

Modification of natural polymers: Part I—Ceric ion initiated graft copolymerization of methyl methacrylate onto *Cannabis* fibre

Ghanshyam S Chauhan, Inderjeet Kaur & B N Misra

Department of Chemistry, Himachal Pradesh University, Summer Hill, Shimla 171 005, India
and

A S Singha & B S Kaith

Department of Applied Sciences, Regional Engineering College, Hamirpur 177 005, India

Revised received 11 August 1998; accepted 22 May 1999

Ceric ion initiated graft copolymerization of methyl methacrylate onto *Cannabis indica* fibre has been carried out. Optimum grafting conditions such as the concentrations of monomer, initiator and nitric acid, amount of water, reaction time and reaction temperature have been evaluated. The grafted copolymers and the ungrafted *Cannabis* fibre have been characterized by IR spectroscopy, thermal gravimetric analysis and swelling studies in DMF, water and *n*-butanol. The trend in the swelling behaviour of the grafted samples (DMF > water > *n*-butanol) is different from that observed for the ungrafted sample (water > DMF > *n*-butanol). The grafted samples show improved thermal stability in contrast to ungrafted fibre. The plausible mechanism for grafting reactions is suggested and the explanation for the trends in grafting parameters are given.

Keywords: *Cannabis indica*, Ceric ammonium nitrate, Graft copolymerization, Methyl methacrylate, Swelling behaviour, Thermal behaviour

1 Introduction

In recent times, there has been a marked thrust on the research activities relating to the modification of natural polymers. Grafting provides a clean and efficient technique to impart desirable properties to the backbone polymers. Modified polymers retain many of the intrinsic properties of the natural polymers and the incorporation of grafted polymers affords improved strength, water repellency, colour fastness and many other attributes deficient in natural polymers. Cellulose and its derived forms are the potential backbones which can be modified to have products for various end-uses.

Grafting of MMA onto cellulose and celluloses is well investigated by chemical and radiation methods. Initiation of grafting by redox reactions employing ceric ions has been extensively studied for grafting of MMA and its binary mixture with other vinyl monomers onto cellulose and celluloses^{1,2}. Haque *et al.*³ grafted MMA onto jute fibre and reported the effects of temperature, initiator concentration and lignin content of jute on graft yields. Percentage grafting of MMA onto beaten cellulose was reported to decrease on beating⁴. Cotton and polyester were graft copolymerized with MMA in aqueous solution in the

presence of HNO₃ by Ibeagi *et al.*⁵ Lin *et al.*⁶ grafted MMA onto bamboo cellulose and evaluated optimum conditions for maximum grafting. Taga and Inagaki⁷ reported that C₂-C₃ glycol groups of the cellulose are the active sites for grafting of MMA. Ceric ion initiated grafting of MMA onto cotton cellulose is also reported recently by Casinos⁸. Okieimen and Ogbeifun⁹ grafted acrylonitrile (AN) and MMA individually and as binary mixture onto carboxymethyl cellulose and reported that smaller amount of polyacrylonitrile is grafted from the mixture of monomers even at higher feed of AN. Comparatively higher reactivity of MMA for thiocarbamate-N-bromosuccinimide redox initiated grafting onto ferrous cellulose has been reported by Magdy¹⁰ in order of reactivity to grafting of different monomers as MMA > Methyl acrylate > AN. Mansour and Basta¹¹ reported that MMA showed maximum reactivity when MMA, ethyl acrylate, allyl chloride, allyl alcohol, methyl acrylate and AN were grafted onto cellulose by ionic xanthation method. Ghosh and Dev¹² grafted MMA and acrylamide mixture onto dialdehyde cellulose obtained from cotton in limited aqueous phase and reported that modification of fibre properties depends on the extent of grafting. Thermal properties of cellulose and cellulose-

sics have been reported to improve upon impregnation of phosphorus or halogen compounds and grafting of vinyl monomers¹³⁻¹⁶. In our earlier work, we have studied thermal analysis of some cellulose fibres like cotton, rayon and jute and their graft copolymers with MMA¹⁷. The grafted fibre showed higher initial decomposition temperature (IDT) than the original fibre. Stability of ungrafted fibre vary in the order of cotton > jute > *Cannabis* > rayon while in case of grafted fibres, the order of stability was found to be cotton > *Cannabis* > jute > rayon.

