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Surface modification of ramie fibers using microwave assisted graft copolymerization followed by *Brevibacillus parabrevis* pretreatment

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ABSTRACT

Ramie fibers usually display poor interfacial adhesion when reinforced in hydrophobic polymer matrices. Hydrophilic nature of natural fibers becomes the most crucial issue in composites engineering. Surface modification of natural fibers has been found to be very effective in improving the fiber-matrix adhesion. In the present paper, we have reported the microwave assisted grafting of binary vinyl monomer mixtures on to ramie fibers (*Boehmeria nivea*) and bacterial cellulase assisted pre-treatment of ramie fibers using bacteria *Brevibacillus parabrevis*. The effects of these pretreatments on some properties of ramie fibers are discussed in the present paper. The modified fibers were characterized by scanning electron microscopy (SEM), X-ray diffraction, and TGA/DTA techniques to determine their morphology, crystallinity and thermal stability. Surface of ramie fiber becomes rough on grafting with synthetic polymers, whereas biologically modified ramie fibers showed the enhanced softness and smooth appearance due to the removal of gum materials and other impurities from the surface of fibers. Both the treatments have slightly changed the thermal stability and crystallinity of ramie fibers. Copyright © 2013 VBRI press.

Keywords: Ramie fibers, graft copolymers, cellulase, morphology, thermogravimetric analysis.

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Introduction

The development of commercially viable "green products" based on natural resources for both matrices and reinforcements is on the rise. Cellulose is probably one of the most ubiquitous and abundant biopolymers on the planet and has been used as a renewable raw material in a wide range of applications **[1-3]**. In order to develop composites with better mechanical properties and environmental performance, it becomes necessary to increase the hydrophobicity of the natural fibers and to improve the interface between matrix and natural fibers. The compatibility and dispersability of fiber and matrix can be improved by developing a hydrophobic coating of a compatible polymer on the surface of filler before being mixed with polymer matrix **[4]**.

Thus, the renewed interest in the natural fibers has resulted in a large number of modifications to bring it at par and even superior to synthetic fibers. Various greener methods have been explored such as plasma treatment, chemical treatment, treatments using fungi, enzymes and bacteria **[5, 6]** to improve the compatibility between natural fibers and hydrophobic polymer matrices. As the cellulosic fibers bear hydroxyl groups, therefore, they are amenable to modifications by different treatments.

Enzymes have attracted much interest because of the diversity of their application **[7]** in the bio processing of natural fibers such as biopolishing of fabrics to enhance softness and smooth appearance **[8]**, and for altering the morphology of natural fibers. Natural and man-made cellulosic fibers can be improved by an enzymatic treatment method called biopolishing. Biopolishing is a process of removal of gum and loose protruding fibers from the surface of fibers by enzymatic method, which results in smooth surface of the fibers **[9, 10]**. Enzymes used for biopolishing are actually a complex of cellulase enzymes. Cellulase refers to a group of enzymes which, acting together, hydrolyze cellulose. The enzyme performs a controlled hydrolysis of 1, 4-β-D-glycosidic linkage of the cellulosic fibres in order to modify the fabric surface. They are natural catalysts for the modification of cellulosic materials. Cellulases are inducible enzymes which are synthesized by microorganisms during their growth on cellulosic materials **[11]**. Many microorganisms including fungi and bacteria had been found to degrade cellulose and other plant cell wall fibers **[12]**. Bacteria, due to their high diversity, faster growth and capability to produce highly thermostable enzymes, are ideal for cellulase production **[13]**.

Natural polymers have received much scientific attention because of number of applications and grafting of synthetic polymers onto natural polymers is one of the best methods for modifying the surface properties of natural polymers **[14-21]**. Grafting of natural fibers with synthetic polymers can enhance their adhesion to polymer matrices. This is due to alteration of the characteristics of the surface topography, removal of non-crystalline constituents of the fibers such as hemicellulose (which is hydrophilic), lignin and pectin **[22]** and the removal of waxes and fatty acids present on the surfaces which can adversely affect interfacial bonding **[23]**.

Surface modification of natural fibers using chemical treatments becomes less attractive because of a number of limitations. So alternative methods should be adopted for the surface modification of natural fibers and environmentally friendlier methods are an excellent alternate for this **[6]**. The objective of this paper is to compare chemical modification of ramie fibers with environment friendly enzymatic treatment. There is scanty information in the literature about pretreatment of ramie fibers with bacterial cellulase. So in this paper, we have reported the graft copolymerization of ramie fibers with binary vinyl monomers and treatment with bacterial cellulase, and effect of these pretreatments on morphology and other properties of original fibers have been studied.

