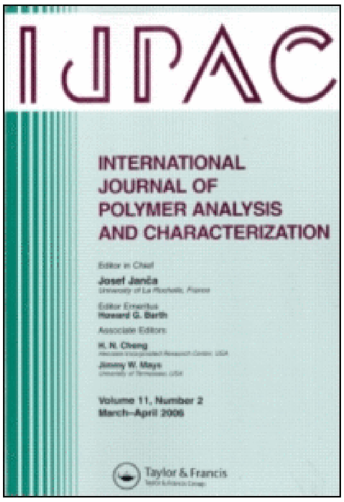
This article was downloaded by:
On: *21 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



International Journal of Polymer Analysis and Characterization
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646643

Synthesis and Characterization of Graft Co-Polymers of Flax Fiber with Binary Vinyl Monomers

B. S. Kaith[a]; Susheel Kalia[a]
[a] Material Science Laboratory, National Institute of Technology (Deemed University), Hamirpur, India

To cite this Article Kaith, B. S. and Kalia, Susheel(2007) 'Synthesis and Characterization of Graft Co-Polymers of Flax Fiber with Binary Vinyl Monomers', International Journal of Polymer Analysis and Characterization, 12: 5, 401 — 412

To link to this Article: DOI: 10.1080/10236660701543676

URL: http://dx.doi.org/10.1080/10236660701543676

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

International Journal of Polymer Anal. Charact., 12: 401–412, 2007
Copyright © Taylor & Francis Group, LLC
ISSN: 1023-666X print
DOI: 10.1080/10236660701543676

Downloaded At: 15:54 21 January 2011

Synthesis and Characterization of Graft Co-Polymers of Flax Fiber with Binary Vinyl Monomers

B. S. Kaith and Susheel Kalia
Material Science Laboratory, National Institute of Technology
(Deemed University), Hamirpur, India

Abstract: Grafting of flax fiber with binary vinyl monomer mixtures such as methylmethacrylate (MMA)/ethyl acrylate (EA), MMA/acrylonitrile (AN), and MMA/acrylic acid (AA) was carried out. At a pressure of 8 Kg/cm^2 under optimum reaction conditions 41.74% grafting resulted. Maximum grafting (109.9%) was found with MMA + EA binary monomer mixture. Synthesized graft co-polymers were characterized with FT-IR spectroscopy, scanning electron microscopy (SEM), TGA/DTA techniques, and X-ray diffraction (XRD). Thermal stability of flax-g-poly(MMA/AA) was found to more than that of flax fiber and other graft co-polymers. On grafting, percentage crystallinity decreases rapidly with reduction in its stiffness and hardness. Flax fiber showed the highest value of percentage crystallinity (76.96 %) and crystallinity index (0.7005) in comparison to flax-g-co-polymers.

Keywords: Flax; Flax-g-co-polymers; Grafting; IR; SEM; TGA/DTA; XRD

INTRODUCTION

Desirable and targeted properties can be imparted to natural or synthetic polymers through graft co-polymerization in order to meet the requirements of specialized applications. This has led to a new class of materials

Received 14 June 2007; accepted 29 June 2007.

Address correspondence to B. S. Kaith, Material Science Laboratory, National Institute of Technology (Deemed University), Hamirpur – 177 005 (H.P.), India. E-mail: bskaith@yahoo.co.in; kaith@nitham.ac.in

called specialty polymers, which play an important role in many frontline technological applications.