The fibres obtained from the stem and branches of *Cannabis indica* have been used by the locals of Himalayas for ages in making ropes, baskets, mats and specialty footwears. The fibre contains 70% cellulose on dry-to-dry basis. However, the fibre suffers from such drawbacks as biodegradation, weathering damage and loss of strength. In the present study, an attempt has been made to modify the *Cannabis indica* fibre through grafting methyl methacrylate (MMA) by ceric ion initiation method in order to improve its strength and resistance to weatherability. The effects of monomer concentration, initiator concentration, HNO₃ concentration, reaction time, temperature and amount of water on per cent grafting have been studied to evaluate the optimum conditions for maximum grafting. Extent of swelling by graft copolymers in different solvents and the thermal behaviour of the graft copolymers have also been studied.

2 Materials and Methods

2.1 Purification of Materials

The fibre isolated from the stem of *Cannabis indica* was immersed in water at 50°C for 24h and then dried in an oven at 50°C. MMA (Merck) was washed with 5% NaOH and dried over anhydrous Na₂SO₄. The dried monomer was distilled and the middle fraction was used. Ceric ammonium nitrate (CAN) of reagent grade was used as such. Cellulose was estimated by ammonia method¹⁸.

2.2 Graft Copolymerization

Cannabis indica fibre (1.0g) was immersed in 100 ml of distilled water and the known amounts of monomer, initiator and HNO₃ were added to the reaction mixture. The contents were refluxed at 45°C for 2h. The optimum reaction conditions for maximum grafting were evaluated as a function of the concentrations of monomer, initiator and HNO₃, amount of water, reaction time and reaction temperature. Homo-

polymer was removed from the fibre by repeated solvent extractions using acetone until a constant weight was obtained. The graft copolymer, free of homopolymer, was dried in an air oven at 50°C. Swelling behaviour of ungrafted and grafted fibres was studied in DMF, H₂O and n-butanol as reported elsewhere¹⁹. The per cent grafting (P_g) and per cent swelling (P_s) were calculated as follows:

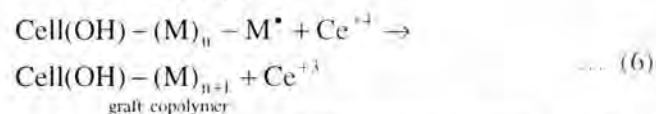
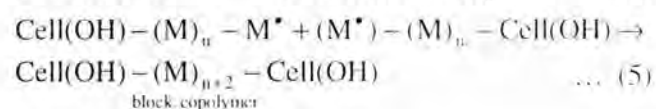
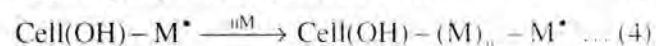
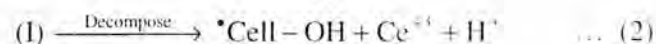
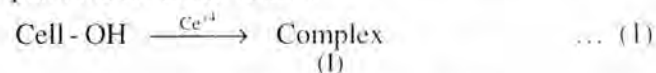
$$P_g = [(W_1 - W_0)/W_0] \times 100$$

$$P_s = [(W_s - W_0)/W_0] \times 100$$

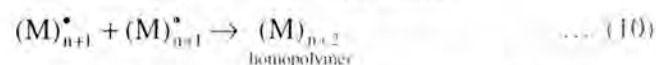
where W₁ is the weight of graft copolymer; W₀, the weight of initial fibre sample; W_s, the weight of swollen graft copolymer; and W_m, the dry graft copolymer weight.

3 Results and Discussion

The C₂, C₃ and C₆ hydroxyl and C-H groups in cellulose are the sites for grafting. Ceric ion forms complex with hydroxyl groups and C₂ and C₃ glycolic hydroxyl groups, are the preferred sites for complex formation. The complex disproportionates to generate free radical sites where MMA can be grafted. The following mechanism of grafting is proposed to explain the observed results:



Initiation of monomer by complex formation with ceric ion is also possible:



The initiation of monomer via complex formation with ceric ion explains homopolymer formation along with grafting reactions. Thus, graft yield and homo-

polymer formation are the functions of both monomer and initiator concentrations.