Experimental

Materials

Ramie fibers were obtained from Ramie Research Station (ICAR), Sorbhog, Assam (India). Bacteria strain Brevibacillus parabrevis (MTCC No. 2708) was purchased from Institute of Microbial Technology, Chandigarh, India. Yeast extract, beef extract, peptone and agar were purchased from Hi media. Glucose, methyl methacrylate, ethyl acrylate, acrylonitrile, acrylic acid, vinyl acetate, NaOH, NaCl, ferrous ammonium sulphate and hydrogen peroxide were purchased from S D Fine-Chem Ltd., India and were used as received.

Purification of ramie fibers

Ramie cellulose fibers (RCF) were washed with detergent in order to remove impurities and then Soxhlet extracted with acetone for 24 hours in order to remove waxes and other impurities and were dried at room temperature.

Grafting of binary vinyl monomer mixtures on to ramie fibers

Ramie fibers (500 mg) were activated by immersing in 100 ml distilled water for 24 hours prior to its grafting under the influence of microwave radiations. A definite ratio of FAS-H_2O_2 mixture was added to the reaction medium, which was followed by addition of binary vinyl monomer mixture, keeping MMA as the principal monomer. Optimum reaction conditions for maximum graft yield were obtained with grafting of principal monomer (MMA) on to ramie fiber prior to the grafting of binary vinyl monomer mixtures. Different binary vinyl monomer mixtures used were MMA+EA, MMA+AN, MMA+AA and MMA+VA. The reaction mixture was stirred and transferred to the microwave equipment operating at 210W microwave power for a specific time interval. The graft copolymers were soxhlet extracted so as to remove homopolymer. The graft copolymer obtained was dried in the hot air oven at 50 °C until a constant weight was obtained.

The percent graft yield (P_g) was calculated as follows:

$$P_g = \frac{W_2 - W_1}{W_1} \times 100$$

Where, W_1 and W_2 are the weights of original and grafted ramie fibers, respectively.

Pre-treatment of ramie fibers using Brevibacillus parabrevis bacteria

For bacterium growth, standard growth medium for Brevibacillus parabrevis (MTCC No. 2708) was prepared and pH was adjusted to 7.2 with sodium hydroxide. The starter culture was first autoclaved at 121 °C for 45 minutes and then inoculated with the bacterium strain in static conditions at 29±1 °C in an incubator. Glucose (1.5 g) was added into the culture medium to produce culture media. After 24 hours of bacteria Brevibacillus parabrevis incubation in static cultures, some of the suspension material was used to start agitated cultures. Under these conditions, strings of materials started appearing and were harvested by filtering with gauze on the third day. All products were kept in vacuumed desiccators with anhydrous calcium sulfate until characterization.

Ramie fibers (0.5 g) were put in 250 mL Erlenmeyer flasks containing 90 ml of culture medium which composed of 4 g/L glucose, 2 g/L yeast extract,1 g/L beef extract, 5 g/L peptone, 5 g/L NaCl and 20 g/L agar for bacteria *Brevibacillus parabrevis*. This formulated media was found to promote the bacterial medication of ramie fibers with stable pH. After autoclaving at 121 °C for 20 minutes, the flasks were inoculated with 10 ml of 24 hours old broth of a previous culture of bacteria *Brevibacillus parabrevis*. The reaction was conducted under agitated conditions on a shaking plate (150 rpm) in an environmental chamber at 30 °C for three days. After the fermentation, the modified ramie fibers were purified in 0.1M NaOH at 80 °C for 20 minutes to remove all microorganisms, medium components, and soluble polysaccharides. After filtration, they were then thoroughly washed in distilled water until neutral pH.

