

SYNTHESIS OF GRAFT COPOLYMERS OF BINARY VINYL MONOMER MIXTURES AND FLAX FIBRE USING FAS-KPS REDOX SYSTEM

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ABSTRACT

In this work, we have reported the study of graft copolymerization of methylmethacrylate (MMA)/Methylacrylate (MA) and MMA/acrylonitrile (AN) binary monomer mixtures onto Flax fibres and evaluation of the different parameters like swelling, moisture absorbance and thermal behaviour of the grafted and ungrafted fibres.

Key words: Graft co-polymers, Methylmethacrylate, Acrylonitrile, Methylacrylate, Redox

INTRODUCTION

Modification of both natural and synthetic fibres through graft copolymerization is a convenient method for incorporation of new and desired properties into textiles without drastically affecting the basic properties of the substrate¹⁻³. Different natural fibres like jute, wood, bamboo, sisal, cotton, coir, wheat straw etc. have been studied for the preparation of composites by several workers⁴⁻¹⁹.

Flax containing about 85% cellulose is one of the most important cellulosic materials and offers tremendous potential for its use as modified natural fibre for its applications in varied fields. However, no such exhaustive studies have been carried out on this natural polymer (variety DPL-21). In this paper, we have studied the graft copolymerization of different vinyl monomer mixtures with MMA as principal partner. The effects of concentrations of MMA, FAS-KPS ratio and reaction time and temperature were studied for getting maximum graft yield. In further studies, the concentration of the associate partner of binary mixture was varied keeping the optimum reaction conditions obtained with MMA, constant, so as to get the maximum percent grafting with the binary mixture. Evaluation of swelling, moisture absorbance and thermal behaviour of the grafted and ungrafted fibres was also carried out.

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EXPERIMENTAL

Material and its purification

The Flax fibre was refluxed for 72 hrs. with acetone using Soxhlet and was made free from impurities. Monomers were purified by giving washings with 5% NaOH and subsequently, they were dried over anhydrous sodium sulphate, which was followed by distillation. Potassium persulphate (BDH) was used as received and ferrous ammonium sulphate (BDH) was recrystallized from hot water prior to its use.

Graft co-polymerization

Activation of Flax fibre (0.4 g) was done at room temperature by immersing it in 100 mL of distilled water for 24 hrs. prior to carrying out graft copolymerization. Known amounts of binary monomers containing MMA as principal partner (for which optimum reaction conditions were initially worked out) were added to the Flax fibre and water mixture. The reaction mixture was stirred for 90 min at 55°C in the presence of optimum amount of FAS-KPS. Poly (MMA) and Poly (MA) were completely removed from the graft copolymer by extraction with acetone whereas poly (AN) was removed by extraction with DMF. Graft co-polymer thus obtained was dried at 50°C to a constant weight. The percentage grafting (P_g) and percentage efficiency (P_e) (Table I) were calculated as per the methods reported earlier⁸.

Swelling, moisture absorbance, IR and thermal studies

Swelling studies were performed in DMSO, DMF, H₂O and n-propanol as per the method reported in earlier work¹¹. Moisture absorbance studies were carried out at different humidity levels ranging from 20% to 95% and the percent moisture absorbance (% Mabs) was calculated^{11, 12}.

The IR spectra of Flax fibre and its graft co-polymers were taken in KBr pellets on Bomem, Hartmann and Braun (MB-Series) spectrometer.

Thermogravimetric analysis (TGA) was carried out on Perkin Elmer thermal analyser under nitrogen atmosphere at a heating rate of 10°C/min.

Characterization of graft co-polymers

In IR spectra, Flax fibre showed a broad peak at 3420 cm⁻¹ due to bonded -OH and at 2925.5, 1458.6 and 1055.87 cm⁻¹ arising -CH₂, C-C and C-O stretching, respectively, whereas in case of binary vinyl monomer mixture graft copolymers, additional bands at 1734 cm⁻¹ (due to carbonyl group of vinyl monomer), and 2240 cm⁻¹ (C=N of AN) were obtained.

On comparing the scanning electron micrographs of Flax (Fig. 1) and its copolymers with binary monomer mixtures (MMA/MA; Fig. 2 and MMA/AN; Fig. 3), it has been found that

upon grafting, a considerable amount of polymer is deposited onto Flax surface in both the cases.