3.1 Effect of Monomer/Initiator Concentration

Structure, reactivity and concentration of monomer affect the population of monomer and its macroradicals. MMA forms complex with ceric ions in an organized array and cellulose provides a matrix for the same. Thus, the initial increase in monomer concentration leads to increase in graft yield (Fig. 1). Very sharp increase in the graft yield with increase in monomer concentration is the result of autoacceleration effect. However, further increase in monomer concentration leads to decrease in grafting since higher simultaneous initiation of monomer chains at the cost of generation of active sites on the polymer backbone leads to the formation of homopolymer by mutual annihilation of monomer macroradical chains.

The effect of change of initiator concentration is shown in Fig. 2. Maximum grafting of 45.5% is observed at 0.01 moles/L of CAN and consequent increase in concentration leads to a decrease in P_g . Similar behaviour for grafting of MMA onto cotton has been reported by Sharma and Daruwalla²⁰. This trend in P_g can be explained by the fact that at higher concentration, Ce^{+4} forms more complexes with polymer backbone as well as the monomer. Higher complexes population results in premature decay and hence a fall in grafting.

3.2 Effect of Nitric Acid Concentration

Variation of P_g as a function of HNO_3 concentration is shown in Fig. 3. After an initial increase, P_g decreases at higher concentrations. It is also evident that at lower concentration of acid, very low variation in P_g is observed. Thus, the lower concentrations of acid catalyze the grafting reactions, but the coagulation of homopolymer and the enhancement of termination of cellulose active sites alongwith the wastage of monomer in side reactions lead to a decrease in P_g as concentration of acid is increased. Similar effect has been reported by El-Alfy *et al.*²¹ for grafting of allyl methacrylate onto cotton cellulose. Sood *et al.*²² proposed that ceric ion exists as $[Ce-O-Ce]^{+6}$, $[Ce]^{+4}$ and $[CeOH]^{+3}$ in reaction medium and on addition of acid these complex ions change to Ce^{+4} which can penetrate easily into cellulose matrix and form complex.

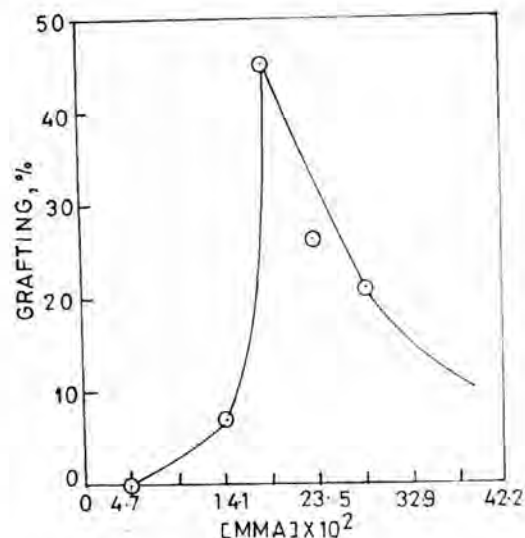
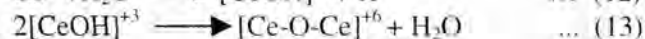
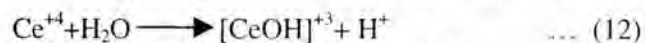


Fig. 1—Effect of monomer concentration on grafting [*Cannabis* fibre, 1g; CAN conc., 10×10^3 mol/l; HNO_3 conc., 17.44×10^2 mol/l; temperature, 25°C; time, 120 min; and H_2O , 100 ml]

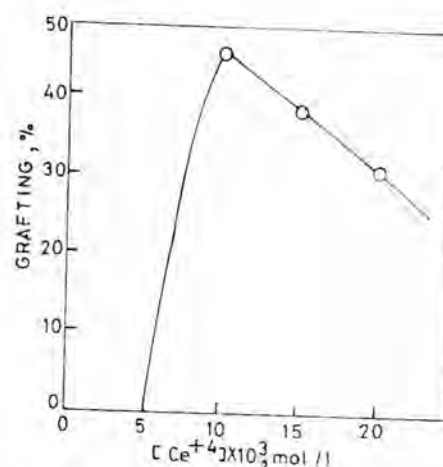


Fig. 2—Effect of ceric ammonium nitrate concentration on grafting [*Cannabis* fibre, 1g; MMA conc., 22.21×10^2 mol/l; HNO_3 conc., 17.44×10^2 mol/l; temperature, 25°C; time, 120 min; and H_2O , 100 ml]