Chauhan et al.[1] graft co-polymerized a binary mixture of styrene and maleic anhydride onto cellulose extracted from *Pinus roxburghii* needles. The grafting reaction was initiated with gamma rays in air by the simultaneous irradiation method. Grafting parameters and reaction rate achieve maximum values when the molar ratio of styrene and maleic anhydride is 1:1. Thermal behavior of graft co-polymers showed that all graft co-polymers exhibit single-stage decomposition with characteristic transitions at 161°–165°C and 290°–300°C. Graft co-polymerization of methacrylate (MA), ethyl acrylate (EA), and ethyl methacrylate on carboxymethyl cellulose by the use of ceric ion in aqueous medium at 35°C has been carried out by Okieimen and Ogbeifun.[2] It has been observed that the frequencies of grafting of monomers were not of the same order of magnitude even though the reaction conditions were the same. Ali et al.[3] prepared the high α-cellulose from a fast-growing annual plant, *Hibiscus sabdariffa*. Grafting of acrylonitrile (AN) onto high α-cellulose was carried out, and the graft co-polymers were characterized with infrared (IR) spectroscopy and scanning electron microscopy (SEM). Karlsson and Gatenholm[4] have prepared cellulose fiber-supported hydrogels of HEMA by using the ozone-induced graft co-polymerization method and studied the effect of various process parameters during ozone treatment on the ability to form hydroperoxides on the cellulose fibers. Abdel-Razik[5] reported the homogeneous grafting of dichloro dimethyl silane onto ethyl cellulose. Grafting of some acrylates and methacrylates onto cellulose and silk in the absence of radical initiator was studied. It has been found that polymerization of methacrylates proceeded more easily than that of acrylates and grafting was much higher onto silk than cellulose.[6]

In the present study, flax has been modified through graft co-polymerization with binary vinyl monomers. Flax-g-co-polymers thus prepared were characterized with IR, thermogravimetric analysis/differential thermal analysis (TGA/DTA), SEM, and X-ray diffraction (XRD) techniques.

Downloaded At: 15:54 21 January 2011

EXPERIMENTAL SECTION

Materials

Flax fiber (*Linum usitatissimum*) was obtained from the Department of Agronomy, CSK HP Agriculture University, Palampur (India). Monomers were washed with 5% sodium hydroxide followed by water and were dried over anhydrous sodium sulphate. The dried monomers were distilled and the middle fraction was used. A Libror AEG-220 (Shimadzu) electronic balance was used for weighing.

IR spectra, thermal analysis, SEM, and XRD of the samples were recorded with a Perkin Elmer RXI Spectrophotometer, Thermal Analyzer (Linseis L-81 11), Electron Microscopy Machine (LEO 435VP), and Bruker D_8 Advance, respectively. Strength of fibers was measured with a Stelometer (MAG, FO501).

Methods

Graft Co-Polymerization of Binary Vinyl Monomer Mixtures onto Flax Fibers

A 0.5 g amount of flax fiber was immersed in 100 mL of distilled water for 24 h prior to grafting. A known amount of binary monomer mixture and a definite ratio of initiator (FAS-H_2O_2) were added to the reaction mixture. The reaction mixture was stirred and transferred to an autoclave at a definite pressure for a definite time interval (120 min). Various reaction parameters were optimized and the separation of homo-polymer from the grafted fibers was carried out so as to get maximum graft yield. Graft co-polymers obtained were dried in a hot air oven at 50°C till constant weight was obtained. The percentage grafting (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 the original flax fibers and the grafted flax fibers, respectively.

Infrared Spectroscopy (IR)

IR spectra of the ungrafted and grafted flax fiber were taken with KBr pellets on a Perkin Elmer RXI Spectrophotometer.

Scanning Electron Microscopy (SEM)

Scanning electron microscopic studies of flax and its graft co-polymers were carried out on an Electron Microscopy Machine (LEO 435VP). Since cellulose is nonconducting material, it was gold plated to have an impact. Scanning was synchronized with the microscopic beam in order to maintain a small size over a large distance relative to the specimen. The resulting images had a great depth of the field. A remarkable three-dimensional appearance with high resolution was obtained. The scans could easily verify the fact that cellulosic fibers lying apart in the raw sample started forming bundles in the graft co-polymers.

Downloaded At: 15:54 21 January 2011

Thermogravimetric Analysis/Differential Thermal Analysis (TGA/DTA)

Thermogravimetric analysis and differential thermal analysis studies were carried out in air at a heating rate of 10°C/min on a thermal analyzer (Linseis, L-81 11).

