

## GRAFTING OF STYRENE ONTO CELLULOSE

Pankaj K. Aggarwal <sup>1\*</sup>, Ajay Karmarkar <sup>2</sup>, Syed Noeman Taqui <sup>3</sup>

<sup>1</sup>Institute of Wood Science & Technology, Mallewaram, Bangalore- 560 003

<sup>2</sup>Konkan Speciality Polyproducts Pvt Ltd, Mangalore- 575011

<sup>3</sup>Department of Chemistry, University of Malaya, Kuala Lumpur, Malaysia

\*\*\*

**Abstract - Bio-fiber - thermoplastic composites are gaining acceptance due to renewed interest in the environment. The trend towards recycling, protection of natural resources and bio-degradability is the driving force behind the increased use of such composites. However, the different polarity of these two unlike materials reduces the interfacial adhesion between them and limits their uses. This problem can be overcome by using a coupling agent. The alternative approach of increasing the interfacial adhesion is to graft vinyl monomer onto cellulose. In this paper results of a study made on grafting styrene onto wood pulp in presence of a comonomer (acrylonitrile) using Mn<sup>3+</sup> ions as an initiator is presented. Effect of monomer concentration, initiator concentration and temperature on grafting efficiency, polymer loading and total conversion was studied in detail. Thermal property of the grafted product was evaluated by TGA. The grafted product was characterized using FTIR and SEM.**

grafting reaction was found to depend strongly on the concentration of initiator [39-41]. Mehrotra and Ranby [42] used trivalent complexes of manganese ions to graft methyl methacrylate and acrylonitrile onto starch which gave a most efficient grafting process. As compared to starch, cellulose is a partly crystalline and strongly hydrogen bonded substrate and therefore it is much less acceptable to grafting than starch. With this objective, Ranby and Gadda [24] described successful grafting process of acrylonitrile onto wood fiber using Mn<sup>3+</sup> ion. As acrylonitrile is not conventionally used for structural applications, one of the objectives of this study is to use styrene monomer for grafting of cellulose. The concurrent formation of homopolymer in most cases [22] and the lack of reproducibility in these largely heterogeneous reactions [23] are some of the problems which still remain to be solved. Razil [12, 13] successfully applied the same process to graft acrylonitrile onto cellulose/ starch. The advantages of using Mn<sup>3+</sup> ions as initiator is high grafting efficiency at pH 6.0. Low acidities are necessary to avoid acidic hydrolysis of carbohydrate chains during graft copolymerization reactions. Considering the above advantages, Mn<sup>3+</sup> ions were selected as initiator for the present study.

Grafting of styrene onto cellulose using Mn<sup>3+</sup> ions is not effective because of limited solubility of styrene monomer in water. Therefore, in this study a new approach was followed for grafting styrene onto wood pulp surface by using acrylonitrile in small quantities as a co-monomer. The present work explores a method to improve the quality of interface between the reinforcing wood fibers and polystyrene matrix, so that optimum stress transfer can take place between high modulus wood fiber and low modulus plastic to study the effect of the grafting parameters on grafting efficiency, polymer loading and total conversion.

## 2. EXPERIMENTAL

### 2.1 Design of experiment

It was of interest to study the effect of three factors viz., initiator concentration, monomer concentration and temperature at 3 levels each on grafting parameters. A factorial design was employed for the analysis of results. Thus a total of 3\*3\*3=27 experiments were performed. The details of levels are shown below:

- F1: Initiator at three levels; 1, 2 and 3 mmol/L  
F2: Monomer concentration 2g, 4g and 6g per batch of 2g of cellulose  
F3: Temperature 45°C, 60°C and 80°C

The reason for selecting factorial design was that it is more efficient than one factor at a time experiment. In this study, an interaction was expected between the three factors besides main effect of each factor. Hence, a factorial design was used.

## 2.2 Materials

Mixed bleached kraft pulp of *Eucalyptus tereticornis* and *Acacia auriculaeformis* was supplied by Mysore Paper Mills, Bhadravathi, Karnataka. The pulp was washed several times with distilled water, filtered in a Buckner funnel and stored in a desiccator to avoid any exchange of moisture with atmosphere. 30 gm of pulp in three replicates was oven dried for more than 72 hours. This oven dry pulp was used for the experiments.

