracture for the clay loaded composite as shown in Fig 5. Elements such as Al, Na and Si, which are mainly from the silicate nanoclay, are detected indicating that the nanoclay has been successfully incorporated into the composite

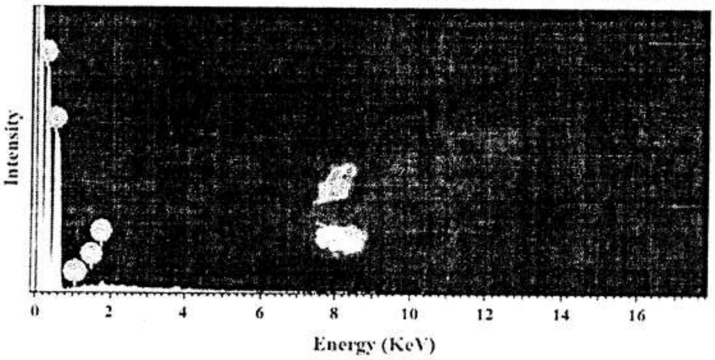

**Fig 5** Energy dispersive X-ray analysis of S/J/G50/M.

### *5. Mechanical property study*

The flexural and tensile properties of composites with varying percentage of glutaraldehyde and clay are shown in Table 2. It is observed that both the flexural and tensile modulus and

**Table 2** Flexural and tensile properties of (a) S/J, (b) S/J/G30, (c) S/J/G40, (d) S/J/G50, (e) S/J/G60, (f) S/J/G70, (g) S/J/G50/M1, (h) S/J/G50/M3 and (i) S/J/G50/M5.

| | Flexural Properties | | Tensile Properties | |
|---|---|---|---|---|
| Sample | Strength (MPa) | Modulus (MPa) | Strength (MPa) | Modulus (MPa) |
| S/J | 27.67 (±1.22) | 1141.9 (±1.57) | 12.59 (±1.26) | 755.38 (±16.74) |
| S/J/G30 | 28.31 (±1.34) | 1336.2 (±1.16) | 18.62 (±1.84) | 1117.10 (±13.46) |
| S/J/G40 | 37.8 (±2.31) | 1641.6 (±2.11) | 19.88 (±0.96) | 1192.53 (±17.32) |
| S/J/G50 | 39.5 (±2.14) | 2234.0 (±1.96) | 22.54 (±1.03) | 1352.18 (±15.34) |
| S/J/G60 | 45.8 (±1.12) | 2575.6 (±1.32) | 22.65 (±1.31) | 1358.81 (±10.79) |
| S/J/G70 | 51.4 (±1.32) | 2620.1 (±1.13) | 24.64 (±2.07) | 1478.53 (±14.08) |
| S/J/G50/M1 | 69.8 (±1.31) | 3777.0 (±2.09) | 28.42 (±0.74) | 1705.47 (±11.67) |
| S/J/G50/M3 | 82.0 (±1.76) | 4516.3 (±1.54) | 32.40 (±1.37) | 1944.78 (±17.62) |
| S/J/G50/M5 | 90.7 (±2.54) | 6434.1 (±2.09) | 40.53 (±2.31) | 2344.67 (±12.78) |

* Each value represents average five samples.

strength increased with the increase in the concentration of glutaraldehyde. The mechanical properties of composite are found to increase with the increase in the concentration of GA. The mechanical properties of the clay treated samples are found better compared to the clay untreated samples. The higher the percentage of clay, the higher is the mechanical properties. The increase in mechanical properties is due to the restriction in the mobility of the intercalated polymer chains present inside the silicate layers of clay.

### *6. Thermal property study*

The influence of GA and nanoclay on the thermal properties of the synthesized composites is investigated by TGA, as shown in Fig 6. Decomposition temperature values ($T_D$) of the crosslinked S/J composite are higher than uncrosslinked S/J composite. The higher the crosslinker concentration, the higher is the $T_D$ value. The $T_D$ values are improved further when clay is added to it. The increase in thermal stability of the synthesized nanocomposites is attributed to the hindered diffusion of volatile decomposition products within it.

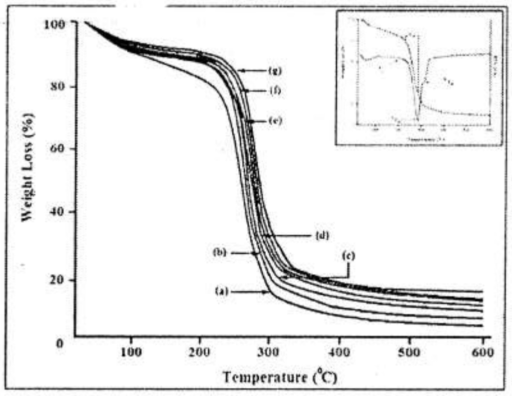

**Fig 6** TGA thermograms of (a) S/J, (b) S/J/G30, (c) S/J/G50, (d) S/J/G70, (e) S/J/G50/M1, (f) S/J/G50/M3 and (g) S/J/G50/M5. TGA and DTG for curve-C are shown in the inset.

### *7. Limiting Oxygen Index study*

The LOI values of the S/J composites with different percentage of crosslinker and clay are presented in the Table 4. From that table, it is observed that LOI value increased with

**Table 4** Limiting Oxygen Indices (LOI) and Flaming Characteristics of the prepared composites.

| Samples | LOI (%) | Flame description | Smoke & Fumes | Char |
|---|---|---|---|---|
| S/J | 22 (±2.0) | Candle like Flame | Small and black smoke | Little |
| S/J/G30 | 29 (±1.0) | Small localised flame | Small and black smoke | Little |
| S/J/G40 | 38 (±3.0) | Small localised flame | Small and black smoke | Little |
| S/J/G50 | 39 (±1.0) | Small localised flame | Small and black smoke | Little |
| S/J/G60 | 44 (±2.0) | Small localised flame | Small and black smoke | Little |
| S/J/G70 | 47 (±1.0) | Small localised flame | Small and black smoke | Little |
| S/J/G50/M1 | 51 (±2.0) | Small localised flame | Small and black smoke | Higher |
| S/J/G50/M3 | 56 (±3.0) | Small localised flame | Small and black smoke | Higher |
| S/J/G50/M5 | 61 (±2.0) | Small localised flame | Small and black smoke | Higher |

* Each value represents average five samples.

then added to the above MMA-g-SF and 5% glycerol (w/w of SF) is added. The stirring is continued for another 3 h at room temperature. 50% (w/w of SF) glutaraldehyde (GA) is added to the slurry. This slurry is used for fabrication of composite. The different composition of the samples is shown in the table 1 given below:

**Table 1** Composition of plasticized SF based composite (wt. %)

| Sample | Jute | GA | Glycerol | SF | MMA | MMT |
|---|---|---|---|---|---|---|
| J/G/SF | 75 | 50 | 5 | 100 | - | - |
| J/G/SF-g-MMA | 75 | 50 | 5 | 100 | 5 | - |
| J/G/SF-g-MMA/N1 | 75 | 50 | 5 | 100 | 5 | 1 |
| J/G/SF-g-MMA/N3 | 75 | 50 | 5 | 100 | 5 | 3 |
| J/G/SF-g-MMA/N5 | 75 | 50 | 5 | 100 | 5 | 5 |