X-Ray Diffraction (XRD) Studies

X-ray diffraction studies were performed on a diffractometer (Bruker AXS D_8 Advance) under ambient conditions using Cu Kα (1.5418°A) radiation, a Ni filter, and a scintillation counter as detector at 40 KV and 40 mA on a rotation between 5° and 50° at 2θ scale at 1 s step size and increments of 0.01° with 0.5° or 1.0 mm of divergent and anti-scattering slit. A small particle size of each sample of flax-g-co-polymers and flax fiber was made. Each sample was homogeneously mixed prior to subjecting it to X-ray diffractometry. The sample holder was made of PMMA polymer and consisted of a round central cavity. The outer diameter of the holder was 50 mm, the central cavity had a diameter of 25 mm, which retained the sample height of 1 mm, and the holder height was 8.5 mm. The holder was then held in the vertical position and the sample was tapped gently. A glass slide was clipped up to the top face of the sample holder first, so as to form a wall of the sample in symmetry to the holder walls. This procedure was repeated until the cavity was filled. Finally, the glass slide was carefully removed without disturbing the sample surface. Powder outside the central cavity was removed with tissue paper. Corrundum was the reference used to calibrate the instrument.

The randomly oriented powdered sample with a uniform surface was exposed to X-rays from all possible planes of the sample, and then the scattering angle of the diffracted X-rays was measured with respect to the angle of the incident beam. Continuous scans were taken and relative intensity was obtained. Crystalline index (C.I.), which measures the orientation of the cellulose crystals in a fiber to the fiber axis, 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 18° corresponds to the amorphous material in cellulose material.[7] Percentage crystallinity (%Cr) and crystalline index (C.I.) were calculated as follows:[8–10]

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

$$\mathrm{C.I.} = \frac{I_{22} - I_{18}}{I_{22}}$$

Downloaded At: 15:54 21 January 2011

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

Fiber Strength

Strength of fiber bundles was determined with a fiber bundle strength tester (Stelometer) using standard test method ASTM D-1445-95 (Flat Bundle Method). A definite number of fibers (five) were taken in a bundle that was put in the Stelometer. Total strength (gms/tex) required to break the fiber bundle was measured and calculated as follows:

$$\text{Strength}(\text{Kg/mg}) = \frac{\text{Total strength of fiber in Kg}}{\text{Total weight of fiber in mg}}$$

$$\text{Strength (gms/tex)} = \text{Strength (Kg/mg)} \times 15.0 \text{ (constant factor)}$$

$$\text{Actual Strength (gms/tex)} = \text{Strength (gms/tex)} \times \text{Humidity correction factor}$$

where the humidity correction factor at RH 53% is 1.0756.

Downloaded At: 15:54 21 January 2011

RESULTS AND DISCUSSION

C_2, C_3, and C_6 hydroxyls and the C–H groups are the active sites for grafting in cellulosic fibers. The grafting onto flax fibers in the presence of FAS-H_2O_2 takes place according to the mechanism proposed by Bhattacharya and Misra.[11]

Effect of Concentration of Binary Monomer Mixtures on Percent Grafting

Graft co-polymerization of binary vinyl monomer mixtures such as methylmethacrylate/EA (MMA/EA), MMA/AN, and MMA/acrylic acid (MMA/AA) onto flax fiber under pressure using MMA ($1.96 \times 10^{-3}\,\text{mol}\,\text{L}^{-1}$) as the principal monomer showed 109.9% (EA = $2.30 \times 10^{-3}\,\text{mol}\,\text{L}^{-1}$), 94.32% (AN = $3.79 \times 10^{-3}\,\text{mol}\,\text{L}^{-1}$), and 55.94% (AA = $2.91 \times 10^{-3}\,\text{mol}\,\text{L}^{-1}$) grafting, respectively (Table I).

Higher percent grafting has been observed in the case of MMA/EA and MMA/AN binary mixtures than in MMA/AA, which is due to the presence of a strong acceptor monomer in the binary mixtures MMA/EA and MMA/AN. The low graft yield with MMA/AA was due to the fact that AA is more strongly associated with water, thereby resulting in decreased free radical sites and hence resulting in low graft yield.

Table I. Effect of concentrations of different binary monomer mixtures on P_g (weight %)

Reaction condition	Binary monomers	Concentrations ($\times 10^{-3}$ mol L^{-1})	P_g (weight%)
Under pressure	MMA + EA	1.96 + 2.30	109.9
	MMA + AN	1.96 + 3.79	94.32
	MMA + AA	1.96 + 2.91	55.94

Characterization of Graft Co-Polymers

Fourier Transform-Infrared (FT-IR) Spectroscopy

Flax fiber showed broad peaks at 3422.8 cm^{-1} due to bonded –OH and at 2918.8, 1653.5, and 1058.7 cm^{-1} arising from $-CH_2$, C–C, and C–O stretching, respectively. Graft co-polymers showed additional peaks at 1735.5 cm^{-1} due to the carbonyl group of EA, at 2364.9 cm^{-1} due to the nitrile group of AN, and at 2358.3 cm^{-1} due to the –OH group of AA.