Most chemicals were analytical grade reagents. Acrylonitrile and styrene however contained monomethyl ether of hydroquinone as inhibitor. The inhibitor was removed by washing the monomer twice with equal volume of 0.5 M aqueous NaOH solution. The monomer was then washed several times with distilled water till the solution became neutral. Any water remaining in the monomer was removed by storing the monomer over calcium chloride in a desiccators overnight. The washed and dried monomer was stored in dark bottles in refrigerator at 4°C. All other reagents were used as received.

## 2.3 Preparation of the initiator

Concentration of MnSO<sub>4</sub>.H<sub>2</sub>O and KMnO<sub>4</sub> in aqueous solutions were selected such that for each desired Mn<sup>3+</sup> concentration in the reaction vessel, 5 ml of KMnO<sub>4</sub> was required to oxidize 5 ml MnSO<sub>4</sub> solution as shown in Table 1.

**Table - 1:** Quantities of MnSO<sub>4</sub>.H<sub>2</sub>O and KMnO<sub>4</sub> for the preparation of the Manganic Pyrophosphate initiator

MnSO <sub>4</sub> .H <sub>2</sub> O per 25 ml aqueous solution (gms)	0.406	0.812	1.217
KMnO <sub>4</sub> per 25 ml aqueous solution (gms)	0.095	0.189	0.284
Resulting concentration of Mn <sup>3+</sup> ions in reaction vessel, mmole/ltr	1.0	2.0	3.0

For a particular concentration of Mn<sup>3+</sup> ions desired in reaction vessel, 25 ml solution of Mn<sup>2+</sup> ions, prepared according to Table 2 was added to a solution of sodium pyrophosphate (Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub>.10H<sub>2</sub>O) prepared by dissolving 2.676 grams of Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub>.10H<sub>2</sub>O in 50 ml distilled water. The pH of the resulting solution was adjusted to 6.0 by adding few drops of concentrated H<sub>2</sub>SO<sub>4</sub> and using pH meter. The pH values of the solution were checked against standard buffers supplied by Merck. The Mn<sup>2+</sup> ions were then oxidized to Mn<sup>3+</sup> ions by titrating potentiometrically with aqueous KMnO<sub>4</sub> solution (Mn<sup>7+</sup> ions) by the method of Lingane and Karplus [43] according to the reaction (eqn. 1):



The weight of KMnO<sub>4</sub> dissolved in 25 ml of distilled water corresponded to the desired concentration of Mn<sup>3+</sup> ions in reaction vessel. About 5 ml of permanganate solution was required for each 5 ml MnSO<sub>4</sub> solution. A total of 60 ml of initiator solution of each Mn<sup>3+</sup> concentration was prepared. Out of this 60 ml solution, 25 ml was used as initiator for every batch.

## 2.4 Graft co-polymerization

Bleached kraft pulp (2 grams) was dispersed in 225 ml of acidified distilled water in a reaction vessel. The vessel was equipped with a stirrer and a nitrogen bubbler.

A 25 ml portion of initiator solution (pH 6.0) of the total 60 ml prepared as previously described and corresponding to the concentration of Mn<sup>3+</sup> ions desired in the reaction vessel was taken in the dropping funnel with 0.5 ml of surfactant. A desired quantity of washed and dried styrene was also taken in the same funnel. Styrene monomer and initiator solution were placed in the same dropping funnel since at pH 6.0 the manganic pyrophosphate initiator does not attack the monomer at all. One gram of acrylonitrile was also added to the reaction vessel and the contents were vigorously stirred. Acrylonitrile was added because it is difficult for styrene alone to graft onto cellulose and very low polymer loading was achieved when styrene alone was used. A brisk stream of oxygen free nitrogen was bubbled through the contents of the reaction vessel and through the initiator solution containing styrene monomer placed in the dropping funnel. This was continued for 30 minutes. When the desired temperature was reached, the contents of the dropping funnel were emptied into the reaction vessel and the total content of the reaction vessel were further bubbled with ultra pure nitrogen for 15 minutes. The reaction vessel was then sealed with Teflon tape and stopcock. A nitrogen filled balloon was placed over reaction vessel to ensure inert atmosphere during the reaction period. The reaction was allowed to proceed for 12 hrs. After termination of polymerization by opening the seal of reaction vessel and letting air into

the vessel, the reaction product was washed thoroughly with distilled water and ethanol. The washed product was filtered again using a Buckner funnel and dried to constant weight in a forced air circulated oven maintained at 60°C.