RESULTS AND DISCUSSION

It has been observed that in case of materials containing cellulose, C₂, C₃ and C₆ -OH groups and C-H sites are the active centers for grafting of polymeric chains onto polymeric back-bone. Potassium persulphate takes part in the redox reaction with Fe²⁺, which can be explained through the following chemical reaction:



Interaction of SO₄^{-*} with H₂O generates OH^{*} and these free radicals are responsible for grafting of polymeric chains onto the Flax back-bone thereby resulting in the formation of copolymer along with homopolymer¹³

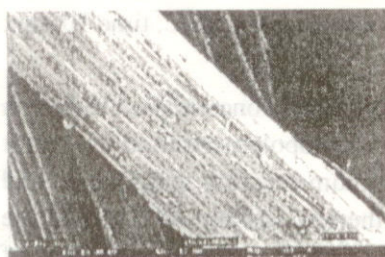


Fig. 1 Scanning electron micrograph of Flax Fibre



Fig. 2 Scanning electron micrograph of Flax-g-poly (MMA/MA) (Sample 5 of Table 1)

Fig. 3 Scanning electron micrograph of Flax-g-poly (MMA/AN) (Sample 13 of Table 1)

Table 1. Effects of concentration variation of [MMA] / [MA] and [MMA] / [AN] binary monomer mixtures of percent Graft yield on grafting onto Flax fibre under optimum reaction conditions*

Sr. No.	Binary Mixtures	$\times 10^3 \text{ mol/L}$ (molar concentration)	P _g	P _e
1.	[MMA] + [MA]	2.94 + 1.10	30.50	3.13
2.		2.94 + 1.66	36.98	3.38
3.		2.94 + 2.21	34.10	2.82
4.		2.94 + 2.76	36.23	2.73
5.		2.94 + 3.31	38.73	2.67
6.		2.94 + 3.87	32.70	2.08
7.		2.94 + 4.42	26.25	1.56
8.	[MMA] + [AN]	2.94 + 1.519	48.28	5.16
9.		2.94 + 2.278	51.33	4.95

Sr. No.	Binary Mixtures	$\times 10^3$ mol/L (molar concentration)	P_g	P_e
10.		2.94 + 3.038	52.50	4.62
11.		2.94 + 3.797	45.73	3.69
12.		2.94 + 4.557	75.33	5.63
13.		2.94 + 5.316	76.75	5.33
14.		2.94 + 6.075	55.75	3.62

* Temp ($^{\circ}\text{C}$) = 55; Time (min) = 90; FAS-KPS (molar ratio) = 0.75:1; Maximum P_g of MMA onto Flax = 40.23

Optimization of various reaction parameters for grafting of principal monomer (MMA) onto Flax

Extensive studies were made to optimize the various reaction parameters like reaction time and temperature, concentrations of monomer and initiator. It has been observed that maximum grafting (40.23%) was obtained under optimum conditions of: temperature, 55°C ; time 90 min; MMA, 2.94×10^3 mol/L and FAS/KPS, 0.75:1.

After reaching maximum P_g of 40.23%, further increase of MMA concentration results in decreased graft yield, which could be due to predomination of homopolymerization over graft co-polymerization. Decrease in percent grafting beyond optimum reaction temperature and time is due to increase in the viscosity of reaction medium thereby causing difficulty in the mobility of the radicals to the polymeric back-bone active sites as well as due to occurrence of more other side chain reactions along with excessive homopolymerization.

Effect of molar ratio of FAS-KPS

The molar ratio of FAS-KPS plays an important role for getting maximum graft yield of 40.23%, 38.73% and 76.75%, with graft copolymerization of MMA, MMA/MA and MMA/AN onto Flax fibre, respectively. The optimum molar ratio for the maximum graft yield is 0.75:1 of FAS-KPS. It has been observed that percent grafting decreases with further increase in molar ratio which is due to the fact that at higher molar ratio, more Fe^{3+} ion are generated and these ions result in the termination of growing chains. If FAS-KPS molar ratio is less than critical value, then there is decrease in P_g because of lesser generation of OH^- ions.

Effect of binary monomer mixture concentration

It has been observed that binary mixtures of MA and AN with MMA as principal monomer, for which the optimum reaction conditions were evaluated, show 38.73% (MA: 3.31×10^3 mol/L) and 76.75% (AN: 5.316×10^3 mol/L) grafting, respectively.

Higher graft yield has been observed with MMA/AN binary mixture as compared to MMA/MA. This occurs due to the fact that AN being a strong acceptor monomer contributes towards maximum grafting whereas MA being the donor monomer, has lesser tendency to

undergo graft copolymerization. Moreover, MA being less water soluble monomer (6 parts/100 mL of water) as compared to AN (7.3 parts/100 mL of water) has less accessibility to reach the active sites of the polymer back-bone; thereby producing lower percent graft yield than AN¹⁴

Swelling studies on raw Flax and its graft copolymers

The swelling behaviour of MMA/MA graft co-polymer varies as a function of P_g and follows the trend: DMSO > DMF > H₂O > n-propanol whereas in case of ungrafted fibre the trend is: H₂O > DMSO > DMF > n-propanol. It could be due to greater affinity of water of hydroxyl groups present in the raw Flax cellulose, resulting in more penetration of water into cellulose matrix as compared to other solvents (Fig. 4).