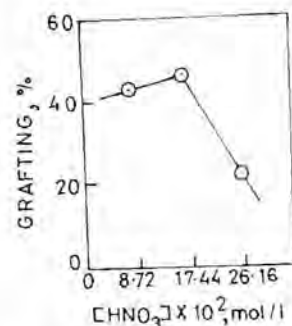


Fig. 3—Effect of nitric acid concentration on grafting [*Cannabis* fibre, 1g; MMA conc., 22.21×10^2 mol/l; CAN conc., 10×10^3 mol/l; temperature, 25°C; time, 120 min; and H_2O , 100 ml]

From Eq. (12) it is evident that the population of Ce^{+4} should increase on addition of acid, leading to increased graft yield. However, when the acid concentration increases further, it, being an oxidizing agent, leads to more side reactions.

3.3 Effect of Reaction Time and Temperature

The effect of temperature on P_g is shown in Fig. 4. It is observed that increase in temperature leads to enhanced swelling of the trunk polymer, increased diffusion of the growing monomer macroradical chains to active sites and enhanced decomposition of the complexes of Ce^{+4} both with monomer and cellulose. However, at higher temperature ($55^\circ C$), P_g decreases as the termination and chain reactions predominate the grafting process. In the present study, the fibre did not only lose weight but also became brittle and lost strength when the reaction temperature was increased to $65^\circ C$ and $70^\circ C$. It is explained by considering the fact that the fibre loses weight and strength as the water-soluble constituents of the fibre are driven out. It is also supported by the control experiment that the fibre loses weight up to 18.2% when it is treated in water at $65^\circ C$. It is further substantiated from the primary thermograms of grafted and ungrafted *Cannabis* fibre as an inflexion is observed between $30^\circ C$ and $150^\circ C$ due to the loss of water which is absent in the grafted sample. The effect of variation of reaction time is shown in Fig. 5. It is observed that grafting increases steadily when the reaction time is increased to 120 min. However, further increase in the reaction time decreases P_g . This trend in P_g is explained by the fact that as the time increases the monomer, backbone and initiator interactions increase, but with further increase in time the graft yield is reduced since the grafting reactions are overtaken by more homopolymer formation as well as by other side reactions.

3.4 Effect of Amount of Water

Fig. 6 shows the effect of amount of water on the graft yield. As the amount of water in reaction medium increases from 75 ml to 150 ml, P_g first increases and then shows a sharp decrease. The presence of water helps in the opening of cellulose backbone and makes it more accessible to the monomer. Apart from loosening of cellulose hydrogen bonding and swelling of trunk polymer, there also exists a possibility of formation of water-cellulose-monomer complex. Hence, an optimum amount of water is use-

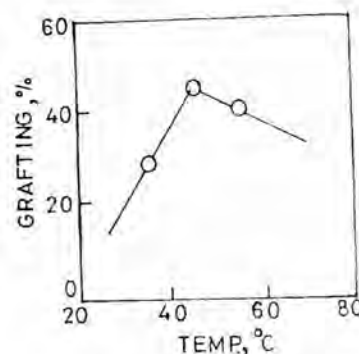


Fig. 4—Effect of temperature on grafting [*Cannabis* fibre, 1g; MMA conc., 22.21×10^2 mol/l; CAN conc., 10×10^{-3} mol/l; HNO_3 conc., 17.44×10^2 mol/l; time, 120 min; and H_2O , 100 ml]

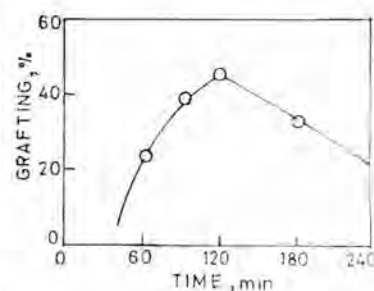


Fig. 5—Effect of reaction time on grafting [*Cannabis* fibre, 1g; MMA conc., 22.21×10^2 mol/l; CAN conc., 10×10^{-3} mol/l; HNO_3 conc., 17.44×10^2 mol/l; temperature, $25^\circ C$; and H_2O , 100 ml]

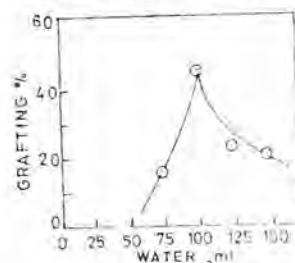


Fig. 6—Effect of amount of water on grafting [*Cannabis* fibre, 1g; MMA conc., 22.21×10^2 mol/l; CAN conc., 10×10^{-3} mol/l; HNO_3 conc., 17.44×10^2 mol/l; temperature, $25^\circ C$; and time, 120 min]

ful for attaining the higher level of P_g , but higher amount of water affects the above advantages as monomer molecules and growing monomer chains lead to lower accessibility to the active sites on the backbone polymer. This effect is more pronounced in the present case as MMA is insoluble in water.

