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MODIFICATION OF FLAX FIBRE THROUGH GRAFT COPOLYMERIZATION WITH METHYL METHACRYLATE AND EVALUATION OF SWELLING, MOISTURE ABSORBANCE AND THERMAL BEHAVIOUR

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Flax fibre has been modified through grafting of methyl methacrylate in presence of potassium persulphate and ferrous ammonium sulphate as reaction initiators. Maximum graft yield of 40.23% was obtained at optimum reaction conditions and the graft copolymer was subjected to evaluation of swelling behaviour in different solvents, moisture absorbance under different humidity levels and thermal stability behaviour. The graft copolymers synthesized were characterized by usual spectroscopic techniques.

Keywords: Flax, methyl methacrylate, graft copolymer, swelling, thermal stability

Introduction

Incorporation of different desired properties onto polymeric materials through grafting is an active area of current interest. Grafting offers scope for developing new cellulosics for various end uses. Modification of fibrous proteins and cellulosics by this method has been reported by various workers [1-5]. Thermal degradation behaviour of cellulosics is very important [6, 7]. Hurduc and Schneider [8], Varma and Narashima [9] and Mukherjee and Sanyal [10] have reported the thermal behaviour of MMA grafted viscose cellulose and cotton with decrease in thermal stability of the grafted fibres as compared to that of ungrafted one. Kokot *et al.* [11] studied the effect of reaction medium, lattice structure and degree of polymerization on thermal stability of different cotton samples. UV and ceric ammonium nitrate initiated cotton graft copolymers were reported to exhibit lesser thermal stability with increase in add-on [12].

Flax one of the most important cellulosic material containing about 85% cellulose content, offers tremendous potential for cost effective technologies. However, no much work has been reported on this fibre. In this paper studies on the graft copolymerization of methyl methacrylate (MMA) onto flax and evaluation of different parameters such as optimum reaction conditions, swelling, moisture absorbance and thermal behaviour have been reported.

Experimental

Purification of Materials

Flax fibre was purified by refluxing with acetone for 72 hrs. in Soxhlet. Methyl methacrylate was purified by giving washings with 5 % NaOH and subsequent drying over anhydrous sodium sulphate which was followed by distillation. Middle fraction was used for grafting. Potassium persulphate(KPS) (BDH) was used as received and ferrous ammonium sulphate (FAS) (BDH) was recrystallized from hot water before use.

Graft Co-polymerisation

0.5 g of flax fibre was kept immersed in 100 ml of distilled water for 24 hrs. prior to graft copolymerization. Known amount of FAS-KPS was added to the reaction medium which was followed by the addition of MMA in small quantities. The reaction mixture was stirred constantly for a particular time interval at a definite temperature. Optimum reaction conditions were evaluated. Homo-polymer was separated by Soxhlet extraction with acetone for 48 h. Graft co-polymer thus obtained was dried at 50 °C to a constant weight. The results have been shown in

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Table 1 Optimization of reaction conditions for maximum graft copolymerization of MMA onto flax

Sr. No.	Temp (°C)	Time (min)	[MMA] x 10^{-3} mol/L	Molar Ratio FAS:KPS	P_g	P_e
1.	45	120	1.96	0.5:1	25.00	5.10
2.	55	120	1.96	0.5:1	33.53	6.84
3.	65	120	1.96	0.5:1	32.53	6.64
4.	75	120	1.96	0.5:1	25.00	5.10
5.	85	120	1.96	0.5:1	25.00	5.10
6.	55	60	1.96	0.5:1	32.45	6.62
7.	55	90	1.96	0.5:1	35.00	7.14
8.	55	120	1.96	0.5:1	33.53	6.84
9.	55	150	1.96	0.5:1	27.98	5.71
10.	55	180	1.96	0.5:1	26.95	5.50
11.	55	210	1.96	0.5:1	25.00	5.10
12.	55	90	1.96	0.25:1	38.13	7.78
13.	55	90	1.96	0.75:1	38.75	7.91
14.	55	90	1.96	1:1	35.05	7.15
15.	55	90	1.96	1.25:1	31.73	6.47
16.	55	90	1.96	0.75:1	26.25	5.36
17.	55	90	1.96	0.75:1	26.50	5.41
18.	55	90	1.96	0.75:1	25.00	5.10
19.	55	90	1.96	0.75:1	26.25	5.36
20.	55	90	0.98	0.75:1	25.03	5.11
21.	55	90	1.47	0.75:1	26.45	5.40
22.	55	90	2.45	0.75:1	27.60	5.63
23.	55	90	2.94	0.75:1	40.23	8.21
24.	55	90	3.43	0.75:1	28.75	5.87
25.	55	90	3.92	0.75:1	25.00	5.10

Table 1. The percentage grafting (P_g) and percentage efficiency (P_e) were calculated as follow :

$$P_g = \frac{W_g - W_{ung}}{W_{ung}} \times 100$$

$$P_e = \frac{W_g - W_{ung}}{W_m} \times 100$$

where W_{ung}, W_g and W_m are the weights of un-grafted fibre, grafted fibre and monomer.