Characterization of modified ramie fibers

IR spectra of the original and modified ramie fibers were taken with KBr pallets on Perkin Elmer Spectrophotometer over a range of 4000-500 cm^{-1}. Scanning electron microscopic analysis of original and modified ramie fibers was carried-out on Electron Microscopy Machine (LEO 435 VP) in order to study the morphological changes as a result of surface modification. Thermo gravimetric analysis and differential thermal analysis were carried-out in nitrogen atmosphere at a heating rate of 10 ºC/minute using Perkin Elmer, (Pyris Dimond) thermal analyzer. X-ray diffraction studies were performed under ambient condition on X-ray diffractometer (Brucker D_8 Advance). Crystallinity was determined by using the wide angle X-ray diffraction counts at 2θ angle close to 22° and 18˚. The counter reading at peak intensity at 22° is said to represent the crystalline material and the peak intensity at 18º corresponds to the amorphous material in cellulose. Percentage crystallinity (%Cr) was calculated as follow **[24, 25]**:

$$\%Cr = \frac{I_{22}}{I_{22}+I_{18}} \times 100$$

Where, I_{22} and I_{18} are the crystalline and amorphous intensities at 2θ scale close to 22° and 18˚, respectively.

Results and discussion

Ramie fibers were immersed in water for 24 hours so as to open the active sites for grafting of copolymers. Grafting was carried-out by using solvent-monomer mixtures rather than pure monomer, which enhances the deep penetration of monomer inside the polymer matrix. C_2, C_3 and C_6 hydroxyl groups and C-H groups are the active cites for grafting in cellulosic fibers **[18]**. The grafting onto ramie fibers in presence of FAS-H_2O_2 (Fenton's reagent) takes place as per the mechanism proposed by Bhattacharya and Misra **[26]** and can be found elsewhere **[18]**.

Action of bacterial cellulase on ramie fibers resulted in stripping of fiber surface through hydrolysis of β 1, 4-glycosidic bond which removes subsequent layers or fibrils of the fiber by the mechanism of peeling effect leaving the fiber less hydrophilic and easier to drain **[27, 28]**. Increase in drainage has also been attributed to decrease in amount of amorphous and gel like polysaccharide layer on the surface **[29]** as well as removal of fuzz formation increases the commercial value of ramie fibers **[30]**. Slow kinetics of enzymatic degradation of crystalline cellulose allow fabric and fiber properties to be improved without excessive damage **[31]**.

Effect of concentrations of binary vinyl monomer mixtures on percent grafting

It is evident from **Table 1** that graft copolymerization of binary vinyl monomer mixtures (MMA+EA, MMA+AN, MMA+AA and MMA+VA) on to ramie fibers under the influence of micro-wave radiations using MMA (1.96×10^{-3} mol L^{-1}) as principal monomer, showed 64.4% (EA = 1.38×10^{-3} mol L^{-1}), 113.4% (AN = 3.03×10^{-3} mol L^{-1}), 50.0% (AA = 2.91×10^{-3} mol L^{-1}), 56.0% (VA= 2.16×10^{-3} mol L^{-1}) grafting, respectively.

High percentage grafting has been observed in the case of MMA+EA and MMA+AN binary mixtures in comparison to MMA+AA and MMA+VA binary mixtures, which is due to the presence of a strong acceptor monomer in the binary mixtures MMA+EA and MMA+AN **[32]**. However, the low graft yield with MMA+AA and MMA+VA was due to the fact that AA is more strongly associated with water which results in decreased free radical sites on the monomeric units and hence resulted in low graft yield **[33, 34]**. Whereas, in case of MMA+VA binary mixtures, two monomers with electron accepting and electron donating ability enter into a charge transfer complex formation thereby reducing the activity of monomers towards grafting **[35]**.

Table 1. Effect of concentrations of different binary monomer mixtures on P_g.

Binary monomer mixture	Concentration (mol/L x 10^{-3})	P_g
	1.96 + 0.92	37.6
MMA+EA	1.96 + 1.38	64.4
	1.96 + 1.84	47.2
	1.96 + 2.30	38.4
	1.96 + 2.76	29.6
	1.96 + 1.51	92.8
MMA+AN	1.96 + 2.27	98.7
	1.96 + 3.03	113.4
	1.96 + 3.79	90.2
	1.96 + 4.55	85.6
	1.96 + 1.45	38.7
MMA+AA	1.96 + 2.18	46.4
	1.96 + 2.91	50.0
	1.96 + 3.64	38.7
	1.96 + 4.37	24.6
	1.96 + 1.08	20.4
MMA+VA	1.96 + 1.62	36.8
	1.96 + 2.16	56.0
	1.96 + 2.70	24.6
	1.96 + 3.24	11.5