***Results & Discussion***

***1. Fourier Transform Infrared Spectroscopy (FT-IR) study***

The interactions between SF, jute, glycerol, MMA, clay and glutaraldehyde are studied by FTIR spectroscopy. FTIR spectra of J/G/SF, J/G/SF-*g*-MMA, and J/G/SF-*g*-MMA/N5 are presented in fig 1. The FTIR spectra for all the samples showed the peaks in the region 3400–3000 cm$^{-1}$, which could be attributed to the –OH and –NH stretching vibrations, respectively. After the addition of MMA into the reaction mixture a new peak at around 1730 cm$^{-1}$ is appeared in curve (b) and (c) attributed due the C=O stretching vibration of MMA which indicated the successful grafting of MMA into SF. It is also observed in the spectrum that the peak intensities in the region 3400–3000 cm-$^{1}$ are decreases which further confirm the interaction of MMA with SF. On addition of MMT, the peak intensity in the region 3400–3000 cm$^{-1}$ corresponding to –OH and –NH stretching vibration is reduced and sharpened. The peak intensities in the region 1030–460 cm$^{-1}$ and 1620 cm$^{-1}$ are also found to enhance. These results further confirmed the interaction of clay particles with GA and SF/J composite

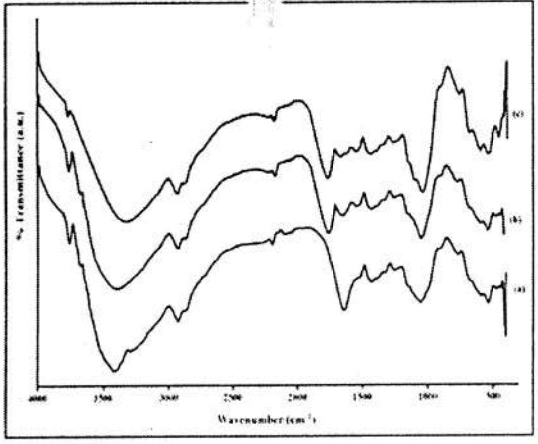

**Figure 1** IR spectrum of (a) J/G/SF, (b) J/G/SF-*g*-MMA, and (c) J/G/SF-*g*-MMA/N5

the increase in the percentage of crosslinker. GA formed crosslinks between jute and starch. The higher the concentration of GA, the higher is the crosslinking. The network structure thus formed would restrict the accessibility of oxygen for the production of degradable components from the composites and hence LOI value would be more. LOI value is enhanced further on addition of nanoclay.

### *8. Dimensional stability test*

The effect of swelling in water vapour at room temperature (~$30^0$ C) and 65% relative humidity for the composite samples for different time periods is shown in Fig 7. In all the cases, the % swelling is found to increase with the increase of time. From the Fig, it is observed that the composites having higher percentage of GA showed more reduction in swelling than the composites containing lower percentage of GA

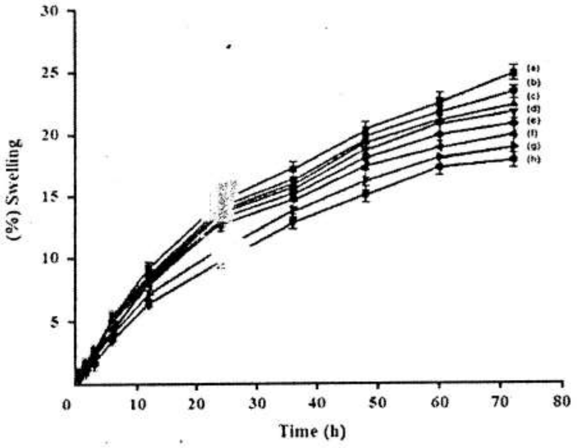

**Fig 7** Swelling behaviour of (a) S/J, (b) S/J/G30, (c) S/J/G40, (d) S/J/G50, (e) S/J/G70, (f) S/J/G50/M1, (g) S/J/G50/M3 and (h) S/J/G50/M5

## *(III) Jute – reinforced – Soy flour-g-MMA Composite*

*Effect of grafting % and Nanoclay concentration*

### Preparation of methyl methacrylate grafted Soy flour

To process Soy flour powder into a suitable resin for fabricating green composites, it is mixed with deionised water in beaker in 1:10 ratio (by weight). Then the slurry is transferred to a 500 ml round bottom flask and stirred with a mechanical stirrer maintaining temperature at 60-70 $^0$C for 1 h. To this slurry, methyl methacrylate (MMA) (3-5% w/w of soy flour) along with aqueous solution of $K_2S_2O_8$ (1% w/w of MMA) is added and the mixture is stirred for 4 h. After the stipulated time the polymer is allowed to cool and kept for further work.

### Dispersion of MMT and preparation of slurry

Montmorillonite (MMT) (1-5%, w/w of SF) is dispersed in 60 ml deionised water in a beaker and stirred with a mechanical stirrer for 12 h. This mixture is sonicated for $^1/_2$ h. The mixture is

### *2. Transmission Electron Microscopy (TEM) study*

TEM analysis is carried out to verify the extent of exfoliation of nanoclay particles in the prepared composites and is presented in figure 2. The dispersion of clay layers as dark lines (shown by arrow mark) is observed in both the images.

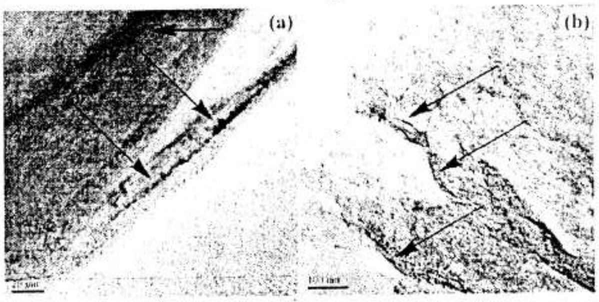

**Figure 1** TEM micrograph of J/G/SF-*g*-MMA/[illegible]5 composite (a) 20 & (b) 100 nm scale.

### *3. Scanning Electron Microscopy (SEM) study*

SEM is performed to know the surface morphology of the prepared composites. Figure 3 represents the SEM micrographs of (a) J/G/SF, (b) J/G/SF-*g*-MMA, (c) J/G/SF-*g*-MMA/N1 and (d) J/G/SF-*g*-MMA/N5. From figure 3 (a) we have seen that the surface of J/G/SF composite is appeared smooth. However, on addition of MMA into the composite the surface appeared rough {figure 3(b)}. Further the roughness of composite surface is increased with the addition of clay particle into it {figure 3 (c) & 3 (d)}. From the figure 3 (c) and 3 (d) it is seen that with the increase in clay percentage the roughness of the composite surface is also increased. The roughness might be due to the adherence of the SF-*g*-MMA or the SF-*g*-MMA /clay to the jute surface.