Swelling, Moisture Absorbance and Thermal Studies

Swelling behaviour studies were carried out in DMSO, DMF, H_2O and n-propanol as per the method reported in earlier work [13]. Moisture absorbance studies were done using Humidity Chamber at different humidity levels ranging from 20 % to 90 % and the percent moisture absorbance (%Mabs) was calculated as:

$$\%Mabs = \frac{W_f - W_i}{W_i} \times 100$$

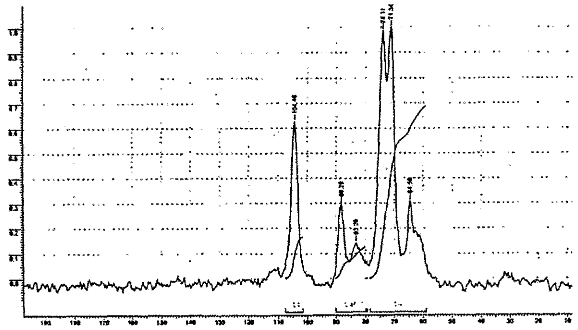

Fig.1 ^{13}C Solid-state NMR of Raw Flax

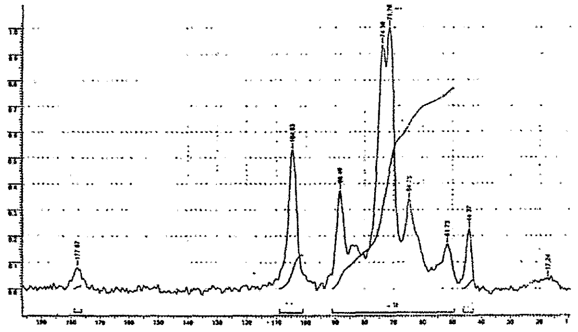

Fig.2 ^{13}C Solid-state NMR of Flax-g-poly (MMA) (Sample 14 of *Table 1*)

where W_i and W_f are initial and final weights of the samples.

Both the grafted and ungrafted samples were subjected to thermo-gravimetric analysis (TGA) studies as per the method reported in the literature [14, 15].

Characterization of Ungrafted and Grafted Fibres

IR spectra of flax fibre and its graft co-polymer were taken in KBr pellets on Bomem, Hartmann & Braun (MB-Series) spectrometer. 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 from -CH_2, C-C and C-O stretching, respectively. An additional band at 1730 cm^{-1} was observed due to the presence of carbonyl group in of Flax-g-poly(MMA).

^{13}C Solid-state NMR (125.76 MHz) of graft copolymer (*Fig.2*) showed additional signals at 177.87 for carbon corresponding to added carbonyl group and 51.73 and 44.37 for methyl and methylene groups of methyl methacrylate in addition to normal peaks at 104.46(C-6), 74.11(C-2) and 71.34(C-3) shown by the ^{13}C NMR spectrum of the Raw Flax (*Fig.1*).

Comparison of scanning electron micrographs of Flax (*Fig.3*) and its copolymer (*Fig.4*) indicates that upon grafting, a considerable amount of polymer is deposited onto flax surface.

A physical mixture of Flax-g-poly(MMA) (1.0 g) was mixed with equal amount of poly(MMA) and was stirred in acetone for about 24 h. Homopolymer recovered after filteration was to the extent of 99 %.