3.5 Characterization of Graft Copolymers

— The IR spectra of *Cannabis indica* fibre and its graft copolymers were taken in KBr pellets on Nicolet IR 750 spectrometer. *Cannabis* fibre shows broad peaks at $3378 cm^{-1}$ due to bonded O-H and at 2921 and $1097 cm^{-1}$, arising from C-H and C-O-C stretching

respectively. The graft copolymers show additional strong bands at 1730cm^{-1} . When the graft copolymers were hydrolyzed with 6 N HCl and the resulting resinous mass was analyzed by IR spectroscopy, a strong band at 1725cm^{-1} was observed.

— Thermogravimetric analysis (TGA) of *Cannabis* fibre and *Cannabis*-g-poly(MMA) was carried out in nitrogen atmosphere at a heating rate of $20^\circ\text{C}/\text{min}$ on Shimadzu TG/DT Simultaneous Analyzer. The decomposition of both the fibres was studied as a function of time and is presented as % weight loss v/s time (Fig. 7). Cellulose decomposes by the primary reactions like thermo-oxidation, dehydration, depolymerization and glucosan formation. Dehydration occurs usually in the region $180\text{--}280^\circ\text{C}$ and it is followed by C-C and C-O bonds random scission. TG curve of *Cannabis* fibre shows three inflexions between 30°C and 150°C , 383°C and 420°C , and 473°C and 518°C . The first region of inflexion seems to be due to the loss of water content of the fibre. The initial decomposition begins at 236°C and continues up to 383°C with a constant weight loss. 70% weight is lost in the range $300\text{--}400^\circ\text{C}$. It precedes 10% weight loss which is due to the loss of moisture. Inflexion between 383°C and 420°C shows that the amorphous region of the cellulose content of the fibre is disturbed with the loss of hydrogen-bonded structure and that the higher temperature ($473\text{--}518^\circ\text{C}$) is required to break down the crystalline region. The overall decomposition of the fibre takes about 36 min. On the other hand, TG curve of *Cannabis*-g-poly(MMA) reveals single-stage decomposition with a very small inflexion between 34°C and 138°C . However, the initial decomposition of the grafted fibre begins at

263°C and continues up to 306°C at a constant weight loss. Beyond $306\text{--}417^\circ\text{C}$, a slight increase in the decomposition rate and weight loss is observed. So, the grafting of MMA onto the fibre results in breaking down of the hydrogen-bonded structure of the backbone, thus leading to single-stage decomposition. Higher initial decomposition temperature (IDT) of 306°C as compared to 259°C of original fibre shows higher thermal stability of the grafted fibre. A comparison of the decomposition temperature (DT) at every 10% weight loss indicates that the difference in successive DT decreases continuously till 60% weight loss and then it increases. In case of grafted fibre, the difference in successive DT shows steady increase, indicating thereby higher energy requirements for every 10% weight loss.

The initial decomposition of the original fibre starts after 22.5 min and goes up to 383°C within next 2 min from 306°C . Complete decomposition of the grafted fibre occurs in 31 min. These observations suggest that grafting may have occurred both in the amorphous and crystalline regions of cellulose. This is evident from the fact that the region of decomposition of crystalline region between 473°C and 518°C in the original fibre is absent in the grafted fibre.

Differential thermal analysis (DTA) curve of the *Cannabis* fibre and its graft copolymer are presented in Fig. 8. The ungrafted fibre shows two exothermic peaks at 370°C and 419°C while the grafted fibre shows a small endothermic peak at 349°C and an exothermic peak at 380°C . The small peak at 370°C with temperature shooting to 382°C is related to the temperature region between 383°C and 420°C of TGA owing to the breakdown of the hydrogen-bonded structure of cellulose in amorphous region. The second exothermic peak at 419°C with temperature shooting to 473°C is due to the decomposition of the crystalline structure of the cellulose.