The grafted product was then carefully weighed and extracted with 750 ml of toluene in a Soxhlet instrument for 72 hrs to remove the homopolymeric product not grafted to the cellulosic pulp. The grafted product was then dried in oven at 60°C for 48 hrs. Weight at different stages i.e., before and after extraction was recorded to calculate the grafting efficiency (GE), total conversion (TC) and polymer loading (PL) which were calculated using eqns. 2-4.

$$G:E:(\%) = [(W_a - W_b) / (W_d - W_b)] * 100 \quad (2)$$

$$P:L:(\%) = [(W_a - W_b) / W_b] * 100 \quad (3)$$

$$T:C:(\%) = [(W_d - W_b) / W_c] * 100 \quad (4)$$

where  $W_a$  is the weight of product after copolymerization and extraction,  $W_b$  is the weight of pulp,  $W_c$  is the weight of monomer charged and  $W_d$  is the weight of product after copolymerization.

All weight being considered on oven dried basis.

## 2.5 Characterization of grafted product

FTIR spectra of both unmodified pulp and grafted pulp were obtained using a Nicolet impact 400 FTIR Spectrometer with co-addition of 64 scans at a resolution of 4 cm<sup>-1</sup> to determine the functional groups present at the surface of the samples before and after grafting. Spectroscopy grade KBr powder was used as a reference substance.

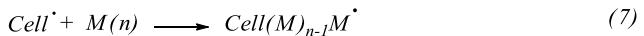
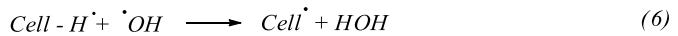
## 3. RESULTS AND DISCUSSIONS

Cellulose in the used native fibers consists of about 60% highly ordered or crystalline nature and interior of the crystalline region is inaccessible to chemical reagents as long as crystalline structure is maintained. The basic unit of organization of native cellulose is a micro fibril about 100 °A in diameter and of great but indefinite length. Modification of cellulose, either chemically or macromolecular modification, increase their usefulness in various applications say as fillers in thermoplastic composites.

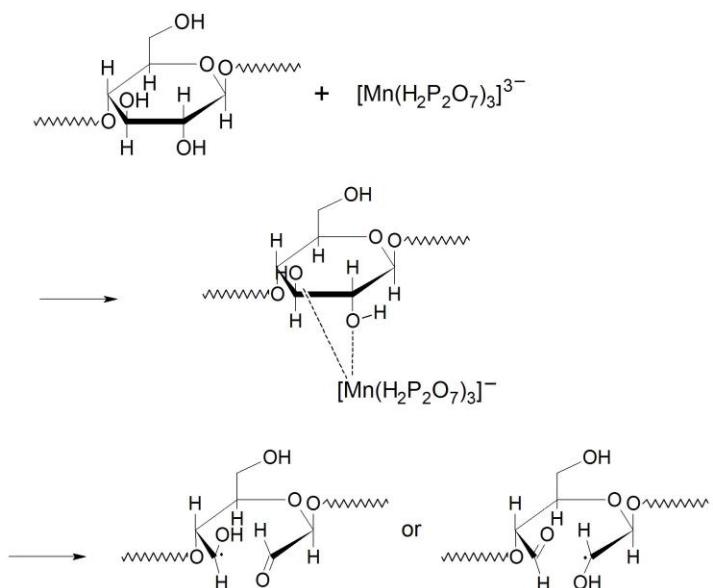
Chemically, formation of macrocellulosic radicals involves the oxidative depolymerization of cellulose with an increase in acidic and reducing groups. The increase in concentration of reducing groups is much greater than the increase of acidic groups. Macrocellulosic radicals initiated by chemical redox system are temperature sensitive and short lived. The formation of graft or block copolymers of fibrous cellulose involves contacting vinyl

monomers (M) in vapour phase or in solution with cellulose (cell-H). Then initiation of copolymerization of monomer with cellulose by ionic, charge transfer, or free-radical processes has been reported.