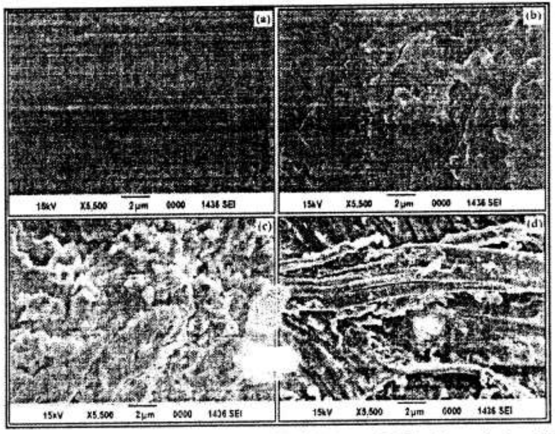

**Figure 3** SEM micrographs (a) J/G/SF, (b) J/G/SF-*g*-MMA, (c) J/G/SF-*g*-MMA/N1 and (d) J/G/SF-*g*-MMA/N5

### *4 Thermal property study*

The influence of MMA grafting and nanoclay on the thermal properties of jute based crosslinked SF composites are investigated by thermogravimetric analysis (TGA) as shown in figure 4. It is seen clearly from the thermograms that the initial decomposition temperature (Ti), maximum

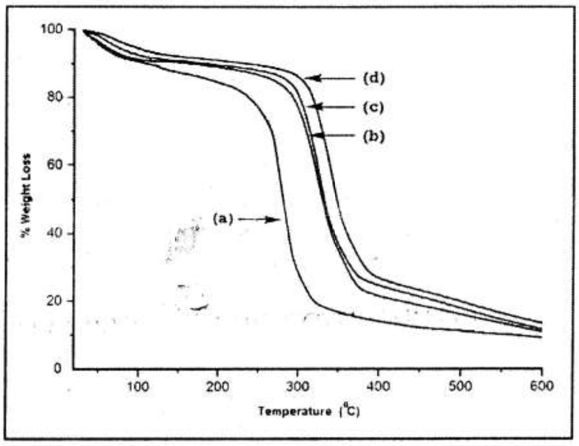

**Figure 4** TGA thermograms of (a) J/G/SF, (b) J/G/SF-*g*-MMA, (c) J/G/SF-*g*-MMA/N1 and (d) J/G/SF-*g*-MMA/N5.

pyrolysis temperature (Tm), decomposition temperature (TD) at different weight loss (%) and residual weight (RW, %) of the composites are improved with the addition of MMA and nanoclay. In figure 4 (a), it is found that the mass loss of SF is 17% before the decomposition temperature, the onset decomposition temperature is 245 °C and the final decomposition temperature is 330 °C. In the figure 4 (b), the mass loss of SF-g- MMA (5%) is 13% before the decomposition temperature, the onset decomposition temperature is 251 °C, and the final decomposition temperature is 377 °C. This indicated that the thermal stability of SF increases after being grafted with MMA. The incorporation of MMT which is inorganic in nature significantly improved the thermal stability of organic materials present within the composites.

### *5. Mechanical Strength Study*

The flexural and tensile properties of the grafted composites with varying percentage of clay are shown in table 3. It is observed that both the flexural and tensile modulus and strength

Table 2 Flexural and tensile properties of (a) J/G/SF, (b) J/G/SF-g-MMA, (c) J/G/SF-g-MMA/N1, (d) J/G/SF-g-MMA/N3, and (e) J/G/SF-g-MMA/N5.

| Sample | Flexural Properties | | Tensile Properties | |
|---|---|---|---|---|
| | Strength (MPa) | Modulus (MPa) | Strength (MPa) | Modulus (MPa) |
| J/G/SF | 13.25 | 3855 | 18.68 | 747.08 |
| J/G/SF-g-MMA | 38.78 | 4492 | 22.37 | 1167.34 |
| J/G/SF-g-MMA/N1 | 43.85 | 5632 | 27.74 | 1352.18 |
| J/G/SF-g-MMA/N3 | 52.60 | 6026 | 32.18 | 1552.77 |
| J/G/SF-g-MMA/N5 | 68.89 | 7876 | 36.32 | 1814.25 |

* Each value represents average five samples.

increased with the increase in the concentration of nanoclay. It is observed from table 2 that except the tensile strength there is significant enhancement on the properties such as tensile modulus, flexural strength and flexural modulus with the increase in nanoclay concentration

The increase in mechanical properties is due to the restriction in the mobility of the intercalated polymer chains present inside the silicate layers of clay.

### *(IV) Jute – reinforced – Starch-g-MMA Composite*

*Effect of grafting % and Nanoclay concentration*

**Preparation of methyl methacrylate grafted starch**

To process starch powder into a suitable resin for fabricating green composites, it is mixed with deionised water in beaker in 1:10 ratio (by weight). Then the slurry is transferred to a 500 ml round bottom flask and stirred with a mechanical stirrer maintaining temperature at 60-70 $^0$C for 1 h. To this slurry, methyl methacrylate (MMA) (3-5% w/w of starch) along with aqueous solution of $K_2S_2O_8$ (1% w/w of MMA) is added and the mixture is stirred for 4 h. After the stipulated time the polymer is allowed to cool and kept for further work.

The various compositions of the grafted composites are shown in the table 1.

**Table 1.** Different composition of the composite samples.

| Sample | Starch | Glycerol | GA | MMA | MMT |
|---|---|---|---|---|---|
| | | | (wt. %) | | |
| S/J | 100 | 5 | 50 | 0 | 0 |
| S/J/MMA3 | 100 | 5 | 50 | 3 | 0 |
| S/J/MMA5 | 100 | 5 | 50 | 5 | 0 |
| S/J/MMA3/M3 | 100 | 5 | 50 | 3 | 3 |
| S/J/MMA5/M3 | 100 | 5 | 50 | 5 | 3 |
| S/J/MMA3/M5 | 100 | 5 | 50 | 3 | 5 |
| S/J/MMA5/M5 | 100 | 5 | 50 | 5 | 5 |

***Results & Discussion:***

***1. Fourier Transform Infrared Spectroscopy (FT-IR) study***

The FTIR analysis of the starch composites is shown in the fig. 1. A broad absorbance band (a) in the region ~3400 cm$^{-1}$ characteristics of O-H stretching vibration is common to all the spectra.

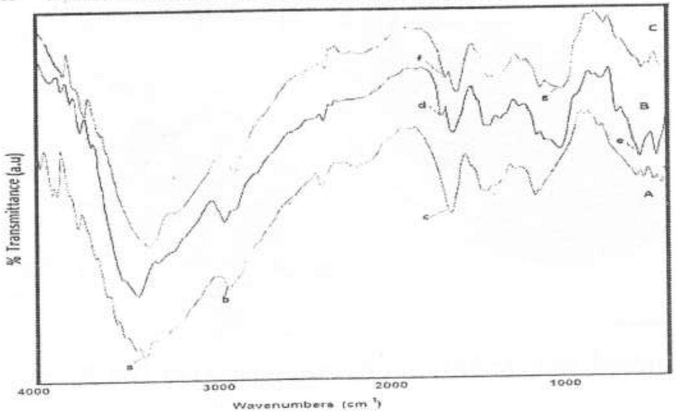

**Fig. 1** IR spectrum of (A) S/J, (B) S/J/MMA, and (C) S/J/MMA/MMT.

The band (b) at 2926 $cm^{-1}$ is attributed to $CH_2$ symmetrical stretching vibrations. The band (c) at 1640 $cm^{-1}$ is assigned to scissoring of two O–H bonds of absorbed water molecules in starch. The bands at 862 and 765 $cm^{-1}$ are due to skeletal stretching vibrations of starch. The curve (B) of starch-g-MMA showed an additional peak at nearly (d) 1730 $cm^{-1}$and (e) 568.71 $cm^{-1}$. The peak (d) is due to the C=O stretching which confirmed the grafting of MMA. The peak (f) is due to the C=O stretching of grafted MMA and the peak (g) at 1039.91 $cm^{-1}$ is the characteristic peak of MMT due to the Si-O-Si stretching in curve C.