The small exothermic peak in the grafted sample may be ascribed to the loss of ether from the grafted poly(MMA) chains as²³:

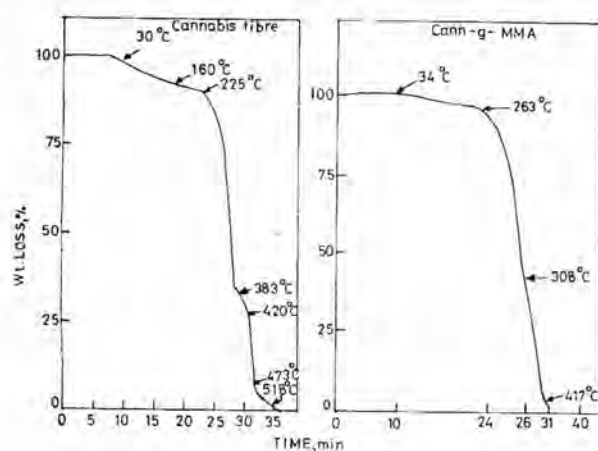
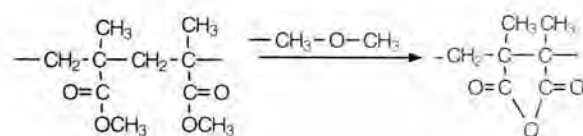


Fig. 7—TG curves of *Cannabis* and *Cannabis*-g-PMMA fibres



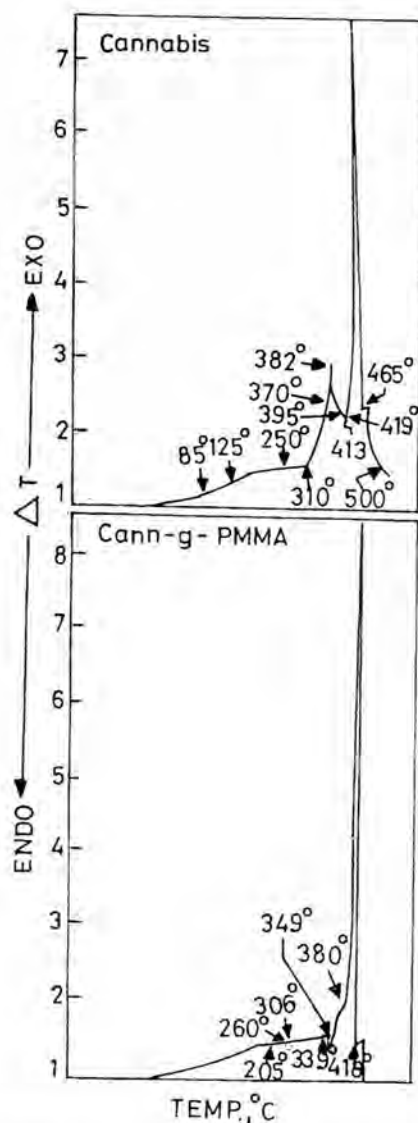


Fig. 8—DTA curves of *Cannabis* and *Cannabis*-g-PMMA fibres

The exothermic peak at 380°C with temperature shooting to 444°C is due to the decomposition of the grafted poly(MMA) chains in addition to the decomposition of the cellulose content of the fibre.

— The swelling behaviour of the ungrafted and grafted samples was studied in DMF, H₂O and *n*-butanol. The results are presented in Fig. 9. The swelling of the grafted samples varies as a function of P_g and the trend for the grafted samples follows in the order: DMF > H₂O > *n*-butanol, while for ungrafted sample, it is H₂O > DMF > *n*-butanol. This is understandable from the fact that water affects the changes in the hydrogen bonding of cellulose by loosening it and penetrates deeper into the matrix. The same phenomenon is not possible for DMF and *n*-butanol.