Scanning Electron Microscopy (SEM)

Scanning was synchronized with the microscopic beam in order to maintain a small size over a large distance relative to the specimen. The scans could easily verify the fact that cellulosic fibers lying apart in the original sample started forming bundles in the graft co-polymers.

A clear-cut distinction between scanning electron micrographs of the original flax and its graft co-polymers, flax-g-poly(MMA/EA), flax-g-poly(MMA/AN), and flax-g-poly(MMA/AA) was observed (Figures 1–4).

Thermal Behavior of Graft Co-Polymers

Thermogravimetric analysis (TGA) of the original flax fiber and graft co-polymers was carried out as a function of weight loss versus temperature. The results of TGA are depicted in Table II. In the case of flax fiber, three-stage decomposition has been observed, with maximum weight loss occurring between 279.9° and 341.8°C (37.0%), 341.8° and 429.3°C (12.57%), and 429.3° and 489.1°C (22.57%). Initial and final decomposition temperatures of original flax fiber are 279.9°C and 489.1°C, respectively (Figure 5). In the case of the prepared graft co-polymers, flax-g-poly(MMA/EA), flax-g-poly(MMA/AN), and flax-g-poly (MMA/AA), the initial decomposition temperatures (IDTs) are 327.3°,

Downloaded At: 15:54 21 January 2011

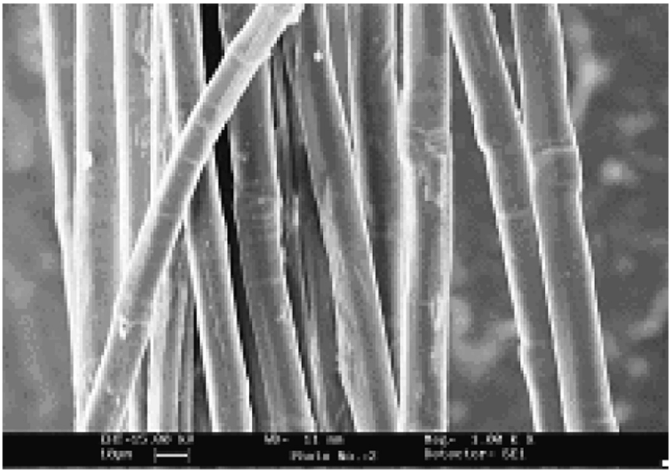


Figure 1. SEM of flax.

Downloaded At: 15:54 21 January 2011

329.8°, and 303.1°C, respectively, and the final decomposition temperatures (FDTs) are 388.1°, 396.9°, and 494.2°C, respectively. It can be observed from the above-mentioned results that graft co-polymers of poly(MMA/AA) with flax fiber prepared under pressure showed higher final decomposition temperature. Therefore, thermal stability of flax-g-poly(MMA/AA) has been found to be higher than that of flax fiber and other graft co-polymers (Figure 6).

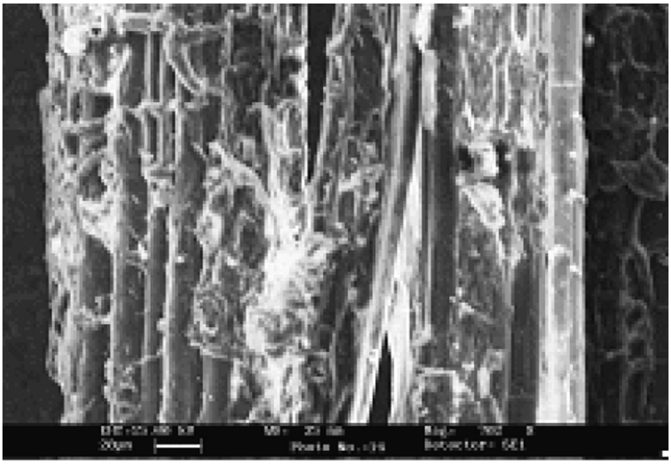


Figure 2. SEM of flax-g-poly(MMA/EA).