Homo-polymerization is usually a problem, particularly when an intermediate radical is formed. In the case where an intermediate radicals is formed, the following reaction eqn. 5 - eqn. 9 could occur [24].



The reaction of Mn<sup>3+</sup> ion in aqueous solution with cellulose involves cleavage of anhydroglucoside ring between carbons C<sub>2</sub> and C<sub>3</sub> with the formation of a short lived radicals as described by Arthur [22] for ceric ion. First Mn<sup>3+</sup> ions form a chelate with cellulose molecule possibly through C<sub>2</sub> and C<sub>3</sub> carbon atoms. The initial formation of complex is followed by transfer of electron from the cellulose molecule to Mn<sup>3+</sup>, thus reducing the manganic ion to manganous ion. A hydrogen atom is oxidized and a free radical is formed on cellulose unit, while the bond between the carbon C<sub>2</sub> and C<sub>3</sub> glucopyranose unit is broken as shown in Fig. 1.



**Fig -1:** Reaction between cellulose and Mn<sup>3+</sup>

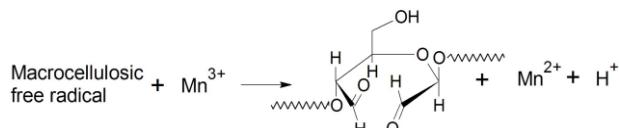
The macro free radical so formed reacts with monomer to initiate copolymerization.

The dissociation of glycol-Mn<sup>3+</sup> complex should be the rate determining step of the reaction. The presence of free radicals have been confirmed by electron spin resonance spectroscopy <sup>24</sup>.

The reaction propagate in the following manner:

Macro-free radical + monomer! Polymer graft on cellulose

Radical termination can occur by reaction of carbon C<sub>2</sub> or C<sub>3</sub> with Mn<sup>3+</sup> to yield Mn<sup>2+</sup> and oxidation of carbon C<sub>2</sub> or C<sub>3</sub> to a reducing group (Fig. 2).



**Fig -2:** Termination of macro-free radical

Homo-polymerization is formed mainly due to various chain transfer mechanisms e.g. chain transfer to monomer itself or to any other species present in the system, followed by homo-polymerization

### 3.1 Effect of Reaction Conditions on Grafting Parameters

The definitions of grafting parameters are as follows:

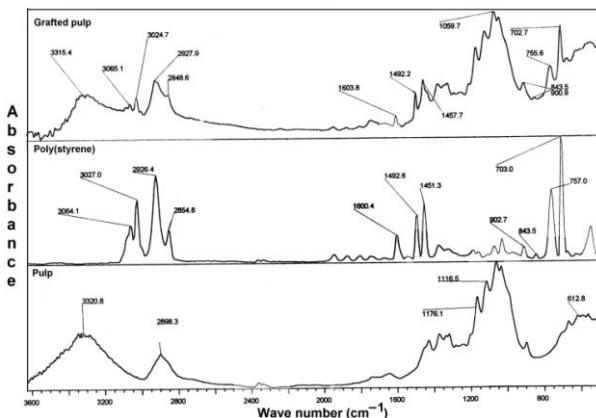
Grafting Efficiency = % of total polymer grafted to the wood pulp

Polymer loading = % of synthetic polymer in graft copolymer

Total conversion = % of monomers converted into polymer

In order to make possible a quantitative evaluation of the copolymer to homopolymer ratio with a reasonable accuracy, it is necessary to work with products having a sufficiently high polymer add on. To satisfy this requirement, a rather high monomer: pulp ratio has been used in this study (1:1, 2:1 and 3:1).