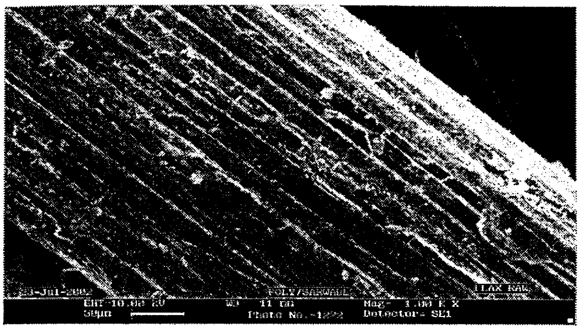

Fig.3 Scanning electron micrograph of Raw Flax

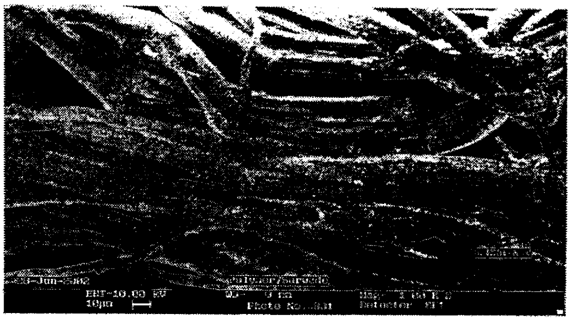

Fig.4 Scanning electron micrograph of Flax-g-poly(MMA) (Sample 14 of *Table 1*)

The solid sample left after filteration was dried to constant weight and it was observed that there was no weight loss. This clearly shows that homopolymer was quantitatively recovered from the reaction mixture.

Results and Discussion

In cellulosic materials like Flax C_2, C_3 and C_6 hydroxyls and C-H groups are active sites for the incorporation of polymeric chains through grafting . Potassium persulphate is known to take part in a redox reaction with Fe^{2+} through the following chemical equation:

$$Fe^{2+} + {}^{-}O_3S-O-O-SO_3^{-} \longrightarrow Fe^{3+} + SO_4^{2-} + SO_4^{-*}$$

In the aqueous medium OH^* are generated by interaction of SO_4^{-*} with H_2O which is responsible for graft copolymerization and homopolymerization [16]. The following mechanistic steps are suggested for explaining the grafting of poly(MMA) onto flax in the presence of FAS-KPS system:

$$SO_4^{-*} + H_2O \longrightarrow HSO_4^{-} + OH^* \qquad (1)$$

$$SO_4^{-*} + FxCell-OH \longrightarrow HSO_4^{-} + FXCell-O^* \qquad (2)$$

$$FxCell-OH + OH^* \longrightarrow FxCell-O^* + H_2O \qquad (3)$$

$$M + OH^* \longrightarrow OH-M^* \xrightarrow{nM} OH-(M)^*_{n+1} \qquad (4)$$

$$\begin{aligned} &OH-(M)^*_{n+1} + FxCell-OH \longrightarrow \\ &\longrightarrow FxCell-O^* + OH-(M)_{n+1} - H \end{aligned} \qquad (5)$$

$$\begin{aligned} &FxCell-O^* + M \longrightarrow FxCell-O-M^* \longrightarrow \\ &\xrightarrow{nM} FxCell-O-(M)^*_{n+1} \end{aligned} \qquad (6)$$

$$\begin{aligned} &FxCell-O-(M)^*_{n+1} + {}^*(M)_{n+1} - OH \longrightarrow \\ &\longrightarrow FxCell-O-(M)_{2n+2} - OH \end{aligned} \qquad (7)$$

$$\begin{aligned} &FxCell-O-(M)^*_{n+1} + Fe^{3+} \longrightarrow \\ &\longrightarrow FxCell-O-(M)_{n+1} + Fe^{2+} \end{aligned} \qquad (8)$$

where FxCell-OH = flax cellulose and M= monomer

It is evident from the above mechanism that both SO_4^{*-} and OH^* may be involved in grafting process. However, initiation of grafting by SO_4^{*-} (2) is unlikely as the concentration of persulphate used is very small, if the grafting is carried-out in absence of swelling agent. On the other hand, SO_4^{*-} in aqueous medium reacts with H_2O to generate OH^* which can initiate the graft co-polymerization and the resulting polymeric chain can abstract hydrogen atom from the back-bone polymer flax to generate the macro-radical (FxCell-O^*) where grafting can take place. Alternately, OH^* can directly generate macro-radical (FxCell-O^*) by hydrogen abstraction. Since initiation of graft co-polymerization is a faster reaction than hydrogen abstraction by OH^* so the generation of macro-radical by the former process is more likely to occur. Termination of growing chains may occur by either process (7) or (8) or both. Since Fe^{3+} is involved in the termination of growing grafted chains, its presence can have great impact on graft yield. Fe^{3+} arises from the interaction of FAS with KPS and consequently, the relative amounts of KPS and FAS should influence the percent grafting.

Effect of Molar Ratio of FAS-KPS

Maximum graft yield has been found at the molar ratio of FAS-KPS = 0.75: 1 and further increase in molar ration decreases the percent grafting. This is due to the formation of more Fe^{3+} ion at higher molar ratio which results in the termination of growing grafted chains leading to the decrease in P_g as is evident from the *Eq.(8)*.