### *2. Scanning Electron Microscopy (SEM) study*

Fig. 2 (a) and (b) show the starch-g-MMA and starch-g-MMA-MMT respectively. With the incorporation of MMA the smoothness of the surface decreased as shown in the fig. 9 (a) and hence it leads to good adhesion between the matrix and fibre. From fig. 9 (b) it is evident that MMT particles are adhere to the rough surface of starch-g-MMA-jute composite and all the composites display an oriented fracture probably due to the orientation of crystal clay layered into the starch matrix. The adhesion between the matrix and jute fibre is also very good which is necessary for the composite to give good performance.

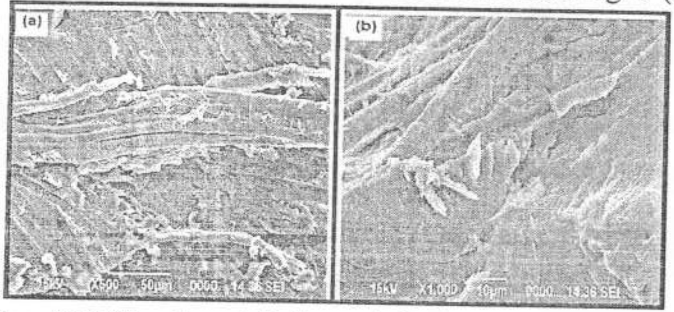

**Fig. 2** SEM micrographs of (a) Starch-g- MMA, and (b) Starch-g- MMA-MMT.

### *3. Transmission Electron Microscopy (TEM) study*

TEM analysis is carried out to verify the extent of exfoliation of nanoclay particles in the prepared composites and is presented in figure 3. The dispersion of clay layers as dark lines (shown by arrow mark) is observed in both the images.

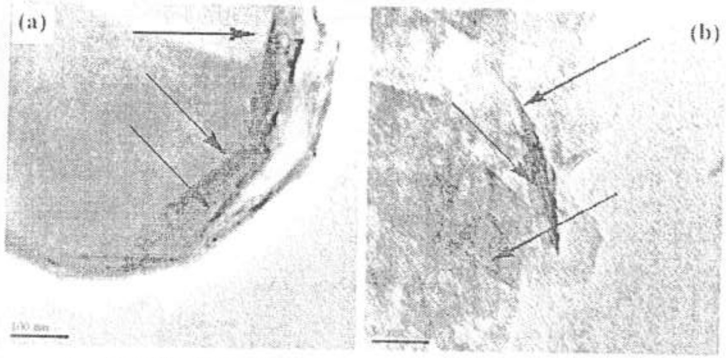

**Figure 3** TEM micrograph of S/J/MMA5/M5 composite (a) 100 & (b) 20 nm scale.

### *4. Thermal study*

The TGA thermograms of (a) S/J, (b) S/J/MMA and (c) S/J/MMA/MMT composites are shown in fig. 4. Fig. 4(a) it is found that the mass loss of composite is 17% before the decomposition temperature, the onset decomposition temperature is 245 $^0$C and the final decomposition temperature is 330 $^0$C. In the fig. 4(b), the mass loss of starch-g- MMA (5%)/Jute composite is 13%before the decomposition temperature, the onset decomposition temperature is 251 $^0$C, and the final decomposition temperature is 375 $^0$C. This indicated that the thermal stability of composite increased after being grafted with MMA. The mass loss of starch-g-MMA-jute composites containing MMT (5 wt %) is found to be 11.5%, the onset and final decomposition temperatures are 271.2 and 379 $^0$C respectively. The result indicated that thermal stability of composite improved due to incorporation of MMT.

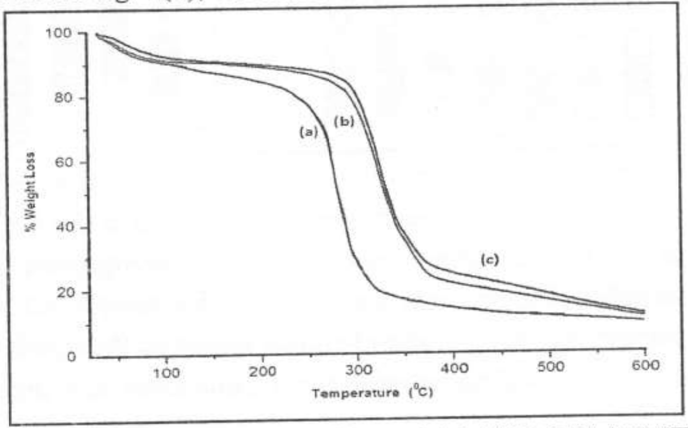

**Fig. 4** TGA thermograms of (a) S/J, (b) S/J/MMA, and (c) S/J/MMA/MMT.

### *5. Mechanical properties study*

*a) Tensile Study*

Fig. 5 shows the tensile modulus and tensile strength of the prepared composite.

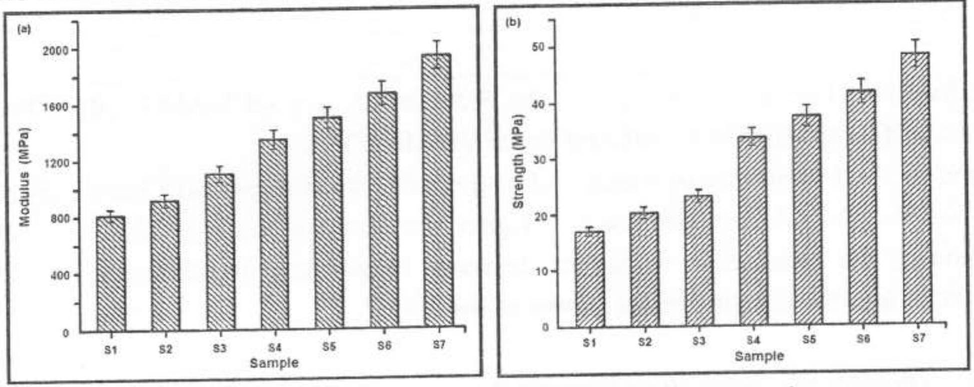

**Fig. 5** (a) Tensile modulus and (b) tensile strength.

*b) Flexural study*

Fig. 6 shows the flexural modulus and flexural strength of the prepared composite.

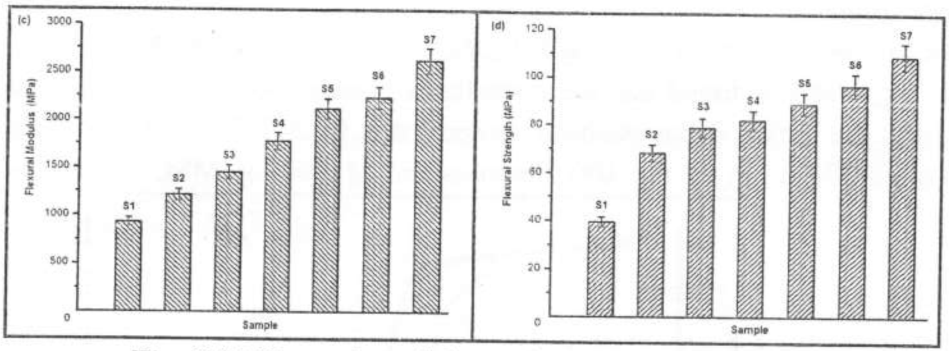

Fig. 6 (c) Flexural modulus and (d) flexural strength.