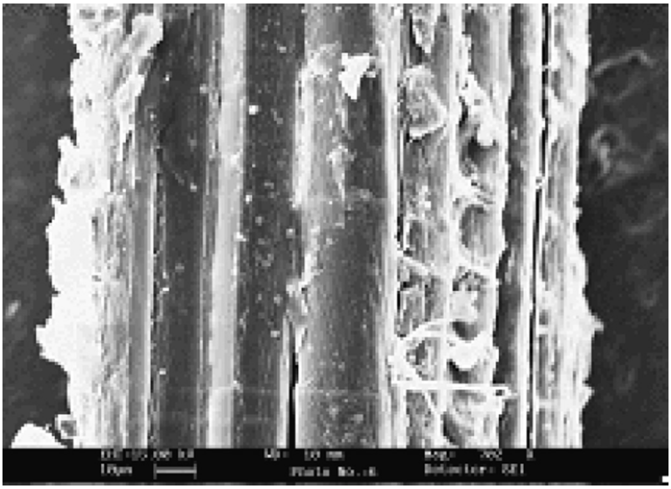


Figure 3. SEM of flax-g-poly(MMA/AN).

TGA results have been supported by DTA studies. DTA of flax fiber showed exothermic peaks at 325.3°C (13.8 μV) and 455.3°C (38.9 μV). These peaks show disturbance in the H-bonded amorphous region and complete breakdown of C–C and C–O bonds of the crystalline region. However, in the case of the graft, a continuous exothermic rise in temperatures has been observed. In the case of flax-g-poly(MMA/AA), sharp exothermic peaks have been observed at 437.3°C (47.6 μV)

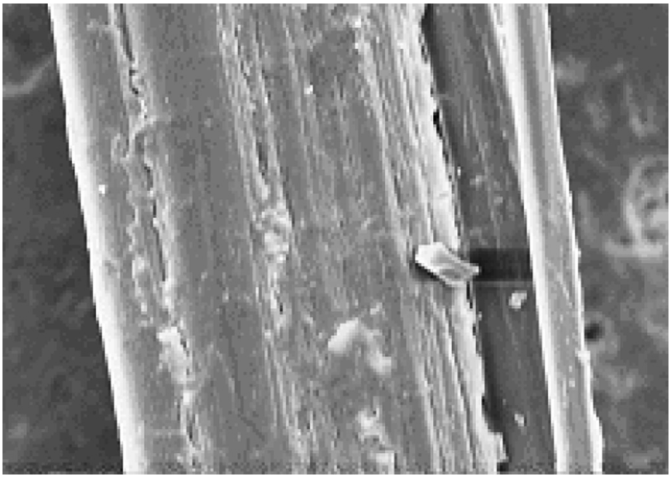


Figure 4. SEM of flax-g-poly(MMA/AA).

Downloaded At: 15:54 21 January 2011

Table II. TGA/DTA of flax and its graft co-polymers

		Thermogravimetric analysis		Differential thermal analysis
Sr. no.	Sample	IDT (°C)	FDT (°C)	Exothermic peaks at temperature (μV)
1.	Flax fiber	279.9	489.1	325.3°C (13.8) 455.3°C (38.9)
2.	Flax-g-poly(MMA/EA)	327.3	388.1	359.8°C (52.2)
3.	Flax-g-poly(MMA/AN)	329.8	396.9	372.6°C (46.9)
4.	Flax-g-poly(MMA/AA)	303.1	494.2	437.3°C (47.6)

(Table II). With increase in percentage of grafting,the original crystal lattice of the fibers gets disturbed, which results in lower final decomposition temperature of the graft co-polymers. Thus, it can be seen that a direct correlation exists between percentage of grafting and crystallinity.

X-Ray Diffraction (XRD) Studies

The X-ray spectrum of flax fiber is more convex than that of graft co-polymers (Figure 7). In the case of flax fiber, the incorporation of monomer chains in the backbone of the flax impaired the crystallinity of flax fiber. Therefore, on grafting, percentage crystallinity decreases rapidly with reduction in stiffness and hardness.