When the molar ratio of the FAS-KPS is less than the critical value, the concentration of OH^* is low and the percent grafting is decreased (*Eq.(3)*). From the above it is evident that molar ratio of FAS-KPS plays an important role for getting maximum grafting.

Effect of Monomer Concentration

It is evident from the above mechanism that initially percent grafting increases with increase in the monomer concentration and after reaching maximum value of 40.20 %, further increase in monomer concentration decreases the graft yield. This happens due to the predomination of homo-polymerization over graft co-polymerization. Homo-polymerization also causes increase in viscosity of the medium thereby decreasing

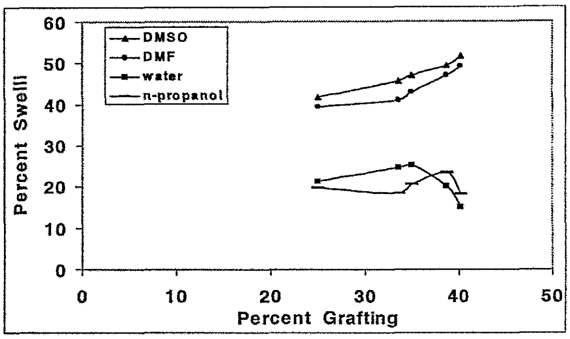

Fig.5 Effect of percent grafting of MMA with flax on swelling behaviour in different solvents

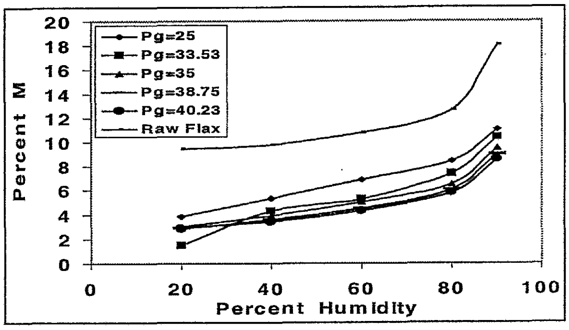

Fig.6 Effect of percent grafting of MMA with flax on moisture absorbance at different humidity levels·

the mobility of the radicals to the active sites on the polymeric back-bone.

Effect of Reaction Temperature and Time

As the reaction temperature is increased from 45 °C to 55 °C, the graft yield is increased. Further increase in temperature beyond 55 °C results in decreased P_g. This is probably due to formation of considerable amount of homopolymer and setting-up of various hydrogen abstraction reactions at high temperature resulting in wastage of monomer by its participation in side reactions.

As it is evident from *Table 1* maximum graft yield is obtained at 90 min. With further increase in reaction time, the graft yield is decreased. This phenomenon can be explained in terms of predominance of homo-polymerization over graft co-polymerization and also due to other side reactions.

Swelling and Moisture Absorbance Behaviour of Flax and its Graft Co-polymer

Swelling studies in different solvents(*Fig.5*) show that behaviour of the graft co-polymer varies as a function of P_g and the trend follows the order: DMSO > DMF > H_2O > n-propanol. In case of original flax the order is: H_2O > DMSO > DMF > n-propanol. It can be due to the fact that water having great affinity for hydroxyl groups and hydrogen bonding present in cellulose, penetrates deeper into the matrix and causes swelling in original fibre which is not possible in case of DMSO, DMF and n-propanol. However, the grafted fibre containing methyl methacrylate chains are solvolysed by DMSO and DMF to the greater extent, hence more swelling in DMSO followed by DMF with increasing P_g has been observed. H_2O and n-propanol cannot interact with methyl methacrylate to the same degree as DMSO and DMF. Therefore, a different pattern for percent swelling in different solvents for the grafted samples is observed. Further, it can be added that during grafting the hydroxyl groups and other active sites of the fibre are substituted with poly(MMA) chains and thus a shift in sorption behaviour of grafted fibre from H_2O to DMSO is observed.

Graft co-polymerization has a great impact on the moisture absorbance behaviour of Flax-g-poly(MMA) vis-à-vis raw fibre. As it is evident from *Fig.6*, moisture absorbance varies at different humidity levels as a function of P_g. Percent moisture absorbance (% Mabs) decreases with increase in P_g. The explaination for this behaviour lies in the fact that with increase in P_g, the sites for maximum moisture absorbance are blocked after incorporation of methyl methacrylate chains through graft co-polymerization which has less affinity for moisture content as compared to hydrogen bondings and –OH groups present in the original matrix. Further, higher % Mabs. in case of original flax can be attributed to the fact that moisture has high interaction with active sites including C_2, C_3, C_6 and free hydroxyl groups present in cellulose thereby softening the matrix and hence more penetration into the lattice of the fibre.

