# GRAFTING MMA ONTO FLAX UNDER THE INFLUENCE OF MICROWAVE RADIATION AND THE USE OF FLAX-g-POLY(MMA) IN PREPARING PF COMPOSITES

**Balbir Singh Kaith[1], Amar Singh Singha[1] and Susheel Kalia[*2],**

[1]Department of Applied Sciences, National Institute of Technology, Hamirpur 177 005 (H.P.) India
[2]Department of Chemistry, Singhania Institute of Law, Management, Science and Technology, Pacheri Bari, Jhunjhunu 333 515 (Raj.) India
[*]susheel_kalia@yahoo.com

## Abstract:

*This paper deals with the graft co-polymerisation of methylmethacrylate (MMA) onto flax fibre under the influence of microwave radiation (MWR). The graft co-polymers are characterised by FTIR spectroscopy, scanning electron microscopy (SEM), thermal analysis (TGA/DTA) and X-ray diffraction (XRD). Graft co-polymers are subjected to the evaluation of some physical, chemical and mechanical properties. Graft co-polymers thus prepared are used in the preparation of phenol-formaldehyde composites. Wear resistance, tensile strength and compressive strength of composites are measured, and it is found that composites reinforced with flax-g-poly(MMA) showed better mechanical properties in comparison to composites reinforced with raw flax.*

## Key words:

*Flax, FAS-$H_2O_2$, grafting, MWR, composites and mechanical behaviour*

## Introduction

Alfrey and Bandel [1] were the first to synthesise graft co-polymers in 1950. They polymerised vinyl acetate in the presence of styrene and vinylidene chloride. The concept of graft co-polymer was actively promoted by Mark [24], who announced new graft co-polymers and thus thoroughly renewed the area of graft co-polymerisation research [14]. During the 1960s the research on grafting remained active. In the early 1970s graft co-polymerisation and its potential was reviewed in several books [4]. Grafting involves the attachment of polymer chains, usually synthetic, to the back-bone polymer. It is a method of increasing the compatibility between synthetic polymers and cellulose [13]. The process of grafting has been explained by Schwab et al. [26]. Modification of fibrous proteins and cellulose through graft co-polymerisation has been reported by various workers [8, 9, 11, 22, 33]. Radical polymerisation has several disadvantages, but grafting onto cellulose still involves radical polymerisation [2, 13, and 23].

Many workers have modified cellulosic fibres through the grafting technique by using different initiating systems. Redox initiators are capable of initiating vinyl polymerisation with few side reactions at low temperature. Fenton's reagent (FAS-$H_2O_2$) is a well known redox initiator for vinyl polymerisation under milder conditions, and has hence been successfully utilised in grafting vinyl monomers onto cellulosic fibres [25]. Resistance to chemicals, solvents and moisture has been incorporated through grafting in natural polymers which are otherwise vulnerable to acids, bases and water [18, 28].

Composites reinforced with cellulosic fibres have received considerable interest in recent years. The advantages of composites reinforced with natural fibres over those reinforced with traditional material are biodegradability [27], better mechanical properties and low density [15]. It has been reported that polypropylene (PP) composites reinforced with wood fibre have properties similar to glass fibre-reinforced PP composites [21]. Joshi et al [16] proposed that composites reinforced with natural fibre are likely to be environmentally superior to those reinforced with glass fibre in many applications. Composites reinforced with cellulosic fibres have been reviewed by Bledzki & Gassan [6]. Fibre-reinforced composites offer numerous technical advantages for engineering, automobiles and other industrial applications. These composites are used in different fields ranging from the material with relatively low mechanical properties for elementary purposes to high-performance material [3, 20, 31,

32, 36]. Kaith et al [19] and Dwivedi et al [10] have reported the reinforcement of polystyrene composites with graft co-polymers of flax fibre. Canche-Escamilla et al [7] have studied the mechanical properties of acrylate-grafted henequen cellulose fibres and their applications in composites, and found that the best results were obtained with poly(MMA) grafted cellulose fibres because of the better fibre-matrix adhesion.

The MWR technique reduces the extent of the physico-chemical stresses to which the fibres are exposed during the conventional techniques [34]. It has been reported that properties of fibres treated under the MWR-assisted technique are the same or even better than those of fibres modified through other conventional techniques [11, 35]. Polyacrylamide was graft co-polymerised onto chitosan and guar gum using MWR, and a maximum grafting of 169% and 66.66% was observed in 1.16 and 0.22 minutes respectively under optimum reaction conditions [29, 30]. Since grafting under MWR is advantageous in terms of time consumption and cost effectiveness, attempts have been made to graft co-polymerised MMA onto flax fibre under the influence of MWR. Graft co-polymers thus prepared are used as reinforcement in the preparation of phenol-formaldehyde (PF) composites.

## Experimental

### Materials

Soxhlet extraction of the flax fibre with acetone was carried out for 72 hrs. Methylmethacrylate (MMA) was washed with 5% sodium hydroxide followed by water, and was then dried over anhydrous sodium sulphate. The dried monomer was distilled and the middle fraction was used. $H_2O_2$ was used as received, and ferrous ammonium sulphate (FAS) was recrystallised from hot water.

A Libror AEG-220 (Shimadzu) electronic balance was used for weighing purposes.

IR spectra of the samples were recorded with KBr pellets on a Bomem, Hartmann & Braun (MB-Series) spectrophotometer. Scanning electron microscopic analysis of the flax and its graft co-polymers were carried-out on an LEO electron microscopy machine (Sr. No. 435-25-20). Thermo-gravimetric analysis and differential thermal analysis studies were carried-out in air on a thermal analyser LINSEIS (L-81 11) at the heating rate of $10^o$C per minute. X-ray diffraction studies were carried out on a Bruker-$D_8$ advance model X-RD.