The mechanical properties of the composites are summarized in the fig. 5 and 6. Tensile strength and modulus as well as flexural strength and modulus of composites increased significantly for all the composite samples. The strength and modulus for sample S/J/MMA5/M5 is the highest and lowest for the sample S/J. The similar chemical nature of the starch matrix and the jute fibers facilitated strong interfacial bonding between them, enhancing their mechanical properties.

### *6. Dimensional stability study*

The results showing the effect of swelling in water vapor at 65% RH and room temperature (30 °C) up to 72 h are presented in fig 7. As expected, grafted sample showed less swelling during the treatment, due to the presence of PMMA polymer. Grafting of MMA polymer to starch decreased the hydrophilicity of starch and as a result less absorption of water vapour is exhibited by the Starch-g-MMA/Jute composite. Higher the concentration of MMA lower is the water absorption of the composite. A further decrease in swelling is observed when MMT clay is incorporated into the composites as shown in the Fig. 7.

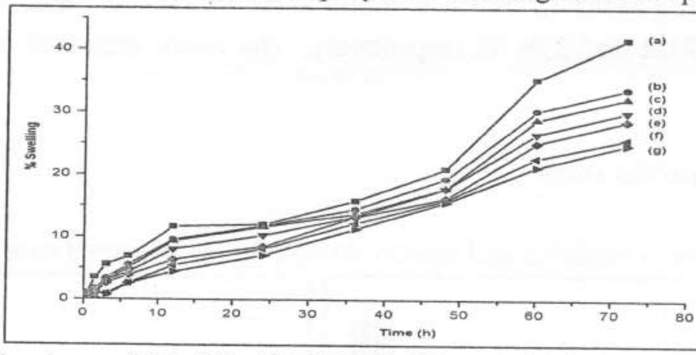

**Fig. 7.** Swelling behaviour of (a) S/J, (b) S/J/MMA3, (c) S/J/MMA5, (d) S/JMMA3/M3, (e) S/J/MMA5/M3, (f) S/J/MMA3/M5 and (g) S/J/MMA5/M5.

### *(V) Jute – reinforced – Soya flour Composite*

*Effect of $TiO_2$ and Nanoclay concentration*

We have prepared the samples as coded in Table 1. The wt (%) of the components viz. SF, glycerol and Jute are kept constant in all the samples where as the wt (%) of $TiO_2$ and nanoclay are varied. The wt (%) of the various components used for the synthesis of the composite are provided in Table 1.

**Table 1** Composition of plasticized soy flour based composite.

| Sample | Soy Flour[a] | Glycerol | GA | Jute | $TiO_2$ | Nanoclay |
|---|---|---|---|---|---|---|
| | (Wt. %) | | | | | |
| S/J/G50 | 100 | 5 | 50 | 75 | - | - |
| S/J/G50/T1 | 100 | 5 | 50 | 75 | 1 | - |
| S/J/G50/T3 | 100 | 5 | 50 | 75 | 3 | - |
| S/J/G50/T5 | 100 | 5 | 50 | 75 | 5 | - |
| S/J/G50/T5/M1 | 100 | 5 | 50 | 75 | 5 | 1 |
| S/J/G50/T5/M3 | 100 | 5 | 50 | 75 | 5 | 3 |
| S/J/G50/T5/M5 | 100 | 5 | 50 | 75 | 5 | 5 |

[a] 20 g of soy flour is assumed to be 100.

***Results & Discussion:***

***1. Fourier transform infrared spectroscopy (FT-IR) study***

The FTIR spectra of the S/J/G50, $TiO_2$, S/J/G50/T5 and S/J/G50/T5/M5 composites are shown in the fig. 1.

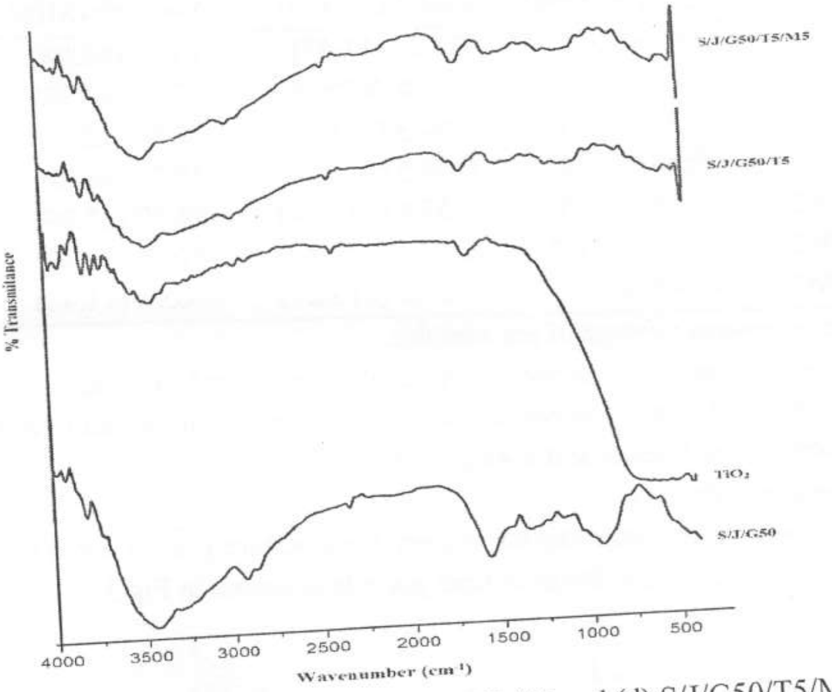

Fig. 1: IR spectra of (a) S/J/G50, (b) $TiO_2$, (c) S/J/G50/T5 and (d) S/J/G50/T5/M5.

Successful incorporation of $TiO_2$ and nanoclay in the composites is revealed by the IR spectrum. The strong absorbance at 1028–418 $cm^{-1}$ is attributed to the Ti-O-Ti stretching of TiO2. The absorbance at 3431 and 1633 $cm^{-1}$ are assigned to the surface hydroxyl groups of TiO2.

***2. Transmission Electron Microscopy (TEM) study***

Fig. 2 represents the TEM micrographs of $TiO_2$ incorporated composites (a) 100 nm scale and (b) 50 nm scale. From the TEM micrographs it can be said that $TiO_2$ nanoparticle has successfully incorporated and well dispersed into the S/J/G50 composite and the average particle size is ~40 nm.

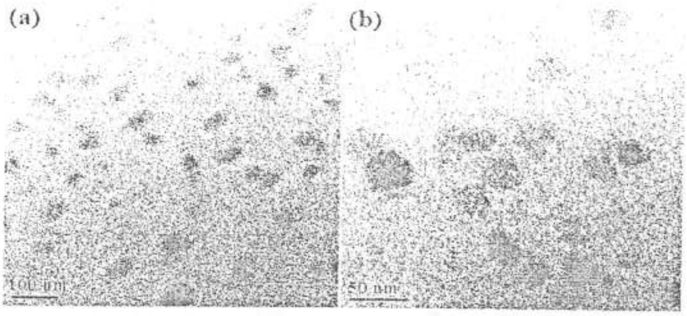

Fig. 2: TEM micrographs of S/J/G50/T5 composites (a) 100 nm and (b) 50 nm scales.

### *3. Mechanical properties study*

Effect of $TiO_2$ on the mechanical properties of the composites is summarized in table 2.