Pre-treatment of ramie fibers utilizing bacterial cellulase

Biopolishing of ramie fibers by utilizing cellulase from bacteria Brevibacillus parabrevis was observed for 3 days, at the pH 7.2 and 1.5 g glucose, which results in enhanced brightness due to the removal of gum materials and small fibrils protruding from the fibers surface **[9, 10]**. In general, glucose has been used as carbon source for bacteria *Brevibacillus parabrevis*. The optimum glucose concentration used for biopolishing was 1.5 gm. At higher glucose concentrations, the amount of gluconic acid increased during the cultivation period. The total amount of gluconic acid produced corresponds to the amount of glucose consumed in the period during which gluconic acid was increasing. This suggested that glucose not consumed by bacteria was metabolized to gluconic acid and other substances. With the increase in glucose concentration, the accumulation of gluconic acid also increased and no more glucose was available for the bacteria to grow **[36]**. Moreover, the accumulated gluconic acid also lowered the pH of the culture media and inhibited cellulase production by deactivating the bacteria.

Amount of extracellular protuberant structures on the fiber due to cellulase production by bacteria Brevibacillus parabrevis increased linearly with culture time upto 3rd day and then decreased. This is due to the fact that after 3rd day most of the glucose was metabolized via gluconic acid to other substances and hence, no more glucose was available for the bacteria to grow. Moreover, the accumulated gluconic acid also lowered the pH of the culture media which deactivated the bacteria resulting in inhibition of bacterial cellulase **[36]**.

Characterization of biologically and chemically modified ramie fibers

Fourier Transform Infrared Spectroscopy (FTIR):

IR spectrum of ramie fibers showed a peak at 3427.09 cm^{-1} due to bonded –OH group and at 2918.06 cm^{-1}, 1644.82 cm^{-1} and 1192.74 cm^{-1} arising from $–CH_2$, C-C and C-O stretching, respectively.

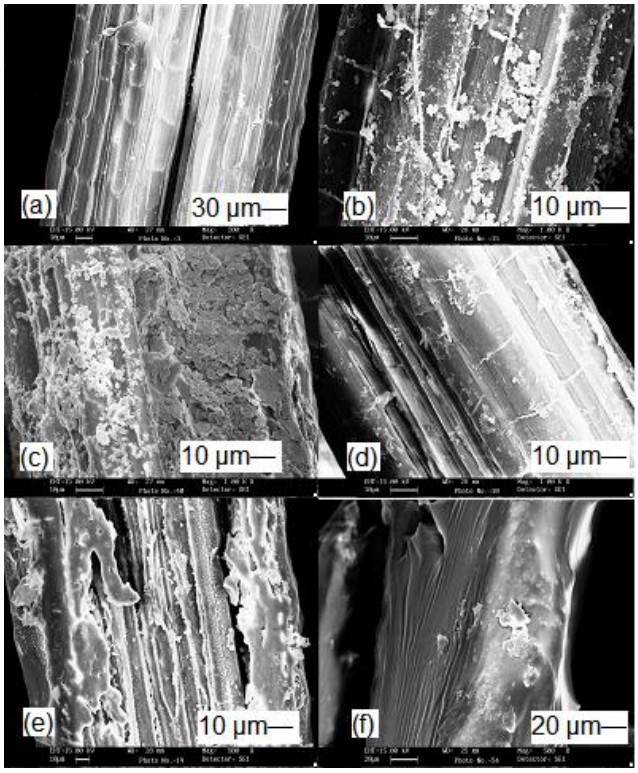

Fig. 1. SEM of (a) original ramie fibers (b) ramie-g-poly(MMA+EA), (c) ramie-g-poly(MMA+AN), (d) ramie-g-poly(MMA+AA), (e) ramie-g-poly(MMA+VA), and (f) bacterial cellulase treated ramie fibers.

In case of ramie-g-poly(MMA+EA), ramie-g-poly(MMA+AN), ramie-g-poly(MMA+AA) and ramie-g-poly(MMA+VA), additional peaks at 1779.35 cm^{-1}, 2253.23 cm^{-1}, 1682.83 cm^{-1} and 1750.13 cm^{-1} due to >C=O of EA, -C≡N of AN, >C=O of –COOH of AA and >C=O of VA, were observed, respectively. An additional peak was

observed at 2695.01 cm^{-1} due to –OH of –COOH of AA **[16, 24]**. This suggests that EA, AN, AA and VA were graft copolymerized onto ramie fiber through covalent linkages **[16, 37]**. In case of *Brevibacillus parabrevis* treated ramie fiber, peaks at 3417.02 cm^{-1}, 2990.69 cm^{-1}, 1643.36 cm^{-1} and 1155.75 cm^{-1} has been observed due to –OH, -CH_2, C-C and C-O stretching. In addition to this, IR spectrum of ramie fiber treated with bacteria *Brevibacillus parabrevis* also showed a peak at 3501.20 cm^{-1}.

