



Study of Morphology of Graft Copolymer of Methacrylic Acid onto Cellulosic Fibres using Electron Microscopy

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ABSTRACT : Graft copolymerization of methacrylic acid (MAA) onto cellulosic fibre derived from *Luffa cylindrica* using chromic acid (CA) as initiator was investigated by carried out the reaction in air. The various parameters such as time, temperature, concentration of monomer and initiator and pH were optimized to get maximum graft yield (89.4%). The samples were characterized with Scanning electron microscopy (SEM) and X-ray diffraction (XRD) techniques. The morphology of grafted co-polymer changed remarkably as compared to the raw cellulosic fibre. XRD data reflects the low values of percentage crystallinity and crystallinity index for grafted fibre in comparison to raw fibre. The crystallite size of grafted fibre decreases significantly which reflects the formation of disorder system in the grafted fibre after copolymerization.

Keywords: *Luffa cylindrica*, methacrylic acid (MAA), Chromic acid, SEM, XRD.

I. INTRODUCTION

With the increasing demand of renewable resources for consumer product the use of renewable resources is highly preferred. Natural fibre is the most abundant raw resource in the world with the number of advantages over the synthetic fibres such as renewability, biodegradability, low cost, low density, non-abrasive character, high toughness, acceptable specific strength, reduce respiratory irritation, etc., which make them a potential reinforcement in eco-composites. Recently much ecofriendly alternative type of fibres and their chemical modifications have been considered by researchers [1-2]. Graft copolymerization is a versatile technique for modifying the properties of cellulose fibre through the incorporation of branches of the synthetic polymers without destroying the desirable properties of natural fibre [3]. A number of methods for surface modification of natural fibre such as mercerization, silane treatment, acetylation, benazoylation, plasma treatment etc. have been reported in literature [4-10]. Among various methods of surface modification of cellulosic fibres graft copolymerization is an attractive method to impart a variety of functional groups on the polymer backbone.

Grafting of vinyl monomers onto the cellulosic materials provides a potential method for altering the physico-chemical and mechanical properties of the polymer substrates. Depending upon the structure of the grafted monomer the cellulosic materials can be made hydrophobic [11], heat resistant [12] and resistance to microbial attack [13]. Natural fibre obtained from coir, sisal, jute, sponge gourds, flax, bamboo, ramie, grasses etc. composed of fibrils along with resinous materials have been used by mankind in order to meet the basic requirements of shelter, food and cloths [14]. *Luffa Cylindrica* belongs to the family cucurbitaceae and grown throughout India, wild in waste lands especially along the coastal area and worldwide as a vegetable sponge. *Luffa*

sponge mainly composed of cellulose, hemicelluloses and lignin. In the present study the grafting of methacrylic (MAA) acid carried onto cellulosic fibre derived from *Luffa cylindrica*. The grafted co-polymer was characterized by SEM and XRD to study morphology and crystallinity.

II. MATERIALS AND METHODS

A. Materials

The raw material used in the present study was *Luffa Cylindrica*. *Luffa cylindrica* fibres were obtained from a dried fruit and local specialty shop. Methacrylic acid (MAA), Acetone, Sodium hydroxide, Chromic acid, Methanol, Methylene blue (MB), $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ and double distilled water used are of analytical grade (AR).

B. Methods

(i) Purification of *Luffa Cylindrica* fibre

The purification of fibre was done by soxhlet extraction using acetone for 72h and the resultant fibre was dried at room temperature than pre-treated with 0.1M sodium hydroxide for 30 min for its purification and to increase its hydrophilicity. Fibres were washed with distilled water until all sodium hydroxide was washed. After washing, *L. cylindrica* fibre was dried in oven at 60°C for 3h and then fibres were stored for further study.

(ii) Grafting copolymerization

0.5g fibre was immersed in the 100 ml of demonized water for 24 hours before grafting with different monomers. Then definite amount of initiator and monomer was added into the flask separately. The mixture was stirred continuously for a definite period of time at a particular temperature. Different reaction parameters such as monomer

concentration, redox initiator concentration, polymerization time, temperature of reaction, pH of reaction mixture were optimized to get the maximum graft yield. Graft copolymer was extracted by washing fibre with methanol to remove attached homopolymer from it. Percent Graft yield (P_g) and percent grafting efficiency (P_e) of grafted samples was calculated as per methods reported earlier [2, 3, 7].

(iii) Scanning Electron microscopy (SEM)

Scanning Electron microscopic studies of *Luffa Cylindrica* fibre and its graft co-polymer was carried-out on electron microscopy machine (LEO 435 VP). The fibres were laid down on the aluminium stub using a conductive tape and were sputter coated with gold in order to prevent charge build-up on the sample.

(iv) X-ray diffraction (XRD) studies

X-ray studies were carried out on Bruker D8 Advance X-ray diffractometer, using Cu K α (1.5418Å) radiation, Ni filter and a scintillation counter as a detector at 40 KV and 40mA on rotation from 5° to 50° at 2° scale. Percent Crystallinity (X_c %) and crystallinity index (C.I.) were calculated as per methods reported [15, 16].

Average crystallite size, more commonly known as particle size L , is related to b , the full width at half maximum (FWHM) of the peak (in radian) was calculated using Scherrer formula as given by:

$$L = \frac{\lambda}{b \cos \theta} \quad \dots(1)$$

where $\lambda = 1.54$ nm is the wavelength of the Cu-K α X-ray radiation used, b is the FWHM of the diffraction peak and θ is the Bragg angle (in radians).