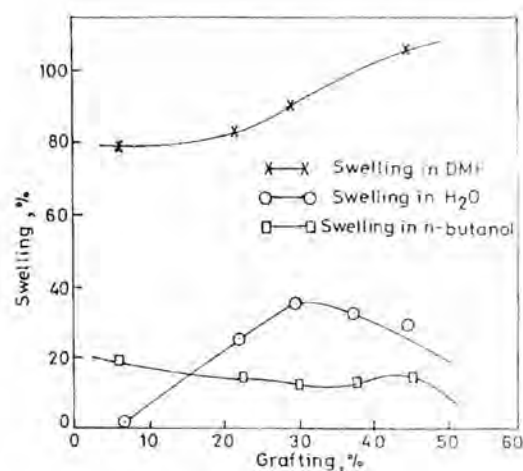


Fig. 9—Swelling as a function of grafting [graft copolymer, 1g; solvent, 10 ml; and time 1440 min]

However, the grafted sample contains methacrylate chains which are solvolyzed by DMF and more swelling in DMF is observed with the increase in P_g . However, water and *n*-butanol can not interact with methacrylate groups to the same extent, hence the observed different patterns for per cent swelling in the grafted copolymers. The swelling behaviour further supports the findings that during grafting the moisture content of the fibre is lost. Therefore, the sorption behaviour of the grafted fibre is shifted from water to DMF.

4 Conclusion

The graft copolymers show higher initial decomposition temperature as compared to original fibre. The grafting of methyl methacrylate shows enhanced thermal stability of the *Cannabis indica* fibre considerably. Similarly, the swelling behaviour of the fibre is significantly changed on grafting due to the opening up of the fibre. The change in these characteristics of the fibre can lead to increase in the spectrum of uses of *Cannabis* fibre.

Acknowledgement

The authors are grateful to the Principal, REC, Hamirpur, for providing facilities to carry out this work.

References

1. Mansour O Y & Nagaty A, *J Polym Sci, Polym Chem Ed*, 13 (1975) 2785.
2. Sharma V N & Daruwalla E H, *J Appl Polym Sci*, 21 (1977) 331.
3. Haque M M, Md. Habiduddowla, Mahmoud A J & Mian A J, *J Polym Sci, Polym Chem Ed*, 18 (1980) 1447.

- 4 Kurosu H & Horike K, *Makuzai Gakkaishi*, 22 (1976) 92; *Chem Abstr*, 85 (1976) 22952u.
- 5 Ibeagi U M, Yabani A M & Ugbohue S C O, *Colloid Polym Sci*, 258 (1980) 1137.
- 6 Lin K C, Lin Y S & Hu C T, *Chem Abstr*, 94 (1981) 158548k.
- 7 Taga T & Inagaki H, *Sen'i Gakkaishi*, 37 (1981) T516; *Chem Abstr*, 96 (1982) 37110u.
- 8 Casinos I, *Angew Makromol Chem*, 22 (1) (1994) 33.
- 9 Okieimen F E & Ogbeifun D E, *J Appl Polym Sci*, 59 (6) (1996) 981.
- 10 Magdi Kandil Zahran, *J Appl Polym Sci*, 62 (1) (1996) 49.
- 11 Mansour O Y & Basta A H, *Polym - Plast Technol Eng*, 34 (3) (1995) 405.
- 12 Ghosh P & Dev Deba Prasad, *Eur Polym J*, 32 (2) (1997) 165.
- 13 Wakayama P, *Chem Abstr*, 95 (1981) 44702w.
- 14 Inagaki N & Katsura K, *J Polym Sci, Polym Chem Ed*, 18 (1980) 441.
- 15 Mukherjee A K & Sanyal S, *Cellul Chem Technol*, 13 (1979) 13.
- 16 Mitra D, Subharwal S & Majali A B, *Therman* (Indian Thermal Society, Jammu), 1998, 222.
- 17 Chauhan Ghanshyam S, Bhatt Sarvjeet S, Kaur Inderjeet, Singha A S & Kaith Balbir, *Therman* (Indian Thermal Society, Jammu), 1998, 196.
- 18 *Encyclopedia of polymer science and technology*, Vol. 3, edited by N Bikales, H Mark & N Gaylord (John Wiley and Sons, New York), 1965, 138.
- 19 Misra B N, Kaur Inderjeet, Gupta Anupam, John Valsamma and Singha A S, *Polym Polym Compos*, 4 (6) (1996) 411.
- 20 Sharma V N & Daruwalla E H, *Cellul Chem Technol*, 13 (1979) 433.
- 21 El-Alfy E, Khalil M I & Hebeisha, *J Polym Sci, Polym Chem Ed*, 19 (1981) 3137.
- 22 Sood D S, Kishore J & Misra B N, *J Macromol Sci Chem*, A 22 (3) (1985) 263.
- 23 Raghunandhan Nair C P, Clouet G & Guilbert Y, *Polym Degrad Stabil*, 26 (1989) 305.