Morphology of original and modified fibers:

Fig. 1 shows the morphology of original fibers, ramie-g-copolymers and biologically modified ramie fibers. Comparison of the scanning electron micrographs reveals a clear cut distinction between original (**Fig. 1a**) and modified ramie fibers. Morphology of ramie fibers was changed after both biological and chemical treatments. Surface of ramie fibers was smooth but on grafting with binary vinyl monomer mixtures it becomes rough (**Fig. 1(b-e) [38]**, whereas biologically modified ramie fibers showed the enhanced softness and smooth appearance due to the removal of gum materials and small fibrils from the surface of fibers (**Fig. 1f**).

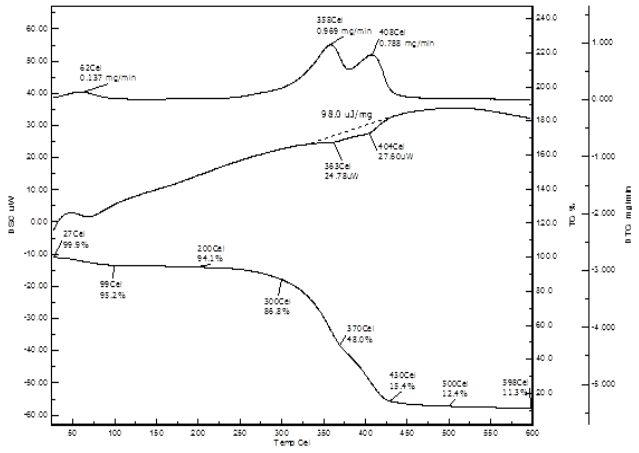

Fig. 2. TGA/DTA of original ramie fibers.

Thermal properties original and modified fibers:

Fig. 2-7 shows the TGA/DTA of original ramie fibers, grafted ramie fibers and biologically modified ramie fibers. In case of ramie fibers (**Fig. 2**), ramie-g-poly(MMA+EA) (**Fig. 3**), ramie-g-poly(MMA+AN) (**Fig. 4**), ramie-g-poly(MMA+AA) (**Fig. 5**), and ramie-g-poly(MMA+VA) (**Fig. 6**), and biologically modified ramie fibers (**Fig. 7**), two stage decomposition has been observed. It has been found that initial decomposition temperature of ramie fibers, ramie-g-poly(MMA+EA), ramie-g-poly(MMA+AN), ramie-g-poly(MMA+AA), ramie-g-poly(MMA+VA) and ramie fibers modified by bacteria *Brevibacillus parabrevis* was around 300 °C, 300 °C, 300 °C, 200 °C, 250 °C and 300 °C, respectively. Whereas, final decomposition temperature of ramie fibers, ramie-g-poly(MMA+EA), ramie-g-poly(MMA+AN), ramie-g-poly(MMA+AA), ramie-g-poly(MMA+VA) and ramie fibers modified by bacteria *Brevibacillus parabrevis* was around 430 °C, 425 °C, 430 °C, 413 °C, 419 °C and 363 °C, respectively.

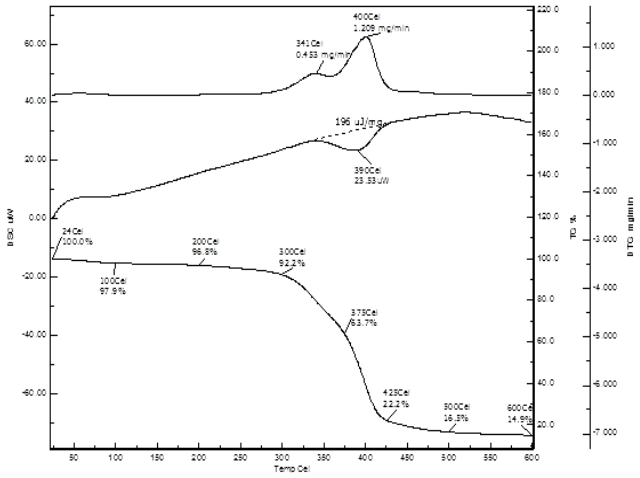

Fig. 3. TGA/DTA of ramie-g-poly(MMA+EA).