The strength of fibres was measured with a Stelometer (MAG, FO501). The wear resistance of the composites was tested on a Wear & Friction Monitor (DUCOM, 20LE). The tensile and compressive strength of samples were tested on a Universal testing machine (Hounsfield, H25KS).

### Graft co-polymerisation of MMA onto flax fibre under the influence of microwave radiation

Flax fibre (500 mg) was immersed in 100 ml of distilled water for 24 hours prior to its grafting under the influence of microwave radiation. A definite ratio of FAS-$H_2O_2$ and a known amount of monomer were added to the reaction mixture. The reaction mixture was stirred and transferred to the microwave oven running at 210W micro-wave power for a specific time interval. The different reaction parameters were optimised and the the homopolymer was separated from the grafted fibre in order to obtain maximum graft yield. The graft co-polymer obtained was dried in the oven at $50^o$C until a constant weight was obtained. The percentage grafting 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 raw and grafted flax respectively.

### Swelling, moisture absorbance, chemical resistance, dye characteristics and fibre strength

Swelling behaviour in different solvents, moisture absorbance at different humidity levels, chemical resistance against acid and base, and the dye characteristics of the grafted and ungrafted samples were examined as per the methods reported earlier [17, 18].

Fibre strength was measured with a Polymeris bundle strength tester (Stelometer). A known weight of fibre bundle was put in the Stelometer and the total strength (gms/tex) required to break the fibre was measured and calculated as follows:

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

Strength (gms/tex) = strength (kg/mg) × 15.0 (constant factor)
Actual Strength (gms/tex) = Strength (gms/tex) × Humidity correction factor,
whereas the Humidity correction factor at RH 53% is 1.0756.

## Preparation of composites

The phenol-formaldehyde (PF) matrix-based composites were prepared by mixing a particular ratio (by weight) of resin with fibre (in the ratio of 1:0.075), which was then placed in an aluminium die of specific dimensions (length 4-8 cm and cross-section 5×5 mm). The sample was cured by heating it in a hot air oven at $80^{\circ}$C for 12 hrs. The composites thus prepared were subjected for the evaluation of different mechanical studies.

## Wear test

The composites were tested for wear resistance as per ASTM D 3702 on a DUCOM machine designed for ISO-9001-2000. Wear resistance was conducted against a hardened steel disc with a hardness of 60 HRC and a roughness of Ra 0.5 µm. The counter-surface was polished using emery paper and cleaned with acetone before each sliding test. Samples (3 cm) for wear test were held against the rotating counter-surface at different speeds (100-600 RPM) and normal loads (1-4 kKg). Each test was conducted for 5 minutes of sliding. Loss of weight was used as a measure of wear.

## Tensile strength test

Tensile strength was tested as per ASTM D 3039. The composite sample of 8 cm length was clamped between two jaws of the universal testing machine. Each end of the jaws covered 2 cm of the sample; the rest of the 4 cm sample was used to study the tensile behaviour. Readings for force and extension were set at zero. The test was conducted at a constant strain rate of order of 5 mm/min. Tensile stress was applied until the sample failed, and the load-extension curve was obtained.

## Compressive strength test

The compressive strength of the samples was studied by using the procedure described in ASTM D 3410. A composite sample of 4 cm was held between two platforms and the strain rate was fixed at 2 mm per minute. The compression stress was applied until the sample failed. The total compression per unit force was noted.

# Results and Discussion

$C_2$, $C_3$ and $C_6$ hydroxyls and the C-H groups are the active cites for grafting in cellulosics. The grafting onto flax in the presence of FAS-$H_2O_2$ is supposed to take place as per the mechanism proposed by Bhattacharya & Misra [5].

### Characterisation of graft co-polymers

The IR spectrum of the flax fibre showed a broad peak at 3,420 cm$^{-1}$ due to the bonded –OH group and at 2,925.5 cm$^{-1}$, 1,458.6 cm$^{-1}$ and 1,055.87 cm$^{-1}$ arising from –$CH_2$, C-C and C-O stretching respectively. However, in the case of flax-g-poly (MMA), an additional peak at 1,730 cm$^{-1}$ due to the >C=0 group was observed. This suggests that MMA has been grafted onto flax fibre through covalent linkages.

Scanning electron micrographs of raw flax and flax-g-poly(MMA) reveals a clear-cut distinction between the ungrafted and grafted flax (Figures 1 and 2).

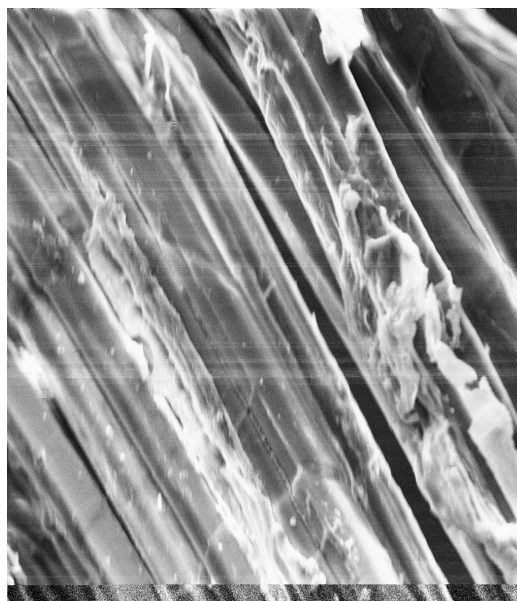**Figure 1**. Scanning electron micrographs of raw flax



**Figure 2**. Scanning electron micrographs of Flax-g-poly(MMA)

Thermo-gravimetric analyses of raw flax (7.0 mg) and flax-g-poly(MMA) (11.0 mg) samples were carried out at a heating rate of $10^{o}$C / minute in air as a function of percentage weight loss versus temperature.