**Table 2** Comparison of the Tensile and Flexural properties of Unfilled and Filled jute based crosslinked SF nanocomposites

| Composite | Tensile Properties | | Flexural Properties | |
|---|---|---|---|---|
| System | Strength (MPa) | Modulus (MPa) | Strength (MPa) | Modulus (MPa) |
| SF/J/G50 | 9.54 (±1.33) | 937.2 (±17.47) | 14.51 (±2.08) | 1701.4 (±11.23) |
| SF/J/G50/T1 | 14.58 (±1.45) | 1121.8 (±15.76) | 27.52 (±1.78) | 2156.1 (±10.34) |
| SF/J/G50/T3 | 23.36 (±2.43) | 1791.3 (±11.64) | 37.86 (±2.13) | 2873.5 (±14.74) |
| SF/J/G50/T5 | 30.64 (±1.78) | 1876.5 (±19.23) | 46.75 (±1.46) | 3534.7 (±13.43) |
| SF/J/G50/T5/M1 | 32.58 (±1.65) | 1955.8 (±13.34) | 68.32 (±1.79) | 4128.8 (±12.82) |
| SF/J/G50/T5/M3 | 52.62 (±1.13) | 2362.9 (±16.38) | 82.19 (±1.12) | 6232.3 (±12.37) |
| SF/J/G50/T5/M5 | 47.45 (±2.11) | 2113.2 (±15.21) | 76.98 (±1.43) | 5789.4 (±11.52) |

* Each value represents average of ten samples.

Tensile strength and modulus as well as flexural strength and modulus of composites increased significantly for all the composite samples. The strength and modulus for sample SF/J/G50/T5/M5 is the highest and lowest for the sample SF/J/G50.

### *4. Dimensional stability test*

The effect of swelling in water vapour at room temperature (~$30^0$ C) and 65% relative humidity for the composite samples for different time periods is shown in Fig 3.

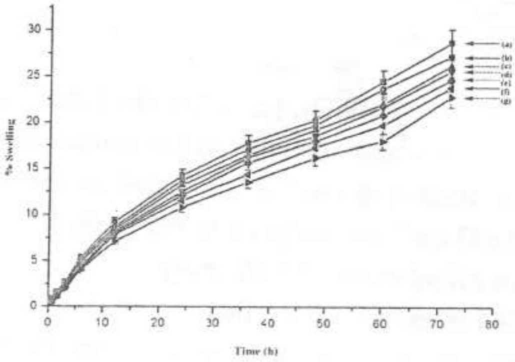

**Fig. 3.** Swelling behaviour of (a) SF/J/G50, (b) SF/J/G50/T1, (c) SF/J/G50/T3, (d) SF/J/G50/T5, (e SF/J/G50/T5/M1, (f) SF/J/G50/T5/M3 and (g) SF/J/G50/T5/M5.

## *(V) Jute – reinforced – Soya flour Composite*

### *Effect of ZnO and Nanoclay concentration*

We have prepared the samples as coded in Table 1. The wt (%) of the components viz. SF, glycerol and Jute are kept constant in all the samples where as the wt (%) of ZnO and nanoclay are varied. The wt (%) of the various components used for the synthesis of the composite are provided in Table 1.

**Table 1** Composition of plasticized soy flour based composite.

| Sample | Soy Flour[a] | Glycerol | GA | Jute | ZnO | Nanoclay |
|---|---|---|---|---|---|---|
| | | | (Wt. %) | | | |
| S/J/G50 | 100 | 5 | 50 | 75 | - | - |
| S/J/G50/Z1 | 100 | 5 | 50 | 75 | 1 | - |
| S/J/G50/Z3 | 100 | 5 | 50 | 75 | 3 | - |
| S/J/G50/Z5 | 100 | 5 | 50 | 75 | 5 | - |
| S/J/G50/Z5/M1 | 100 | 5 | 50 | 75 | 5 | 1 |
| S/J/G50/Z5/M3 | 100 | 5 | 50 | 75 | 5 | 3 |
| S/J/G50/Z5/M5 | 100 | 5 | 50 | 75 | 5 | 5 |

[a] 20 g of soy flour is assumed to be 100.

### *Results & Discussion:*

### *1. Fourier transform infrared spectroscopy (FT-IR) study*

The FTIR spectra of the S/J/G50, $TiO_2$, S/J/G50/T5 and S/J/G50/T5/M5 composites are shown in the fig. 1.

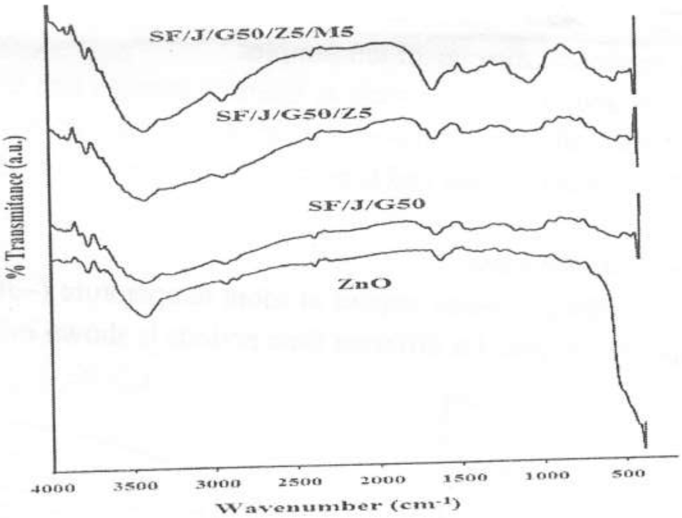

Fig. 1: IR spectra of (a) S/J/G50, (b) $TiO_2$, (c) S/J/G50/Z5 and (d) S/J/G50/Z5/M5.

Successful incorporation of $TiO_2$ and nanoclay in the composites is revealed by the IR spectrum.

### *2. Transmission Electron Microscopy (TEM) study*

Fig. 2 represents the TEM micrographs of ZnO incorporated composites (a) 100 nm scale and (b) 500 nm scale. From the TEM micrographs it can be said that ZnO nanoparticle has successfully incorporated into the S/J/G50 composite and the average particle size is ~50 nm.

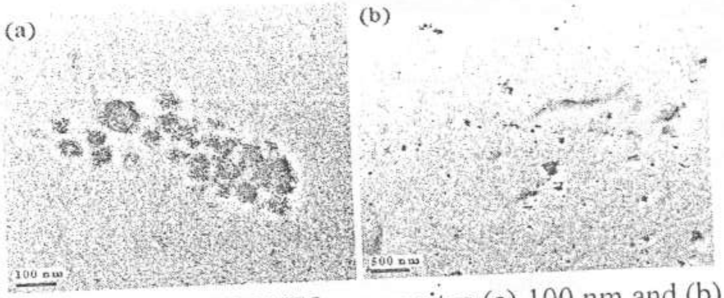

Fig. 2: TEM micrographs of S/J/G50/Z5 composites (a) 100 nm and (b) 500 nm scales.

### *3. Mechanical properties study*

Effect of ZnO on the mechanical properties of the composites is summarized in table 2.