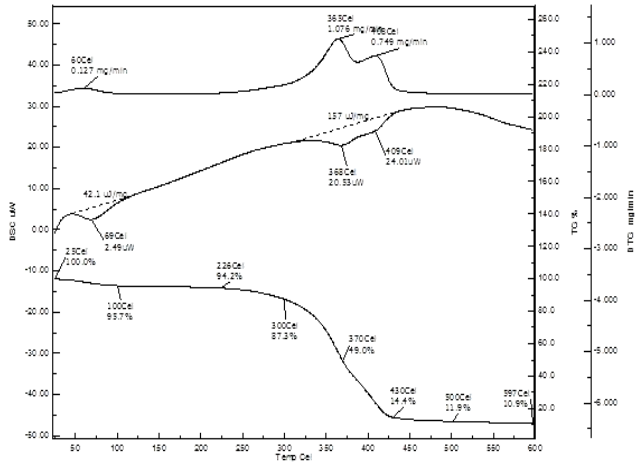

Fig. 4. TGA/DTA of ramie-g-poly(MMA+AN).

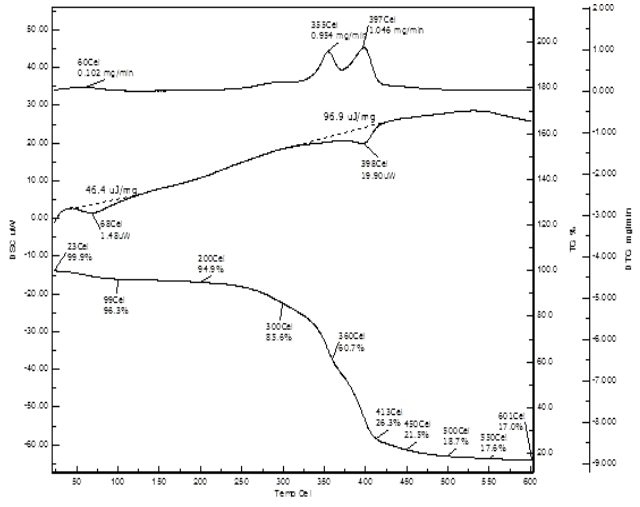

Fig. 5. TGA/DTA of ramie-g-poly(MMA+AA).

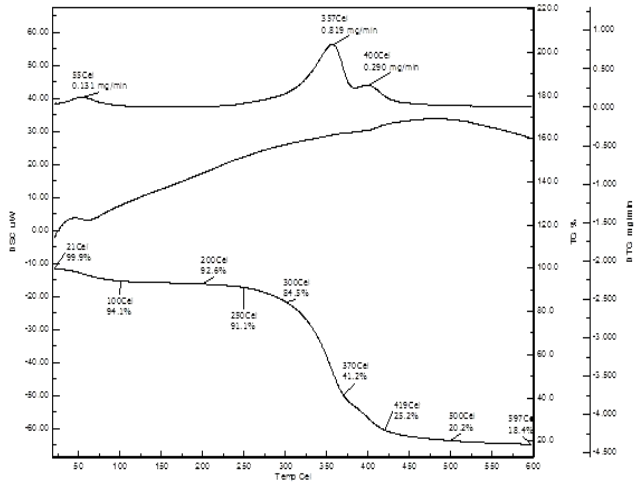

Fig. 6. TGA/DTA of ramie-g-poly(MMA+VA).

Maximum thermal stability (430 °C) has been found in case of ramie fibers and ramie-g-poly(MMA+AN) followed by ramie-g-poly(MMA+EA), ramie-g-poly(MMA+VA), ramie-g-poly(MMA+AA) and ramie fibers modified with bacteria *Brevibacillus parabrevis*. It was found that a chemical treatment decreases the thermal stability of ramie fibers but not altered very much in comparison to original ramie fibers. It is due to the reason that the graft copolymers prepared under the influence of microwave radiations showed negligible disturbances in the crystalline lattice of ramie fiber as the optimum reaction time for grafting under MWR was very low and thus fiber faces no disturbances in its crystal structure, thereby retaining almost similar crystalline structure **[39]**. Whereas in case of modification with bacterial cellulase, thermal stability was found to decreased due to hydrolyses of cellulose by exo-cleavage of β-1, 4-glycosidic linkage **[40]**. Exo-acting cellulases are more active on the crystalline regions of ramie cellulose **[41]**, thereby disturbing the crystalline structure of ramie fiber, which resulted in a decreased thermal stability.