It is evident from Figures 3 and 4 that in the case of original flax fibre, depolymerisation and glucosan formation initially took place between $89.6^{o}$C to $253^{o}$C with 10.42% weight loss. However, in the case of flax-g-poly(MMA) the primary reactions due to depolymerisation and glucosan formation took place up to the temperature of $207.9^{o}$C. It has been found that the initial and final decomposition temperatures of the original flax fibre are $279.9^{o}$C and $489.1^{o}$C respectively, whereas in the case of flax-g-poly (MMA) the initial and final decomposition temperatures are $269.2^{o}$C and $436.2^{o}$C respectively. It is evident that in the case of grafting, the fibre becomes more amorphous, thereby resulting in lower initial and final decomposition temperatures of the graft co-polymers obtained.
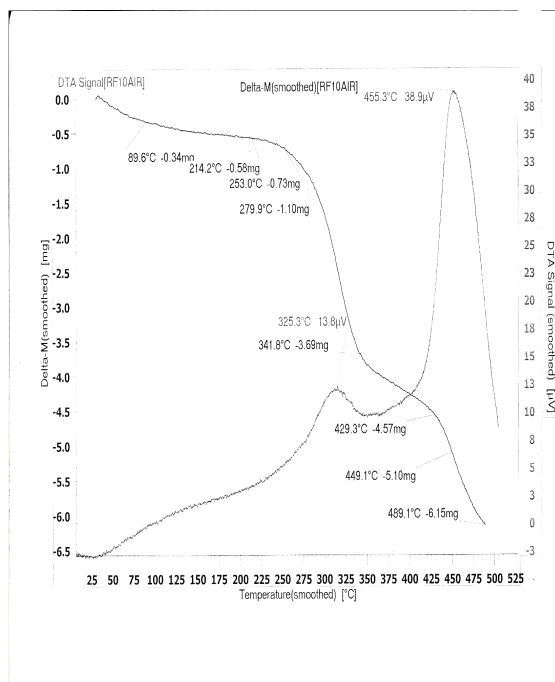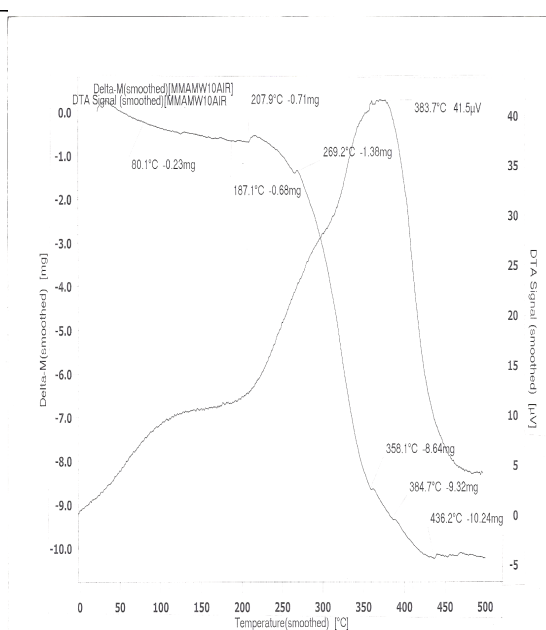


**Figure 3**. TGA-DTA curves of raw flax



**Figure 4**. TGA-DTA curves of flax-g-Poly(MMA)

Differential thermal analysis of the original flax fibre shows exothermic peaks at 325.3°C (13.8 µV), and there was a continuous exothermic combustion of the sample at furnace temperature in the presence of atmospheric oxygen. This peak shows the disturbance in the H-bonded amorphous region. Another sharp exothermic peak was observed at 455.3°C (38.9 µV) which indicates the complete breakdown of C-C and C-O bonds of the crystalline region (Figure 3). However, in the case of flax-g-poly(MMA), a continuous exothermic rise in temperatures was observed, and exothermic peaks at 383.7°C (41.5 µV) were obtained.

XRD studies were carried out under ambient conditions using Cu Kα (1.5418°A) radiation, a Ni-filter and a scintillation counter as a detector at 40 KV and 40 mA on rotation between 12° to 25° at 2θ scale at 1-second step size and increments of 0.01 degree with 0.5° or 1.0 mm of divergent and anti-scattering slits. The results are shown in Figures 5 and 6. Cellulosic fibres possess both crystalline and amorphous regions. The occurrence of both crystalline and amorphous regions indicates that ordered and disordered regions co-exist in crystalline polymers.

It has been observed from Figures 5 and 6 that raw flax on 2θ scale showed peaks at 14.82°, 16.30°, 22.65° and 23.22° , with relative intensities of 43.0, 36.0, 100.0 and 84.0 respectively. Flax-g-poly(MMA) showed peaks at 15.10°, 16.59°, 22.86° and 23.16° with relative intensities of 45.0, 39.0, 100.0 and 99.0 respectively. The diffraction patterns of raw flax and flax-g-poly(MMA) showed that the diffraction peak intensity of raw flax are not significantly reduced after grafting at all angles. This is due to the small amount of disturbance in the crystal lattice of the raw fibre, due to the incorporation of poly(MMA) chains on the active sites of the polymer back-bone during grafting, which thereby results in little morphological transformation and a slight decrease in crystallinity.
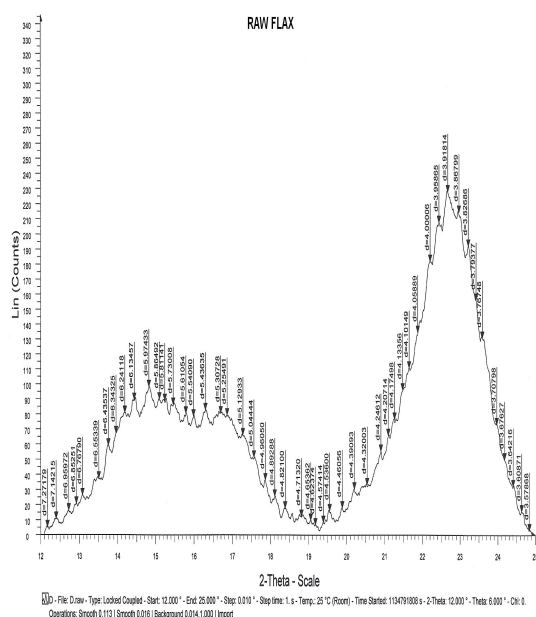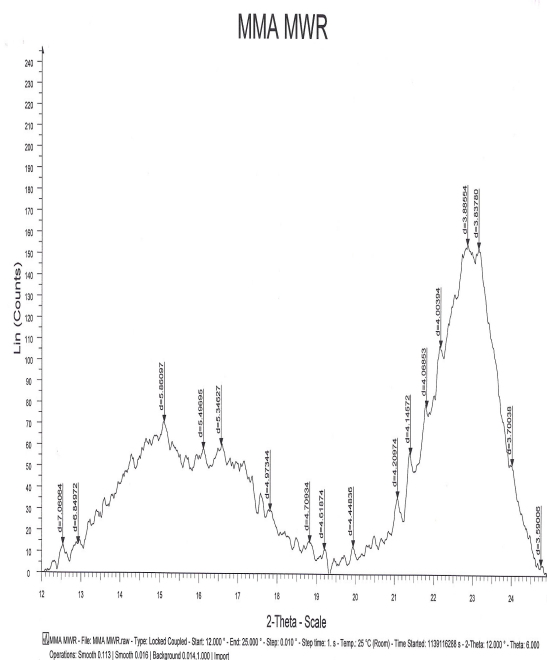