Downloaded At: 15:54 21 January 2011

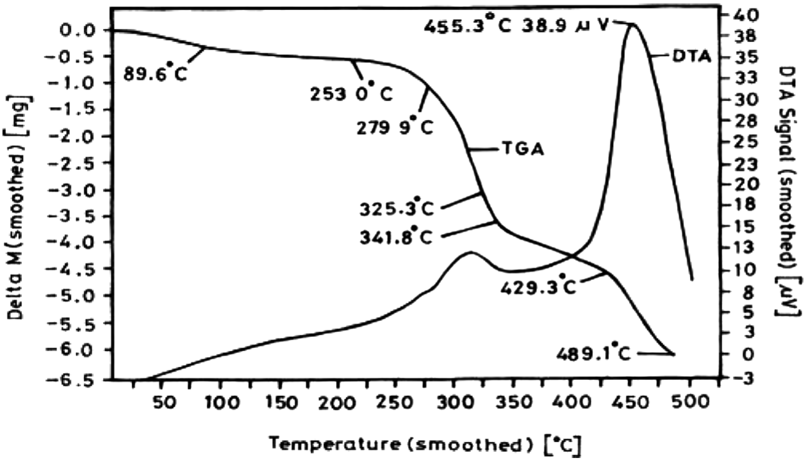


Figure 5. TGA/DTA curves of flax fiber.

Downloaded At: 15:54 21 January 2011

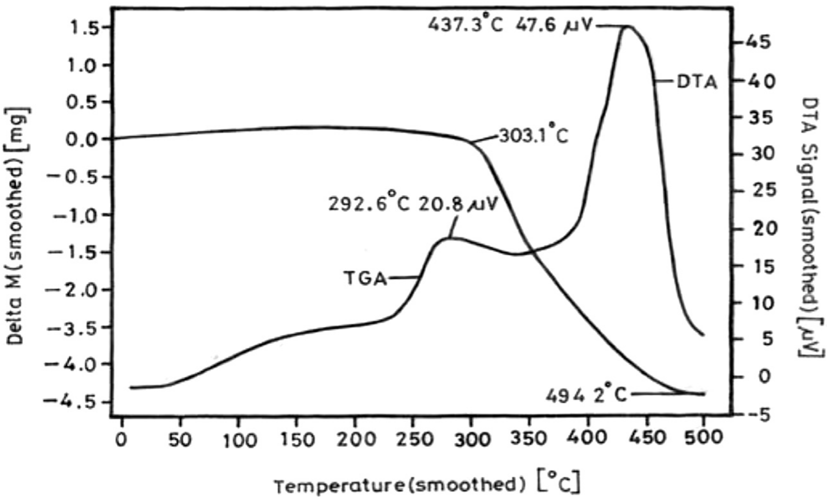


Figure 6. TGA/DTA curves of flax-g-poly(MMA/AA).

Crystalline index gives a quantitative measure of the orientation of the cellulose crystals in fibers. A lower crystalline index in the case of graft co-polymers means poor order of cellulose crystals in the fiber. This is due to misorientation of the cellulose crystals to the fiber axis during grafting as indicated by the lower crystalline index. This result clearly indicates that the cellulose crystals are better oriented in flax fiber, followed by flax-g-co-polymers (Table III).

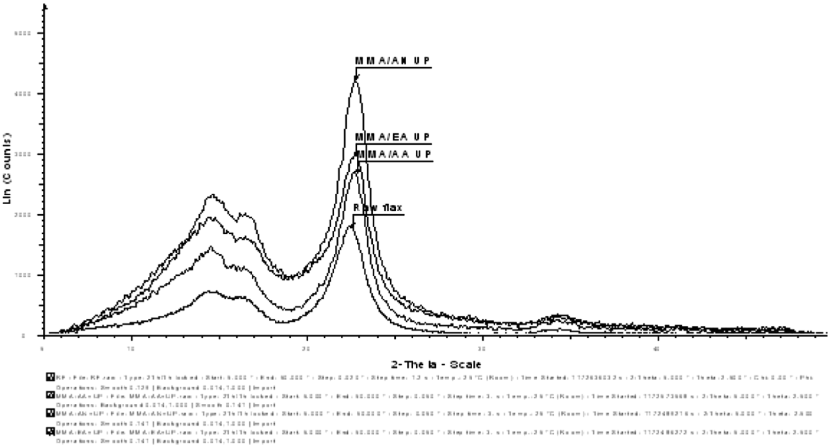


Figure 7. XRD of flax and its graft co-polymers.