When styrene monomer was reacted with initiator under identical conditions, but without wood fiber substrate, no polymerization was observed, whereas conversion of monomer to polymer was significant in the presence of wood fibers. This provided evidence of the chemical attachment of polystyrene chains to wood fibers. The grafted pulp was further characterized by FTIR spectroscopy (Fig. 3). This is evidenced from increase in absorption at around 1492, 1457, 1603 and 2848-3025 cm<sup>-1</sup> in grafted wood pulp. This is accompanied by reduction in the OH absorption at 3300-3400 cm<sup>-1</sup>.



**Fig -3:** FTIR of styrene, pulp and grafted pulp

The copolymerization results are compiled in Table. 2-4. A dropping funnel with a N<sub>2</sub> bubbler eliminated the deviations since all the operations were conducted under sufficiently pure atmosphere of N<sub>2</sub>. It was of interest to see how grafting parameters would vary with Mn<sup>3+</sup> ion concentration, monomer concentration, and the reaction temperature, with the total pyrophosphate solution kept at constant 10 x 10<sup>-3</sup> M. The acidities of the reaction mixture was kept constant at 80 x 10<sup>-3</sup> M H<sub>2</sub>SO<sub>4</sub>.

The main effect and interaction effect of all the three factors was analyzed using ANOVA technique. The data were analyzed as a three way un-replicated factorial experiment with the following factors: initiator concentration at 3 levels, monomer concentration at 3 levels and temperature at 3 levels. Three two way tables were obtained by summing over each factor in turn. Table 2-4 presented the raw data for polymer loading, grafting efficiency and total conversion respectively.

#### 3.1.1 Effect on Polymer Loading

In all the experiments small amount of acrylonitrile (1.0 gm/batch) was added to the reaction system because very low polymer loading was achieved with styrene alone. This may be due to limited solubility of styrene in water. The solubility of styrene in water is 0.027 g/100 ml as against 1.62 g/100 ml for MMA and 7.93 g/100 ml for acrylonitrile.

Statistical analysis was done to analyze the main and interaction effects of factors namely initiator concentration (I), monomer concentration (M) and temperature (T) on polymer loading. The results are described in Table 2.

**Table - 2:** Statistical analysis for polymer loading

Source of Variation	D.F	SS	MS	F	P
Initiator	2	1288.66	644.33	19.010	<0.001
Monomer	2	12606.3	6303.1	185.96	<0.001
Temperature	2	2165.36	1082.6	31.943	<0.001
Residual	8	271.152	33.894	-	-
Total	26	16975.6	652.91	-	-

**Table -3:** Effect of initiator concentration, monomer concentration and temperature on Polymer loading (%)

Initiator concn. (mmol/ltr)	Temp = 45°C			Temp = 60°C			Temp = 80°C			Average	
	Monomer concn. (g)			Monomer concn. (g)			Monomer concn. (g)				
	2	4	6	2	4	6	2	4	6		
1.0	17.0	7.2	6.3	22.1	9.1	7.1	13.2	61.5	5.7	52.20	
2.0	27.5	8.2	7.7	49.3	1.0	7.0	29.8	70.6	6.1	65.17	
3.0	15.6	6.7	4.2	35.4	8.3	7.4	24.6	59.9	4.0	49.25	
Average	20.0	7.4	6.0	35.6	9.3	7.5	22.4	64.1	5.6		
Average	51.7			67.9			47.0			55.5	

There is a significant difference ( $P = <0.001$ ) in the mean values among the different levels of Initiator. The differences are greater than would be expected by chance after allowing for the effects of differences in monomer and temperature. Effect of initiator concentration, monomer concentration and temperature on Polymer loading is given in Table 3.

Fig. 4 indicates that as the initiator concentration increased from 1.0 mmol/l to 2.0 mmol/l, a sharp increase in polymer loading was observed and at initiator concentration between 2.0 and 3.0 mmol/l the polymer loading decreased. The increase in polymer loading may be attributed to more frequent grafts because of higher initiator concentration to AGU ration. While the decrease observed at higher initiator concentration may be due to greater incidences of radical termination according to reactions shown in Fig 2.