Figure 5. XRD studies of raw flax



Figure 6. XRD studies of Flax-g-poly(MMA)

## Effects of various reaction parameters

The optimum reaction conditions for obtaining maximum graft yield were as follows: MMA ($1.96 \times 10^{-3}$ mol L$^{-1}$); FAS-$H_2O_2$ (molar ratio), 1:6; time (min.), 30 and pH, 7.0.

As shown in Figure 7, $P_g$ increases with the increase in monomer concentration; after reaching the maximum value (24.64%), further increase in monomer concentration decreases the graft yield, because of the predomination of homo-polymerisation over graft co-polymerisation. Moreover, the increased viscosity of the reaction medium with homo-polymerisation hinders the path of the free radicals in reaching the active sites, thereby resulting in less graft yield.

The FAS-$H_2O_2$ molar ratio plays an important role in deciding the graft yield (Figure 8). Maximum grafting has been observed at a molar ratio of 1:6; further increase in molar ratio resulted in decrease

of the graft yield, because at higher concentration more $Fe^{3+}$ ions are produced which act as the chain terminator [5].

As is evident from Figure 9, $P_g$ has been found to increase with the increase in reaction time, but after 30 minutes, a decline in $P_g$ is observed. This is due to various hydrogen abstraction reactions being set up as well as an increase in the viscosity of the medium due to homo-polymerisation. $P_g$ has been found to increase with the increase in pH of the reaction medium up to 7.0 pH. A further increase in pH resulted in decreased $P_g$ (Figure 10). This is probably due to the decrease in concentration of free radicals as the OH ions act as the chain terminator, as shown below:

$$\text{Flax - (M)}^{*}_{n+1} + {}^{*}\text{OH} \text{ ----------} \rightarrow \text{Flax – (M)}_{n+1}\text{-OH}$$



**Figure 7.** Effect of MMA concentration on % grafting (Time = 30 min; FAS: $H_2O_2$ = 1.0:6.0; pH = 7.0)



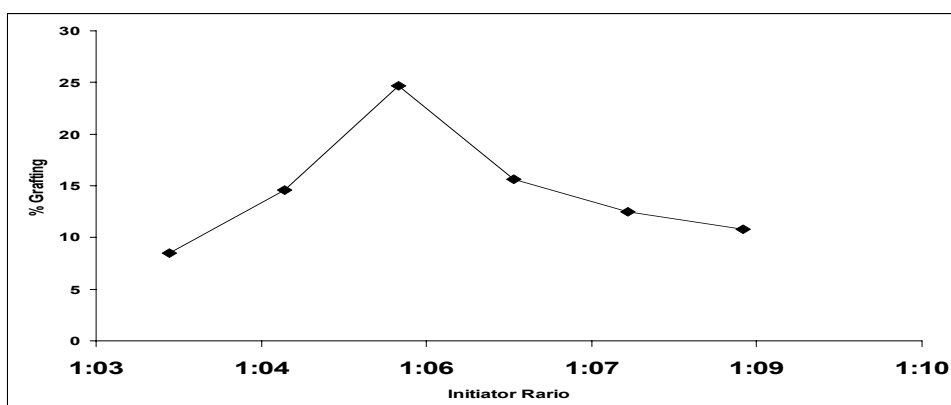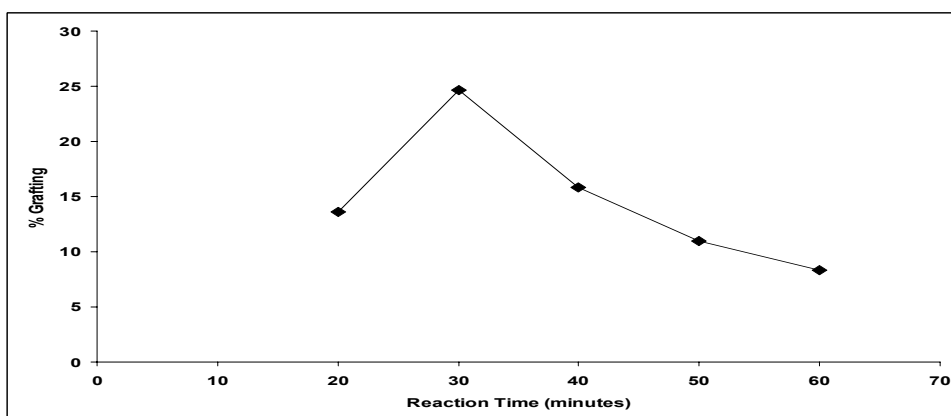**Figure 8**. Effect of FAS-$H_2O_2$ ratio on % grafting (Time = 30 min; MMA = 1.96 x $10^{-3}$ molL$^{-1}$; pH = 7.0)