In case of the grafted fibre containing MMA/MA chains, water and n-propanol can not interact to the same extent as with raw Flax due to blocking of active sites on Flax back-bone by poly (MMA/MA) chains; thus causing change in the sorption behaviour. Poly (MMA/MA) chains grafted on the Flax are more solvolysed by DMSO and DMF as compared to water or alcohol, therefore resulting in more swelling in DMSO followed by DMF with increasing percent grafting. Hence, a different pattern for percent swelling in different solvents for the grafted samples is observed. Similar swelling pattern has been also observed with MMA/AN binary system.

Moisture absorbance behaviour

The moisture absorbance varies at different humidity levels as a function of P_g (Fig. 5). There has been decrease in % Mabs. with increase in graft yield, which is due to the fact that with increase in P_g , the sites for maximum moisture absorbance are blocked after incorporation of poly (MMA/MA) chains through graft copolymerization. Since poly (MMA/MA) chains

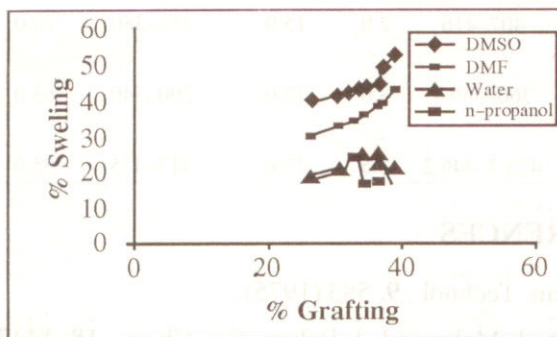


Fig. 4 Effect of percent grafting of binary mixture of MMA/MA with Flax on swelling behaviour in different solvents.

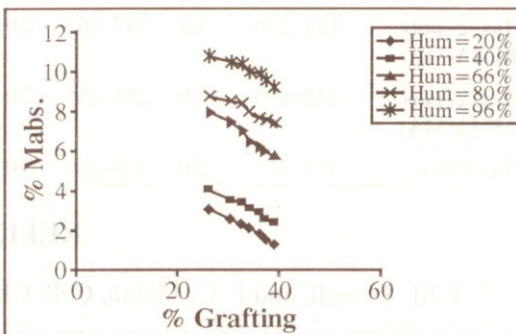


Fig. 5 Effect of percent grafting of binary mixture of MMA/MA with Flax on moisture absorbance at different humidity levels.

have lesser affinity towards water as compared to original matrix, so %Mabs. decreases with increase in P_g . Similar behaviour has been observed with Flax-g-poly (MMA/AN) system.

Thermal behaviour of Flax and its graft co-polymer

In case of TGA studies, the decomposition of both ungrafted and grafted fibres was studied as a function of %weight loss v/s temperature, depolymerization and glucosan formation in the temperature range between 157° C to 253° C, which was followed by the cleavage of C–C and C–O bonds. Initial decomposition which started at 270° C and continued upto 340° C resulted in a constant weight loss of 8.0%. Further weight loss of 23% was observed in the temperature range of 358° C to 380° C. Decomposition at 425.3° C showed that the amorphous region of the cellulose content of the fibre is disturbed with loss of H-bonded structure and a higher temperature of 446.2° C (FDT) was required to break-down the crystalline region.

On the other hand, in case of Flax-g-poly (MMA/MA) fibre, the initial decomposition begins at 247° C (IDT) and continues upto 262° C at a constant loss of 2%. A sharp weight loss of 70% is observed in the temperature range of 278° C to 380° C. Inflexions show that the amorphous region of the cellulose content of the grafted fibre is disturbed with loss of H-bonded structure and a higher temperature (407° C to 416° C, FDT) is required to break-down the crystalline region. Higher IDT of 270° C and FDT of 446.2° C of pure fibre as compared to 247° C (IDT) and 407° C (FDT) of Flax-g-poly (MMA/MA) fibre show a decrease in thermal stability after grafting, which may be due to disturbance in the original crystal lattice of the fibre because of impregnation of monomer chains in the matrix⁸⁻². Similar results have been observed with Flax-g-poly (MMA/AN) (Table 2).

Table 2. Thermal behaviour of Flax fibre and its graft co-polymers

Sample	Primary reactions (°C)	% Wt. loss	IDT (°C)	% Wt. loss	FDT (°C)	% Wt. loss	Final Residue (%)	Region of maximum wt. loss (°C)	% Wt. loss
Flax-g-poly (MMA/MA)	131–200	3.0	247–262	2.0	407–416	2.0	15.0	278–380	70.0
Flax-g-poly (MMA/MA)	150–190	4.0	255–285	2.0	360–369.7	3.0	12.0	290–340	65.0
Flax Fibre	157–253	2.0	270–340	8.0	425.3–446.2	4.5	19.0	417–425	55.0

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