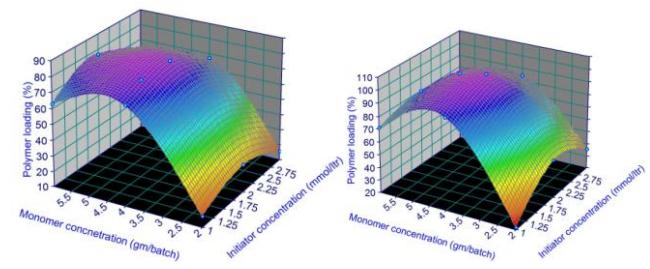
When the monomer concentration was increased from 2 gram per batch to 4 gram per batch (every batch had 2 grams of wood pulp dispersed in 250 ml of total aqueous volume), polymer loading increased sharply with the monomer concentration and decreased slightly at monomer concentration 6 gram per batch (Fig. 5). The increase can possibly be attributed to higher molecular weight of the grafted side chains, because in presence of excess monomer i.e., higher (monomer/total number of initiating radicals) ratio the molecular weight of the grafted polystyrene chains will be higher.

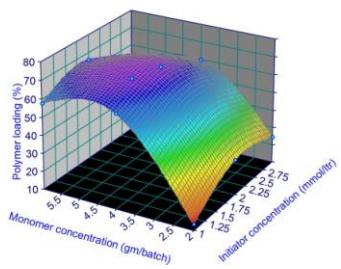
The temperature of the reaction was varied from 45°C to 80°C. The Polymer loading increased strongly in the temperature range 45°C to 60°C. This can be attributed to increase in the rates of polystyrene chain attachment to the cellulose backbone. However a sharp reduction in polymer loading beyond 60°C may be because of increased incidences of radical termination. Thus 60°C appears to ceiling temperature, defined as the temperature at which the rate of propagation reaction is equal to the rate of depropagation reaction for a given system. The equilibrium involved may be expressed as



where  $K_p = k_p / k_p$ . Below the ceiling temperature, increase in the temperature of the reaction has a greater effect on increasing  $k_p$  than  $k_p$ . At ceiling temperature,  $k_p = k_p$ , Altaf and Mansour [44] also noted that the maximum grafting yields for monomer was at a definite temperature for grafting reactions using free radical xanthate-hydrogen peroxide method. They have also reported existence of ceiling temperature in grafting reactions for grafting of poly (ethyl acrylate) onto cellulose using ceric salts as initiator.

It is clear from ANOVA analysis that the interactions I x T, I x M, and M x T have significant effect on polymer loading. This indicate that optimum polymer loading depends on all the three factors i.e., initiator concentration, monomer concentration and reaction temperature. 3D plots of polymer loading versus initiator concentration and monomer concentration at three different temperatures, shown in Fig. 4-6, clearly illustrate this phenomenon.





**Figs. 4-6:** Effect of monomer and initiator concentrations on polymer loading at 45°C, 60°C and 80°C.

It is evident that maximum polymer loading is achieved when the initiator concentration is in the range of 1.5 to 2.25 mmol/l and monomer concentration in the range of 3.5 to 4.5 g/2g batch of wood fibers, and the reaction temperature should be in the range 55-62°C.

### 3.1.2. Effect on grafting efficiency

Table 4 shows the statistical analysis of main and interaction effect of factors namely initiator concentration, monomer concentration and temperatures on grafting efficiency. There is a significant difference ( $P < 0.001$ ) in the mean values among the different levels of initiator. The differences are greater than would be expected by chance after allowing for the effects of differences in monomer and temperature. Effect of initiator concentration, monomer concentration and temperature on Grafting efficiency is provided in Table 5.