**Figure 9**. Effect of reaction time on% grafting (MMA = 1.96×$10^{-3}$ molL$^{-1}$; FAS:$H_2O_2$ = 1.0:6.0; pH = 7.0)

### Physical, chemical and mechanical behaviour of graft co-polymers

It is evident from Figure 11 that swelling behaviour of the samples varied as a function of $P_g$ and followed the following order: propan-2-ol > $CCl_4$ > $H_2O$ > MeOH. In the cases of propan-2-ol and $CCl_4$, swelling has been found to increase with the increase in $P_g$. This is explained by the fact that MMA is more solvolysed with propan-2-ol and $CCl_4$ as compared to $H_2O$ and MeOH. On the other hand, in the case of un-grafted samples, the order is $H_2O$ > MeOH > $CCl_4$ > propan-2-ol. Water and MeOH, which have a greater affinity for hydroxyl groups present in cellulosics as compared to propan-2-ol and $CCl_4$, penetrate deep into the matrix, thereby resulting in more swelling of ungrafted fibre. Therefore, a different pattern for swelling in different solvents for both grafted and un-grafted fibres has been observed.
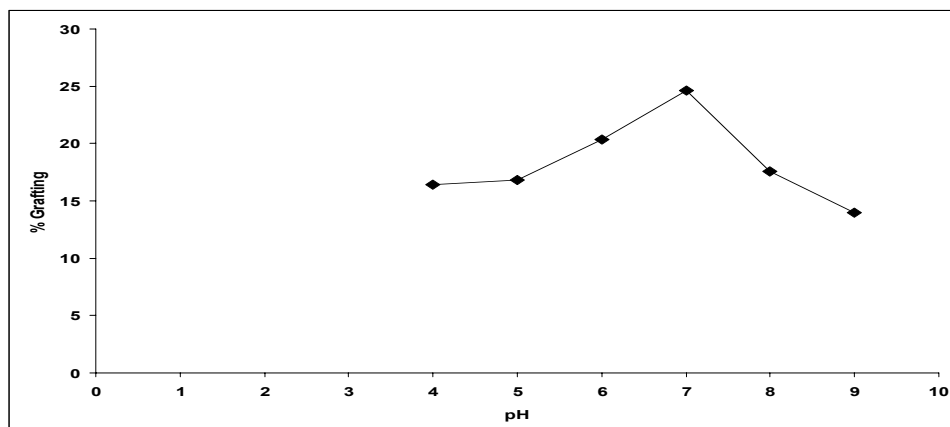


**Figure 10**. Effect of pH on % grafting (Time = 30 min; FAS : $H_2O_2$ = 1.0 : 6.0; MMA = $1.96 \times 10^{-3}$ molL$^{-1}$)
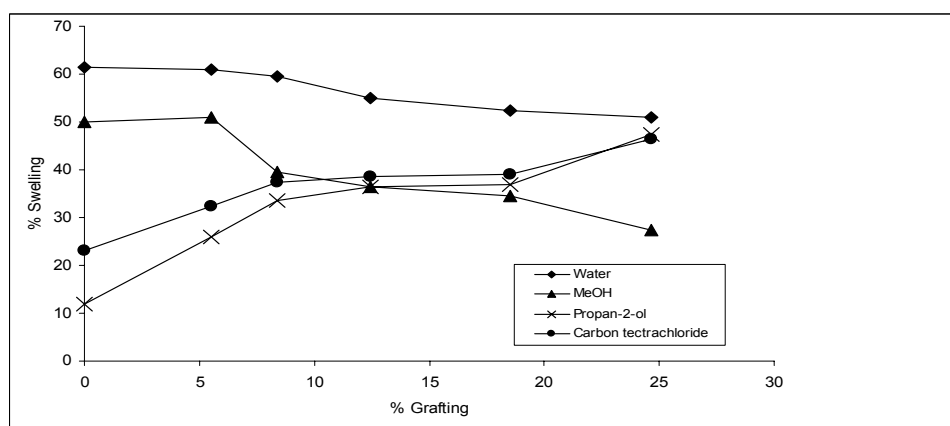


**Figure 11**. Effect of percent grafting of MMA onto flax fibre on swelling behaviour in different solvents

It is evident from Figure 12 that moisture absorbance decreases with the increase in $P_g$. This is because of the lesser affinity of water for MMA, and on grafting most of the active sites became blocked due to the incorporation of poly(MMA) chains.
It has been observed that the chemical resistance of the fibre against 1N HCl and 1N NaOH increases with the increase in $P_g$ (Figure 13 and 14). This is due to the fact that upon grafting with poly(MMA), the active sites which are vulnerable to chemical attack are blocked with the stable long polymeric chains. Thus grafting offers chemical resistance to the overall structure of the fibre.

It is quite evident from Figure 15 that there is a decrease in dye uptake by the fibre with increase in $P_g$. This is explained by the fact that dye absorption takes place on the active sites of the fibre which become blocked due to the grafting of poly(MMA) chains on these sites, thereby resulting in less dye uptake.