**Table 2** Comparison of the Tensile and Flexural properties of Unfilled and Filled jute based crosslinked SF nanocomposites

| Composite System | Tensile Properties | | Flexural Properties | |
|---|---|---|---|---|
| | Strength (MPa) | Modulus (MPa) | Strength (MPa)* | Modulus (MPa) |
| SF/J/G50 | 8.24 (±2.33) | 927.9 (±13.56) | 12.91 (±1.48) | 1691.9 (±14.54) |
| SF/J/G50/Z1 | 15.38 (±2.41) | 1081.3 (±14.36) | 26.82 (±2.18) | 2078.4 (±12.98) |
| SF/J/G50/Z3 | 22.56 (±1.56) | 1841.5 (±17.34) | 35.26 (±1.93) | 2783.1 (±18.44) |
| SF/J/G50/Z5 | 31. 58 (±1.88) | 1956.6 (±12.83) | 48.95 (±1.86) | 3476.4 (±16.89) |
| SF/J/G50/Z5/M1 | 34. 64 (±1.25) | 2095.8 (±13.24) | 69.72 (±1.39) | 4251.8 (±19.65) |
| SF/J/G50/Z5/M3 | 55.64 (±1.49) | 2422.7 (±11.78) | 84.89 (±1.82) | 6223.2 (±17.31) |
| SF/J/G50/Z5/M5 | 49.25 (±2.81) | 2283.9 (±19.41) | 79.18 (±1.93) | 5699.6 (±14.57) |

* Each value represents average of ten samples.

Tensile strength and modulus as well as flexural strength and modulus of composites increased significantly for all the composite samples. The strength and modulus for sample SF/J/G50/Z5/M5 is the highest and lowest for the sample SF/J/G50.

### *4. Dimensional stability test*

The effect of swelling in water vapour at room temperature (~$30^0$ C) and 65% relative humidity for the composite samples for different time periods is shown in Fig 3.

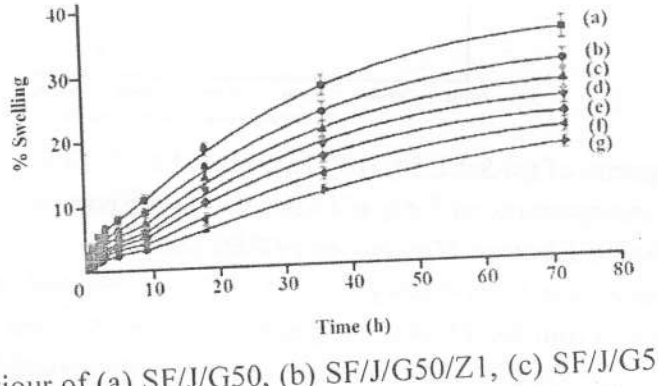

**Fig. 3.** Swelling behaviour of (a) SF/J/G50, (b) SF/J/G50/Z1, (c) SF/J/G50/Z3, (d) SF/J/G50/Z5, (e SF/J/G50/Z5/M1, (f) SF/J/G50/Z5/M3 and (g) SF/J/G50/Z5/M5.

**Publications and manuscripts prepared during the reported period of the project:**

1. Iman, M. and **Maji, T. K.** Effect of crosslinker and nanoclay on starch and jute fabric based green nanocomposites. *Carbohydrate Polymers,* 2012, 89, 290–297.
2. Iman, M. and **Maji, T. K.** Effect of Crosslinker and Nanoclay on Jute Fabric Reinforced Soy Flour Green Composite. *Journal of Applied Polymer Science,* 2012, DOI: 10.1002/APP.37713.
3. Iman, M., Bania, K. K. and **Maji, T. K.** Jute based crosslinked soy flour green nanocomposites reinforced with cellulose whisker and nanoclay. *Biomacromolecules (communicated).*
4. Iman, M. and **Maji, T. K.** Effect of nanoclay on jute fabric reinforced Soy flour-*g*-MMA green nanocomposites. (Manuscript, under preparation).
5. Iman, M. and **Maji, T. K.** Effect of nanoclay on jute based Starch-*g*-MMA green nanocomposites. (Manuscript, under preparation).
6. Iman, M. and **Maji, T. K.** Effect of $TiO_2$ and nanoclay on jute based soy flour green nanocomposites. (Manuscript, under preparation).
7. Iman, M. and **Maji, T. K.** Synergistic effect of ZnO and nanoclay on jute based soy flour green nanocomposites. (Manuscript, under preparation).

**Papers published in Conference Proceedings, Popular Journals etc.**

1. Iman, M and **Maji, T.K.,** Effect of Crosslinker and Nanoclay in Jute-reinforced-Starch composite, ***National Conference on Smart Nanostructures***, January 18-20, **2011**, Tezpur University, Assam, India.

2. Iman, M and **Maji, T.K.**, Effect of Crosslinker and Grafting on the properties of Jute-reinforced-Soy flour composite, ***National Seminar on Recent Advances in Synthesis and Catalysis***, February 10-12, **2011**, Dibrugarh University, Assam, India.

3. Iman, M and **Maji, T. K.,** Effect of Nanoclay on the properties of Jute-reinforced-Starch-g-MMA composites, ***National Conference on 'Chemistry, Chemical Technology and Society'***, November 11-12, **2011**, Tezpur University, Assam, India.

4. Iman, M and **Maji, T. K.,** Property Evaluation of Biodegradable Composites based on Cellulose microcrystalline powder and Natural Polymer, ***International Conference on Nanomaterials & Nanotechnology***, December 18-21, **2011**, University of Delhi, Delhi, India.

Annexure-II

## REQUEST FOR ANNUAL INSTALMENT WITH UP-TO-DATE STATEMENT OF EXPENDITURE

1. Sanction Order No and date: **SR/S5/GC-13/2008 Dated: 06/02/2009**

2. Total Project Cost: **10,56,200.00**

3. Revised Project Cost:
(if applicable)
4. Date of Commencement: **01.04.2009**

5. Statement of Expenditure:
(month wise expenditure incurred during current financial year)

| **Month & year** | **Expenditure incurred/ committed** |
|---|---|
| April, 2011 | 13340.00 |
| May, 2011 | 12000.00 |
| June 2011 | 14000.00 |
| July, 2011 | 14000.00 |
| August, 2011 | 14000.00 |
| September, 2011 | 15920.00 |
| October, 2011 | 14000.00 |
| November, 2011 | 14000.00 |
| December, 2011 | 98478.00 |
| January,2012 | 16140.00 |
| February, 2012 | 22855.00 |
| March, 2012 | 79359.00 |
| Total | 328092.00 |

6. Grant received in each year:
   a. 1st Year : 3,00,000.00
   b. 2nd Year : 4,00,000.00
   c. 3rd Year : 2,50,000.00
   d. Interest, if any :
   e. Total (a+b+c+d): 9,50,000.00

## Statement of Expenditure

(to be submitted financial year wise i.e. DOS* to 31st March of the financial year 2012

| Sr No | Sanctioned Heads | Funds Allocated (indicate sanctioned or revised | Expenditure Incurred | | | Total Expenditure IV + V + VI | Balance as on (date) | Requirement of Funds upto 31st March next year | Remarks (if any) |
|---|---|---|---|---|---|---|---|---|---|
| | | | 1st Year (01st April '09 to 31st March 2010) | 2nd Year (01st April '10 to 31st March 2011) | 3rd Year (01st April '11 to 31st March 2012) | | | | |
| (I) | (II) | (III) | (IV) | (V) | (VI) | (VII) | (VIII) = III – (IV+V+VII) | | |
| 1. | Manpower Costs | 4,90,000.00 | 1,30,248.00 | 1,44,000.00 | 1,64,000.00 | 4,38,248.00 | | Nil | |
| 2. | Consumables | 2,00,000.00 | 66,551.00 | 76,667.00 | 56,782.00 | 2,00,000.00 | | Nil | |
| 3. | Travel | 90,000.00 | Nil | 1,740.00 | 14370.00 | 16,110.00 | | Nil | |
| 4. | Contingencies | 1,00,000.00 | 33,339.00 | 32,389.00 | 34,272.00 | 1,00,000.00 | | Nil | |
| 5. | Others, if any | Nil | Nil | Nil | Nil | Nil | | Nil | |
| 6. | Equipment | Nil | Nil | Nil | Nil | Nil | | Nil | |
| 7. | Overhead Expenses | 1,76,000.00 | 58,666.00 | 58,666.00 | 58.668.00 | 1,76,000.00 | | Nil | |
| 8. | Total | 10,56,200.00** | 2,88,804.00 | 3,13,462.00 | 3,28,092.00 | 9,30,358.00 | 19,642.00 | | |

Name and Signature of Principal Investigator: Tarun K Maji
Date: 12.9.12

TARUN K MAJI )
Professor
Dept. of Chemical Sciences
Tezpur University

13/9/12
Signature of Competent financial authority: ________
(With seal)
Date: ________

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* DOS – Date of Start of project, 01.04.2009.