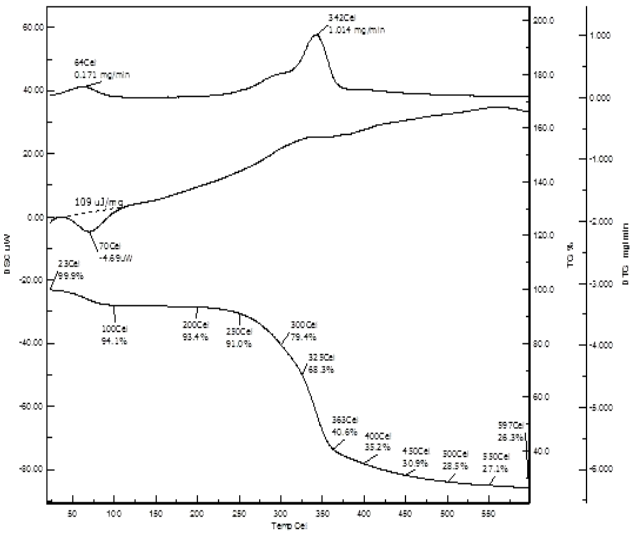

Fig. 7. TGA/DTA of bacterial cellulose treated ramie fibers.

Crystallinity of original and modified fibers:

Table 2 shows the XRD data of original ramie, grafted ramie fiber and biologically modified ramie fibers. It is evident from **Table 2** that percentage crystallinity of ramie fibers, ramie-g-poly(MMA+EA), ramie-g-poly(MMA+AN), ramie-g-poly(MMA+AA), ramie-g-poly(MMA+VA) and cellulase treated ramie fibers was found to be 80.1, 73.7, 74.9, 73.0, 76.7 and 75.5 and 66.6 %, respectively.

Table 2. Crystallinity of original, graft copolymers and cellulase treated ramie fibers.

Fibers	At 2θ Scale		% Cr	C.I
	I_{22}	I_{18}		
Ramie fiber	1929	478	80.1	0.75
Ramie-g-poly(MMA+EA)	1536	514	74.9	0.66
Ramie-g-poly(MMA+AN)	1290	476	73.0	0.63
Ramie-g-poly(MMA+AA)	1582	480	76.7	0.69
Ramie-g-poly(MMA+VA)	1482	479	75.5	0.67
cellulase treated ramie fibers	955	499	66.6 2	0.49

Therefore, %Cr of ramie fibers decreases on chemical and biological modification. A small change in thermal stability is due to the grafting of copolymers, which disturbed the crystalline structure of ramie fibers because of impregnation of monomer chains in the matrix and the fiber becomes amorphous **[42, 43]**. In cellulase treatment, it is due to extracellular cellulase which hydrolyses cellulose by exo-cleavage of β-1, 4-glycosidic linkage **[40]**. Exo-acting cellulases are more active on the crystalline regions of ramie cellulose fibers **[41]**, thereby disturbing the crystalline structure and hence resulted in decreased %Cr. Crystallinity index of ramie fiber, ramie-g-poly(MMA+EA), ramie-g-poly(MMA+AN), ramie-g-poly(MMA+AA), ramie-g-poly(MMA+VA) and biologically modified ramie fibers was 0.75, 0.66, 0.63, 0.69 and 0.67 and 0.49, respectively. A lower crystallinity index in case of biologically and chemically modified ramie fiber means poor order of cellulose crystals in the fiber. This is due to misorientation of the cellulose crystals to the fiber axis during hydrolysis of cellulose by cellulase and incorporation of polymer chain during grafting of copolymers **[44]**.

Conclusion

Surface modification of ramie fibers by utilizing bacteria *Brevibacillus parabrevis* and microwave assisted grafting are effective methods. Both treatments have little effect on thermal stability and crystalline structure of ramie fibers but enhanced the hydrophobicity of fibers. Morphology of

ramie fibers was changed after pretreatments. Surface of ramie fibers becomes rough on graft copolymerization, whereas it becomes soft and bright on biological modification. Surface modification of ramie fibers with bacterial cellulase is a green method and modified fibers can be used as reinforcing material for the fabrication of composite materials.

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