It has been observed that fibre strength increases with the increase in percent grafting. This is due to the fact that the optimum reaction time for obtaining maximum graft yield is quite short, and so grafting results in fewer surface flaws and the crystal lattice of the fibre is not much disturbed, which leads to an increase in fibre strength [34] (Table 1).
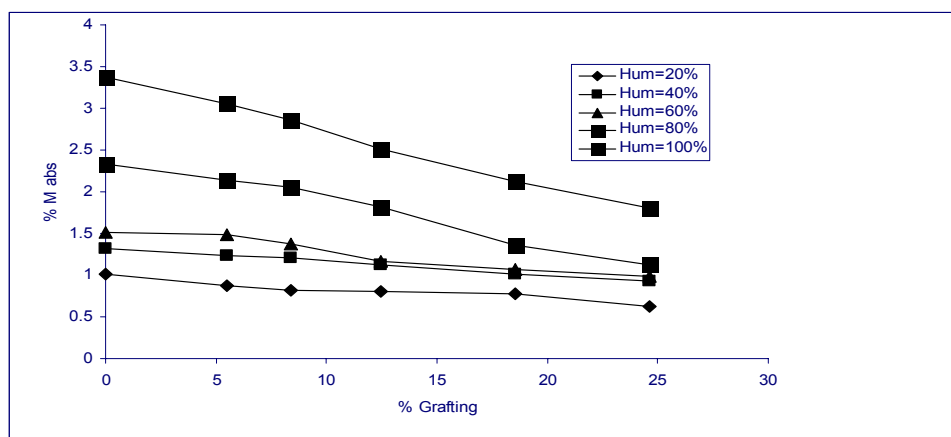


**Figure 12**. Effect of percent grafting of MMA onto flax fibre on moisture absorbance at different humidity levels
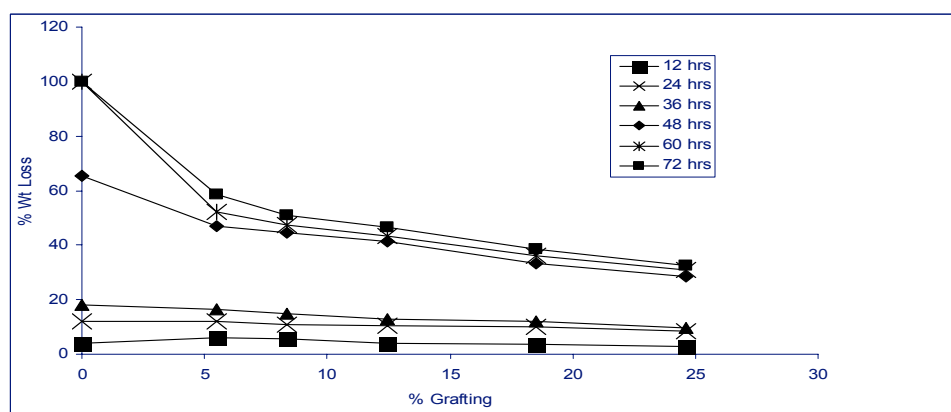


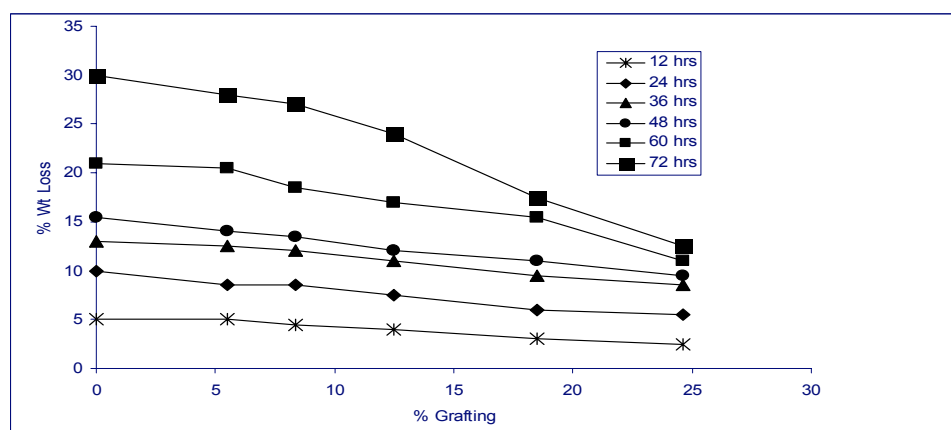**Figure 13**. Effect of percent grafting of MMA onto flax fibre on chemical resistance against 1N HCl



**Figure 14**. Effect of percent grafting of MMA onto flax fibre on chemical resistance against 1N NaOH
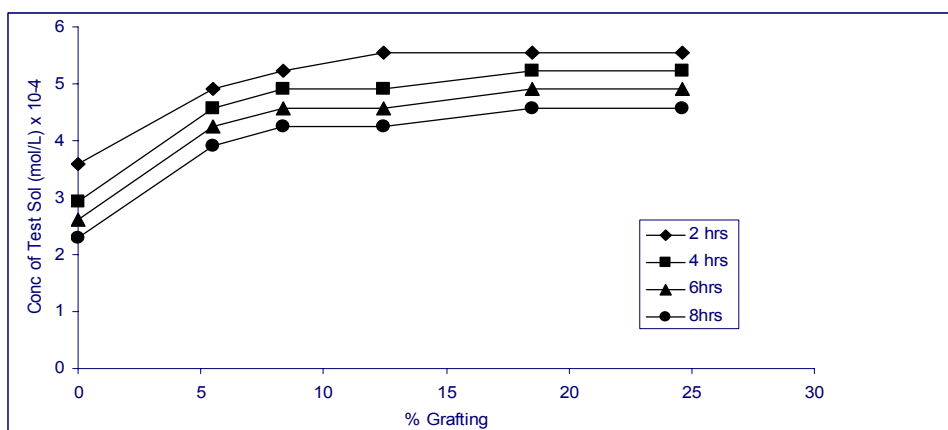
**Figure 15**. Effect of percent grafting of MMA onto flax fibre on absorption of Gentian blue dye

**Table 1**. Effect of percent grafting of MMA onto flax fibre on fibre strength

| Sample code | % grafting | Fibre strength (gms/tex) |
|---|---|---|
| Raw flax | 0 | 28.84 |
| Flax-g-poly(MMA) | 5.52 | 29.90 |
| Flax-g-poly(MMA) | 8.36 | 30.23 |
| Flax-g-poly(MMA) | 12.46 | 32.65 |
| Flax-g-poly(MMA) | 18.52 | 37.03 |
| Flax-g-poly(MMA) | 24.64 | 46.96 |

**Mechanical properties of the phenol-formaldehyde composites using raw flax and flax-g-poly (MMA) as reinforcement**

Wear resistance is maximum with flax-g-poly(MMA) reinforcement followed by raw flax reinforcement and PF. Loss of material in this case is due to abrasion and frictional heat effects which enhances increasing the load (Figure 16).