** **Total fund received Rs. 9,50,000.00 against the allocated fund of Rs. 10,56,200.00.**

Note:

1 Expenditure under the sanctioned heads, at any point of time, should not exceed funds allocated under that head, without prior approval of DST. 2. Figures in Column (VIII) should not exceed corresponding figures in Column (III)

Utilisation Certificate (Annexure III) for each financial year ending 31st March has to be enclosed along with request for carry-forward permission to the next financial year.

Annexure-III

## UTILISATION CERTIFICATE (2 COPIES)
## FOR THE FINANCIAL YEAR – 2011-2012(ENDING 31ST MARCH)

1. Title of the Project/ Scheme: **DEVELOPMENT OF GREEN NANOCOMPOSITE BASED ON NATURAL RESOURCES.**

2. Name of the Institution: **TEZPUR UNIVERSITY.**

3. Principal Investigator: **Professor TARUN KUMAR MAJI.**

4. Department of Science & Technology sanction order No & date sanctioning the project: **SR/S5/GC-13/2008 Dated: 06/02/2009**

5. Head of account as given in the original sanction order:

| | Total (in Rs.) |
|---|---|
| MANPOWER | 4,90,200.00 |
| EQUIPMENT | Nil |
| CONSUMABLES | 2,00,000.00 |
| TRAVEL | 90,000.00 |
| CONTINGENCY | 1,00,000.00 |
| OVERHEADS | 1,76,000.00 |
| TOTAL (in Rs.) | 10,56,200.00 |

| | | |
|---|---|---|
| 6. Amount brought forward from the previous Financial year quoting DST letter no and date in which the authority to carry forward the said amount was given | i. Amount:<br>ii. Letter No: **SR/S5/GC-13/2008**<br>iii. Date **02/07/2010** | **Rs. 97,734.00** |
| 7. Amount received during the financial year (Please give DST letter/order no and date) | i. Amount:<br>ii. Letter/Order No: **SR/S5/GC-13/2008**<br>iii. Dated: **29/7/2012** | **Rs. 2, 50,000.00** |
| 8. Total amount that was available for expenditure (excluding commitments) during the financial year (Sr. No. 6+7) | | **Rs. 3, 47,734.00** |
| 9. Actual Expenditure (excluding commitments) Incurred during the financial year (upto 31st March) | | **Rs. 3, 28,092.00** |
| 10. Balance amount available at the end of the financial year: | | **Rs. 19,642.00** |
| 11. Unspent balance refunded, if any (please give details of cheque no etc.): | | **Rs. 19,642.00** |
| 12. Amount to be carried forward to the next financial year (if applicable): | | **NA** |

## UTILISATION CERTIFICATE

Certified that out of **Rs. 2, 50,000.00** of grants-in-aid sanctioned during the year **2011-2012** in favour of **Registrar, Tezpur University** under this Ministry/ Department letter/ order No. **SR/S5/GC-13/2008** dated **29/07/2012** and Rs **97,734.00** on account of unspent balance of the previous year, a sum of **Rs 3, 47,734.00** has been utilized for the purpose of **Implementing the Project** for which it was sanctioned and that the balance of **Rs 19,642.00** remaining unutilized at the end of the year and the unspent balance refunded via cheque no. dated:

Tarun K Maji
Signature of PI
Date 12·9·12

RUN K MAJI
Professor
Chemical Sciences
University

14/9/12
Signature of Registrar/ Signature of Head
Registrar
Tezpur University
Date

13/9/12
Accounts Officer of the Institute
Date

(To be filled in by DST)

Certified that I have satisfied that the conditions on which the grants-in-aid was sanctioned have been fulfilled/ are being fulfilled and that I have exercised the following checks to see that the money was actually utilised for the purpose for which it was sanctioned:-

Kinds of checks exercised.

1.
2.
3.
4.
5.

Signature:____________
Designation:____________
Date:____________

# Statement of Expenditure

(to be submitted financial year wise i.e. DOS* to 31st March of the financial year 2012

| Sr No (I) | Sanctioned Heads (II) | Funds Allocated (indicate sanctioned or revised (III) | Expenditure Incurred | | | Total Expenditure IV + V + VI (VII) | Balance as on (date) (VIII) = III – (IV+V+VII) | Requirement of Funds upto 31st March next year | Remarks (if any) |
|---|---|---|---|---|---|---|---|---|---|
| | | | 1st Year (01st April '09 to 31st March 2010) (IV) | 2nd Year (01st April '10 to 31st March 2011) (V) | 3rd Year (01st April '11 to 31st March 2012) (VI) | | | | |
| 1. | Manpower Costs | 4,90,000.00 | 1,30,248.00 | 1,44,000.00 | 1,64,000.00 | 4,38,248.00 | | Nil | |
| 2. | Consumables | 2,00,000.00 | 66,551.00 | 76,667.00 | 56,782.00 | 2,00,000.00 | | Nil | |
| 3. | Travel | 90,000.00 | Nil | 1,740.00 | 14370.00 | 16,110.00 | | Nil | |
| 4. | Contingencies | 1,00,000.00 | 33,339.00 | 32,389.00 | 34,272.00 | 1,00,000.00 | | Nil | |
| 5. | Others, if any | Nil | Nil | Nil | Nil | Nil | | Nil | |
| 6. | Equipment | Nil | Nil | Nil | Nil | Nil | | Nil | |
| 7. | Overhead Expenses | 1,76,000.00 | 58,666.00 | 58,666.00 | 58,668.00 | 1,76,000.00 | | Nil | |
| 8. | Total | 10,56,200.00** | 2,88,804.00 | 3,13,462.00 | 3,28,092.00 | 9,30,358.00 | 19,642.00 | | |

Name and Signature of Principal Investigator: Tarun Maji
Date: 12.9.12

TARUN K MAJI
Professor
Dept. of Chemical Sciences
Tezpur University

13/9/12

Signature of Competent financial authority: ____________
(With seal)
Date: ____________

---

* DOS – Date of Start of project, 01.04.2009.

**** Total fund received Rs. 9,50,000.00 against the allocated fund of Rs. 10,56,200.00.**

Note:

1. Expenditure under the sanctioned heads, at any point of time, should not exceed funds allocated under that head, without prior approval of DST i.e. Figures in Column (VIII) should not exceed corresponding figures in Column (III)
2. Utilisation Certificate (Annexure III) for each financial year ending 31st March has to be enclosed along with request for carry-forward permission to the next financial year.