III. RESULTS AND DISCUSSION

The extent of grafting on the natural fibre mainly depends upon the availability of the active sites on the polymeric back bone. The graft copolymerization was carried out by changing the reaction parameters such as reaction time, temperature and concentration of the initiator and monomer within certain limits while keeping the values of the other parameter constant. Table 1 shows the optimized reaction parameters in the presence of air to obtain the maximum graft yield of 89.4 % .

Table 1. Optimization of various reaction parameters for grafting of methacrylate onto cellulosic fibre in the presence of air

Sr. no.	Monomer ($\times 10^{-3}$ mol/L)	Initiator (mol/L)	Solvent (ml)	Temp (°C)	Time(min)	pH	P_g	P_e
1	0.350	5×10^{-4}	100	35	60	7	68%	89.4%
2	0.350	25×10^{-4}	100	60	60	7	4%	25.0%
3	0.467	75×10^{-4}	100	60	60	7	8%	57.1%
4	0.467	75×10^{-4}	100	100	100	7	44%	78.6%
5	0.583	1×10^{-3}	100	100	100	9	8%	50.0%
6	0.700	125×10^{-4}	100	90	120	9	12%	66.7%
7	0.350	5×10^{-4}	100	35	90	7	24%	66.7%
8	0.350	5×10^{-4}	100	60	30	7	4%	40.0%
9	0.350	5×10^{-4}	100	35	60	3	3%	50.0%
10	0.350	5×10^{-4}	100	60	90	7	8%	66.0%

(i) Morphological study

The Fig. 1 and 2 shows the scanning electron micrographs of raw *L. cylindrica* cellulosic fibre and MAA grafted copolymer respectively. It is clear from the figures that surface of grafted fibre is rough and surface of raw fibre is smooth. This roughness of grafted sample is due to the deposition of the poly (MAA) chains on the surface of raw fibre through graft copolymerization.

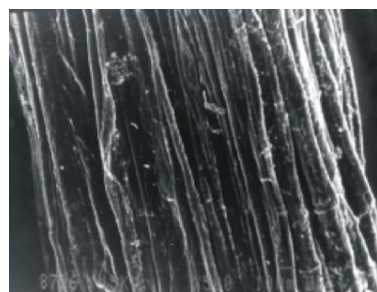
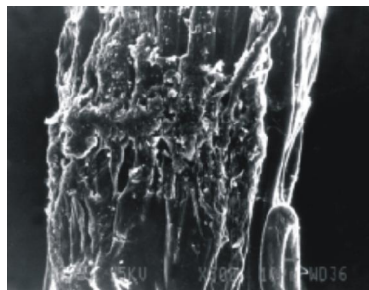


Fig. 1. SEM of raw fibre Figure

Fig. 2. SEM image of *Lc-g-poly(MAA)*

(ii) X-ray Diffraction

The XRD pattern of raw and *Lc-g-poly(MAA)* fibre is shown in Fig. 3. The characteristics peaks of raw fibre were observed at $2\theta = 22.5^\circ$ and 16.18° with relative intensities of 1072 and 506 respectively. Similarly, grafted fibre shows peaks at $2\theta = 17.58^\circ$ and 11.6° with relative intensities of 517 and 274 respectively. The profile of the halos shows that the fibres are semi crystalline in nature with a dominant crystalline phase. It is interesting to note that intensity of the *Lc-g-poly(MAA)* peaks decreases during grafting. This decrease in intensity indicates that crystallinity of *Lc-g-poly(MAA)* fibre decreases. However, the *Lc-g-poly(MAA)* fibre shows broadening of the peak after

grafting suggests convergence of the fibre towards more disordered system. On the other hand, grafting could lead to cross linking, thereby bringing about reduction in the crystalline structure.

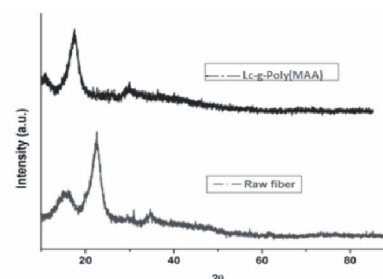


Fig. 3. X-ray diffraction pattern of raw and grafted fibre

It is clear from Table 2 that there is slightly change in the crystallinity and crystallinity index of the fiber during grafting. This may be due to the disorientation of cellulose crystal when MMA chains are incorporated in the active sites of the polymer back bone during grafting. Moreover, grafting occurs mainly in the amorphous region of the fiber. Thus, the mismatching of the crystal lattice to the fiber axis during grafting resulted in graft copolymer with low crystallinity and crystallinity index thereby, increase in molecular weight and cross linking network.

Table 2. XRD parameters of raw fiber and *Lc-g-poly(MAA)* sample

Sample	2θ (deg.)	FWHM (deg.)	Intensity		% of Crystallinity	index (C.I.) Crystallinity	Crystallite size L (Å)
			I_C	I_A			
Raw fibre	22.5	2.68	1072	506	67.9	0.52	33.5
<i>Lc-g-poly(MAA)</i>	17.58	9.6	517	274	65.3	0.47	9.1

The calculated crystallite size (Table 2) of grafted fiber decreases significantly which reflects the formation of disorder system in the grafted fiber after copolymerization.

IV. CONCLUSION

The grafting of MAA has been successfully done onto cellulosic fibre using chromic acid as an initiator in air. XRD spectra revealed that crystallinity decreases after grafting indicates disordering in the copolymers. SEM image show improved surface morphology after grafting onto natural cellulosic *Luffa cylindrical* fibre. Based on the above findings it can be stated that new fibres with improved chemical and morphological properties could be synthesized by optimizing various reaction parameters.

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