Figure 17 demonstrates that composites reinforced with raw flax showed more extension (2.17 mm) in comparison to reinforcement with flax-g-poly(MMA) (2.13 mm) at a load of 150 newtons. However, further extension beyond load > 150 force (N) causes the composite to break. Nevertheless, the PF matrix showed less extension (1.18 mm) but fails at 75 newtons.
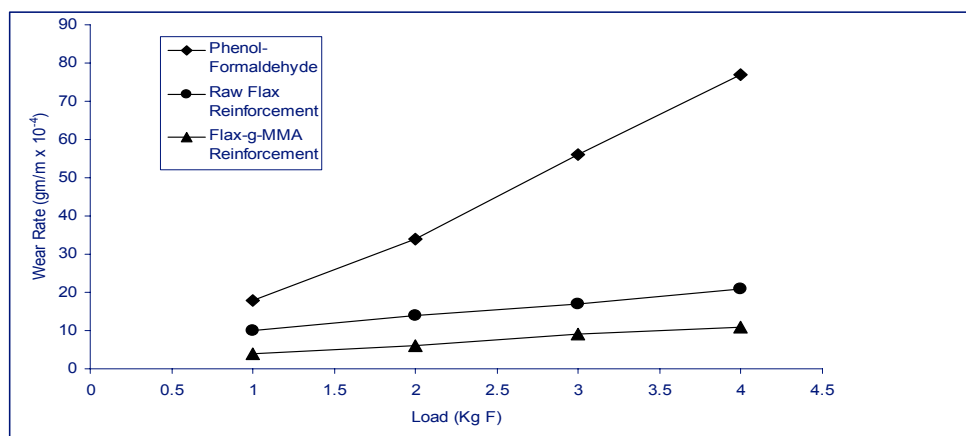


**Figure 16.** Effect of raw flax and flax-g-poly(MMA) reinforcement on wear rate of the phenol- formaldehyde composites

It is evident from Figure 18 that the composite-reinforced flax-g-poly(MMA) showed more compression (2.42 mm) but can bear a load up to 900 newtons, whereas the composite reinforced with raw flax fibre initially showed more compression as compared to the composite reinforced with grafted fibre, but breaks at 300 newtons. The PF matrix fails at 200 newtons with a compression of 0.62 mm.
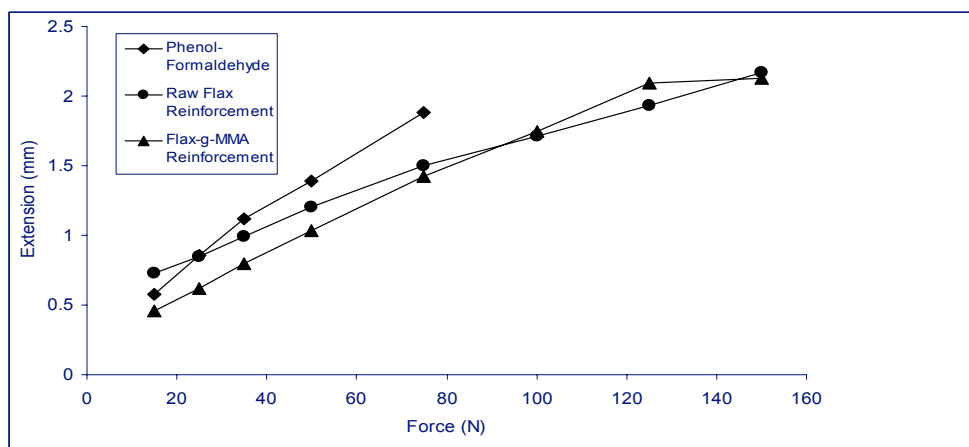
**Figure 17.** Effect of raw flax and flax-g-poly(MMA) reinforcement on tensile strength of the phenol-formaldehyde composites
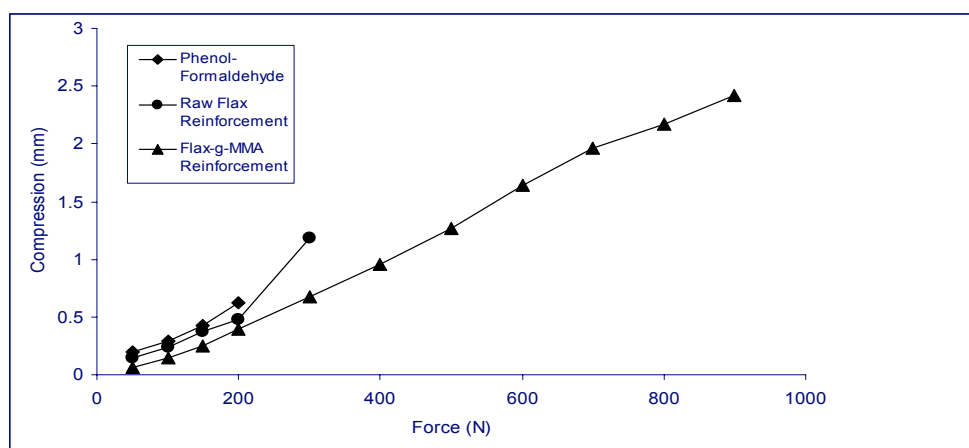
**Figure 18.** Effect of raw flax and flax-g-poly(MMA) reinforcement on compressive strength of the phenol-formaldehyde composites

In the case of graft co-polymers prepared under the influence of MWR, even though the graft yield obtained is less, the optimum reaction time required for obtaining maximum graft yield is also less (30 minutes). This has resulted in fewer surface flaws and hence fewer disturbances in the crystal lattice of the fibre, thereby also resulting in the better mechanical strength of the composites reinforced with flax-g-poly(MMA). Moreover, the fibre strength of the graft co-polymers prepared under the influence of MWR was found to be greater than that of raw flax.