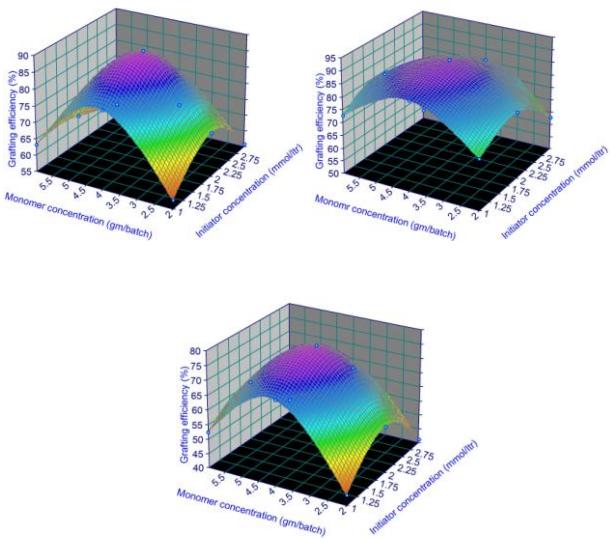
**Table -4:** Statistical analysis for grafting efficiency

Source of Variation	D F	SS	MS	F	P
Initiator	2 4	1168.31 4	584.15 7	37.22 1	<0.00 1
Monomer	2 8	1724.55 8	862.27 9	54.94 2	<0.00 1
Temperature	2 5	1486.70 2	743.35 4	47.36 1	<0.00 1
Residual	8	125.555	15.694	-	-
Total	26 8	4636.18 5	178.31	-	-

**Table - 5:** Effect of initiator concentration, monomer concentration and temperature on Grafting efficiency (%)

Initiat or conc. (mmo l/ltr)	Temp = 45°C			Temp = 60°C			Temp = 80°C			Ave rage	
	Monomer conc. (g)			Monomer conc. (g)			Monomer conc. (g)				
	2	4	6	2	4	6	2	4	6		
1.0	5	7	6	6	8	7	4	6	5	65.7	
	7.	8.	3.	9.	4.	2.	3.	8.	2.		
	6	7	3	4	8	9	5	9	5		
2.0	6	8	7	7	9	7	5	7	6	74.1	
	8.	8.	2.	5.	0.	8.	5.	8.	0.		
	1	1	2	5	2	9	9	0	3		
3.0	5	6	5	6	8	5	4	6	4	58.0	
	5.	3.	9.	2.	0.	3.	1.	1.	4.		
	8	5	0	8	5	3	2	6	5		
Average	6	7	6	6	8	6	4	6	5		
	0.	6.	4.	9.	5.	8.	6.	9.	2.		
	5	8	8	3	2	4	9	5	4		
Average	67.4			74.3			56.3			66.0	

Figs. 7-9 shows the effect of monomer and initiator concentration on grafting efficiency. It is clear from the figures that when initiator concentration was increased from 1 to 2 mmol/ltr, grafting efficiency also increased. When the initiator concentration increases, the rate of polymerization also increases and hence increase in grafting efficiency. Any further increase in initiator concentration approximately beyond 2 mmol/l, the rate of chain transfer, say to monomer also increases. Homopolymer is formed because of chain transfer reactions, hence grafting efficiency exhibited a declining trend. When the monomer concentration was increased from 2 to 4 gms/batch, grafting efficiency increased by 31%. This is due to higher molecular weight of the grafted side chains. When the monomer concentration was increased to 6g/batch the grafting efficiency decreased because of increased incidences of chain transfer to monomer. As discussed earlier, charge transfer to monomer will result in homo-polymerization. However when the temperature was raised from 45 to 60°C, the grafting efficiency increased by 10% only followed by a sharp decrease when the temperature was further increased to 80°C. Thus the increase in temp from 45 to 60°C do not have much influence on grafting efficiency. Increase in temperature beyond ceiling temperature results in sharp decrease in grafting efficiency due to increased incidents of free radical termination.



**Fig -7-9.** Effect of monomer and initiator concentrations on grafting efficiency at 45°C, 60°C and 80°C

Danuealt [38] *et al.* (1986) studied the effect of different parameters on grafting reactions for bleached kraft pulp and the effect of grafted polymer on properties of paper sheets so formed. A maximum of 122% polymer loading and grafting efficiency of 81% was achieved.