Table III. Percentage crystallinity (%Cr) and crystalline index (C.I.) of flax fiber and graft co-polymers

Sr. no.	Sample	P_g	At 2θ scale I_{22}	I_{18}	%Cr	C.I.
1.	Flax fiber	—	1780	533	76.96	0.7005
2.	Flax-g-poly(MMA/EA)	109.9	3018	1847	62.03	0.3880
3.	Flax-g-poly(MMA/AN)	94.32	3591	1876	65.69	0.4776
4.	Flax-g-poly(MMA/AA)	55.94	2692	1302	67.40	0.5163

Table IV. Fiber strength of flax and its graft co-polymers

Sample code	% Grafting	Fiber strength (gms/tex)
Flax fiber	—	28.84
Flax-g-poly(MMA/EA)	109.9	3.89
Flax-g-poly(MMA/AN)	94.32	2.82
Flax-g-poly(MMA/AA)	55.94	5.48

Downloaded At: 15:54 21 January 2011

Fiber Strength

Flax fiber has been found to show maximum fiber strength (28.84 gms/tex) in comparison to graft co-polymers. It has been observed that there is a decrease in fiber strength of flax during grafting. This is due to the fact that there is an increase in surface flaws along with morphological transformations during the grafting process, which results in weakening of the fiber (Table IV).

CONCLUSION

Graft co-polymerization is one of the best methods for modifying the properties of natural fibers. Flax-g-poly(MMA/AA) has been found to show good thermal stability. Crystallinity of flax decreases on grafting with binary vinyl monomers. Cellulose crystals are better oriented in flax fiber, followed by flax-g-co-polymers.

REFERENCES

[1] Chauhan, G. S., L. K. Guleria, B. N. Misra, and I. Kaur. (1999). Polymers from renewable resources. II: A study in the radio chemical grafting of poly

(styrene-alt-maleic-anhydide) onto cellulose extracted from pine needles. *J. Polym. Sci. Part A Polym. Chem.* **37**, 1763–1769.

[2] Okieimen, F. E. and D. Ogbeifun. (1996). Graft copolymerizations of modified cellulose: Grafting of methyl acrylate, ethyl acrylate and ethyl methacrylate on carboxy methyl cellulose. *Eur. Polym. J.* **32**, 311–315.

[3] Ali, F., C. N. Saikia, and S. R. Sen. (1997). Grafting of acrylonitrile onto high α-cellulose extracted from Hibiscus sabdariffa. *Ind. Crops Prod.* **6**, 121–129.

[4] Karlsson, J. O. and P. Gatenholm. (1997). Preparation and characterization of cellulose-supported HEMA hydrogels. *Polymer* **38**, 4727–4731.

[5] Abdel-Razik, E. A. (1994). Homogeneous grafting of dichlorodimethylsilane onto ethyl cellulose. *Eur. Polym. J.* **30**, 313–317.

[6] Imoto, M., K. Takemoto, H. Azuma, N. Kita, and M. Kondo. (1967). Vinyl polymerization. 170: Grafting of some acrylates and methacrylates onto cellulose and silk in absence of radical initiators. *Makromol. Chem.* **107**, 188–195.

[7] Mwaikambo, L. Y. and M. P. Ansell. (2002). Chemical modification of hemp, sisal, jute, and kapok fibers by alkalization. *J. Appl. Polym. Sci.* **84**, 2222–2234.

[8] Agrawal, A. M., R. V. Manek, W. M. Kolling, and S. H. Neau. (2003). Studies on the interaction of water with ethylcellulose: Effect of polymer particle size. *AAPS PharmSciTech* **4**, article 60.

[9] Reddy, N. and Y. Yang. (2005). Structure and properties of high quality natural cellulose fibers from cornstalks. *Polymer* **46**, 5494–5500.

[10] Segal, L. C., A. E. Martin, and C. M. Conrad. (1959). An empirical method for estimating the degree of crystallinity of native cellulose using the X-ray diffractometer. *Tex. Res. J.* **29**, 786–794.

[11] Bhattacharya, A. and B. N. Misra. (2004). Grafting: A versatile means to modify polymers: Techniques, factors and applications. *Prog. Polym. Sci.* **29**, 767–814.

Downloaded At: 15:54 21 January 2011