## Conclusions

Through grafting, it is possible to add water repellence and chemical resistance to the raw flax, although the thermal stability of the flax-g-poly(MMA) was found to be less than that of raw flax. The fibre strength of flax-g-poly(MMA) was found to be greater than that of raw flax fibre.

The swelling behaviour of the graft co-polymers is in accordance with the affinity of the solvents to poly(MMA) chains.

Reinforcing the PF resin with flax-g-poly(MMA) improves the mechanical strength of the composites in comparison to reinforcement with raw flax [7].

## References:

1. Alfrey, T., Bandel, D., Paper presented at 118th Am. Chem. Soc. Meeting, Chicago, Sept. 4, 1950, through Mark, H.F., Rec. Chem. Progr., 1951, 12, 139.
2. Arthur, J.C., J. Adv. Macromol. Chem., 1970, 2, 1.
3. Augl, J.M., Berger, A.E., Nat. SAMPE Tech. Conference, 1976, 18, 8.
4. Battaerd, H.A.J., Tregear, G.W., (eds.), 'Graft Copolymers' Interscience, New York, (1967).
5. Bhattacharya, A., Misra, B. N., Prog. Polym. Sci., 2004, 29, 767.
6. Bledzki, A.K., Gassan, J., Prog. Polym. Sci., 1999, 24, 221.
7. Canché-Escamilla, G., Cauich-Cupul, J.I., Mendizábal, E., Puig, J.E., Vázquez-Torres, H., Herrera-Franco, P.J., Composites: Part A, 1999, 30, 349.
8. Chauhan, G. S., Lal, H., Singha, A. S., Kaith, B. S., Ind. J. Fibr. Text. Res., 2001, 26, 302.
9. Chauhan, G.S., Kaith, B. S., Guleria, L.K., Res. J. Chem. Environ., 2004, 4, 35.
10. Dwivedi, D. K., Singha, A. S., Kumar, S., Kaith, B. S., Int. J. Plast. Tech., 2004, 8, 299.
11. Freddi, G., Massafra, M.R., Beretta, S., Shibata, S., Gotoh, Y., Yasui, H., Tsukada, M., J. Appl. Polym. Sci., 1996, 60, 1867.
12. Haque, M.M., Habibuddowla, M., Mahmood, A.J., J. Polym. Sci. Chem., 1980, 18, 1447.
13. Hebeish, A., Guthrie, J.T., The chemistry and Technology of Cellulosic Copolymers. Heidelberg: Springer Verlag, 1981.
14. Immergut, E.H., Mark, H., Macromol. Chem., 18/1,9, 322 (1956).
15. Joly, C., et al, J. Macromol. Sci. Pure Appl. Chem., 1996, 12, 1981.
16. Joshi, S.V., Drzal, L.T., Mohanty, A.K., Arora, S., Composites: Part A, 2004, 35, 371.
17. Kaith, B. S., Singha, A. S., Kumar, S., J. Polym. Mater., 2003, 20, 195.
18. Kaith, B. S., Singha, A. S., Kumar, S., Misra, B.N., J. Polym. Mater., 2005, 22, 425.
19. Kaith, B. S., Singha, A. S., Dwivedi, D. K., Kumar, S., Kumar, D., Dhemeniya, A., Int. J. Plast. Tech., 2003, 7, 119.
20. King, J., Chaudhary, M., Zahir, S., 20th National SAMPE Symp., SAMPE, Covina, CA, 1984, 29, 392.
21. Krishnan, M., Narayan, R., Mat., Res. Soc. Proceedings, 1992, 266.
22. Mishra, M., Mohanty, A.K., Singh, B.C., J. Appl. Polym. Sci., 1987, 33, 2809.
23. McDowall, D.J., Gupta, B.S. and Stannett, V., Prog. Polym. Sci., 1984, 10, 1.
24. Mark, H.F., Text. Res. J., 1953, 23, 294.
25. Misra, B.N., Dogra, R., Mehta, I.K., Jassal, J.K., J. Polym. Sci. Polym. Chem. Ed., 1979, 17, 1861.
26. Schwab, E., Stannett, V., Hermans, J.J., Grafting onto Cellulosic Fibres, TAPPI., Vol. 44, No. 4, April 1961, pp. 251-256.
27. Simon, J., et al, Polym. Degrad. Stab. 1998, 59, 107.
28. Singha, A. S., Kaith, B. S., Sharma, S. K., Int. J. Chem. Sci., 2004, 2, 37.
29. Singh, V., Tiwari, A., Tripathi, D.N., Sanghi, R., Carbohydrate Polymers, 2004, 58, 1.
30. Singh, V., Tiwari, A., Tripathi, D.N., Sanghi, R., Polymer, 2006, 47, 254.
31. Solanki, A., Ph.D. Thesis, IIT, Delhi, India, 2002.
32. Solanki, A., Chaudhary, V., Varma, I.K., J. Appl. Polym. Sci., 2002, 84, 2277.
33. Trivedi, I.M., Mehta, P.C., Cell. Chem. Technol., 1975, 9, 583.
34. Tsukada, M., Islam, S., Arai, T., Boschi, A., Freddi, G., AUTEX Res. J., 2005, 5, 40.
35. Tsukada, M., Islam, S., Arai, T., Boschi, A., Freddi, G., Int. Nonwovens J., 2001, 10, 4.
36. Visconti, I.C., Polym. Plast. Engg., 1992, 31, 1.

$\nabla\Delta$