Thermal Behaviour of Flax and its Graft Co-polymer

Thermogravimetric analysis (TGA) of flax fibre and Flax-g-poly(MMA) was carried-out on Perkin Elmer Thermal Analyser under nitrogen atmosphere at a heating rate of 10 °C/min. The decomposition of both the fibres was studied as a function of %weight loss v/s temperature (*Fig.7*). Primary reactions like thermo-oxidation, dehydration, depolymerization and glucosan formation decomposes the ungrafted fibre. These processes take place in the region between 157 °C to 253 °C and is followed by the breaking down of C-C and C-O bonds. Initial decomposition begins at 270 °C (IDT) and continues upto 340 °C with a constant 8.0 % weight loss. In the temperature range of 358 °C to 380 °C, 23 % weight loss has been observed. Further decomposition at 425.3 °C shows 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) is required to break-down the crystalline region.

On the other hand, in case of Flax-g-poly(MMA) fibre, the initial decomposition begins at 260 °C (IDT) and continues upto 285 °C at a constant loss of %. A sharp weight loss of % is observed in the temperature range of 295 °C to 310 °C. Inflexions between 330 °C

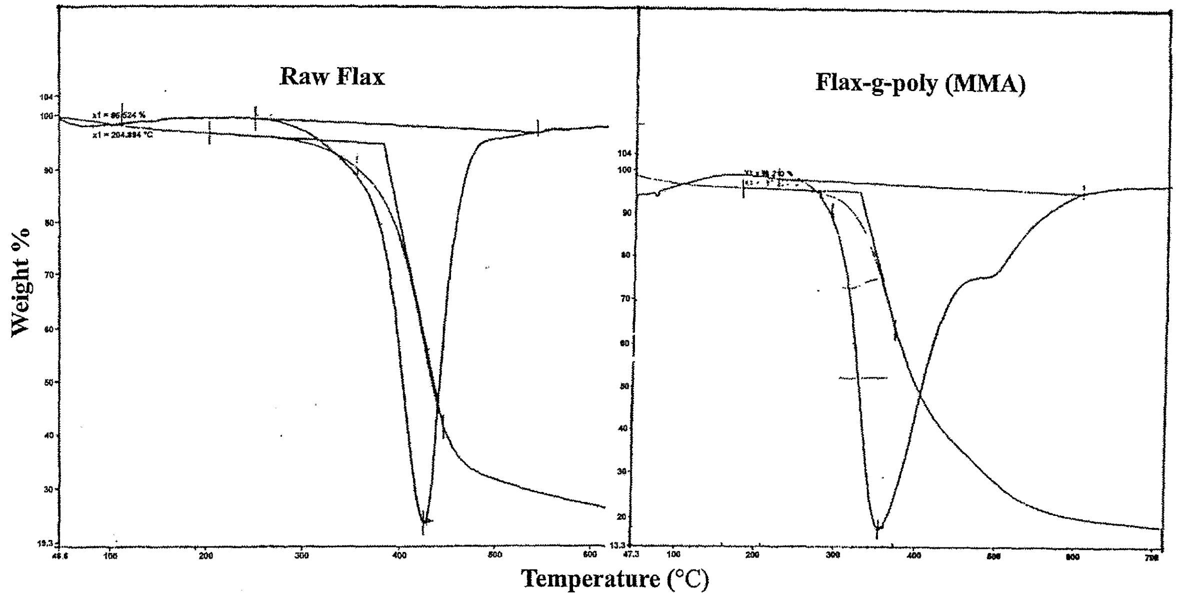

Fig.7 TG curves of flax and flax-g-poly (MMA) (Sample 14 of *Table 1*)

and 365 °C 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 (370 °C to 375 °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 260 °C (IDT) and 375 °C (FDT) of Flax-g-ploy(MMA) 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 matrix. Similar results have also been reported by other workers [8-12].

Conclusion

Graft co-polymerization of methylacrylate onto flax fibre shows that the properties like moisture resistance and swelling behaviour are entirely the functions of P_g. TGA studies show that grafted fibre has lesser thermal stability as compared to that of original fibre. Keeping in view the modified behaviour of the fibre after grafting, new eco-friendly materials can be synthesized to replace the existing non-bio-degradables. These materials could also be used as the precursors for the synthesis of future membranes and gels. A comprehensive research work is already in progress in our Material Laboratory.

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