### 3.1.3. Effect on total conversion

From Table 6, it is clear that the difference in the mean values among the different levels of initiator are not great enough to exclude the possibility that the difference is just due to random sampling variability after allowing for the effects of differences in monomer and temperature. There is no statistically significant difference ( $P=0.094$ ). The difference in the mean values among the different levels of monomers are greater than would be expected by chance after allowing for the effects of differences in initiator and temperature. There is a statistically significant difference ( $P=0.006$ ). The difference in the mean values among the different levels of temperature are not great enough to exclude the possibility that the difference is just due to random sampling variability after allowing for the effects of differences in initiator and monomer concentration. There is not a statistically significant difference ( $P=0.05$ ).

**Table -6:** Statistical analysis for total conversion

Source of Variation	D F	SS	MS	F	P
Initiator	2	347.934	173.96	3.219	0.094
Monomer	2	1104.26	552.13	10.21	0.006
Temperature	2	480.519	240.25	4.446	0.050
Residual	8	432.325	54.041	-	-
Total	26	3285.53	126.35	-	-

**Table -7:** Effect of initiator concentration, monomer concentration and temperature on Total conversion (%)

Initiator conc. (mmol/ltr)	Temp = 45°C			Temp = 60°C			Temp = 80°C			Average	
	Monomer conc. (g)			Monomer conc. (g)			Monomer conc. (g)				
	2	4	6	2	4	6	2	4	6		
1.0	2.9.5	4.3.3	3.2	3.1.9	5.8	3.5	3.0.5	4.7	3.7	37.7	
2.0	4.0.3	4.7.0	3.5.0	6.1	5.7	3.7	5.2	4.5	3.6	46.0	
3.0	2.8.0	5.2.9	2.4.0	5.0	5.7	5.5	4.8	4.8	3.0	44.2	
Average	3.2.6	4.8.7	3.0.9	5.1	5.5	6.6	4.7	4.6	3.4		
Average	37.4			47.5			42.7			42.6	

Effect of initiator concentration, monomer concentration and temperature on Total conversion is given in Table 7. From the above description, it is clear that 55-62°C seems to be temperature range for optimum values of polymer loading and grafting efficiency. The ceiling temperature seems to be 60°C, which is defined as the temperature at which the rate of propagation reaction is equal to the rate of de-propagation reaction for a given system.

## 4. CONCLUSIONS

The results of the above study shows that manganic pyrophosphate can be used very efficiently to initiate grafting of styrene onto wood fibers provided small amount of acrylonitrile is used as co-monomer. Very high grafting efficiencies of the order of 90% can be achieved using this system. In this study, because of use of  $Mn^{3+}$ ,

formation of homopolymer is minimized. From the study we can conclude that:

- Manganic pyrophosphate can be used very efficiently to initiate grafting of styrene onto wood fibers in presence of small quantity of acrylonitrile.
- Formation of homopolymer is minimized.
- Initiator concentration of 1.5-2.25 mmol/l, monomer concentration of 3.5-4.5 gm/batch and temperature range of 55-62°C yields maximum polymer loading and grafting efficiency.

## REFERENCES

- [1]. P.Hamed and A.Y. Coran. *Addition of Plastics: State of the art.* 1(1978) Academic Press, New York.
- [2]. J.A. Meyer. Wood-polymer materials: *Wood Science*, 14(1981)49-54
- [3]. J.A. Meyer. Industrial use of wood polymer material:state of the art. *Forest Product Journal*, 32(1982)24-29.
- [4]. R.M. Rowell and P. Konkol. *Treatments that enhance physical properties of wood, General Technical reportFPL-GTR-55* US Forest Product Laboratory Madison (1987) 12.
- [5]. M.H. Schneider. Wood polymer composites *Wood Fiber Sci.*, 26(1994)142-151.
- [6]. R.C. Gauthier, A.C.Joy, H. Coupas and M. Escoubes. Interphases in polyolefin/cellulosic fibre composites: Chemical coupling, morphology, correlation with adhesions and aging in moisture. *Polymer Composite*, 19(1998)287-300.
- [7]. PankajK. Aggarwal, N. Raghu, A. Karmarkar and Shakti Chauhan.Jute-Polypropylene composites using m-TMI-grafted-Polypropylene as a coupling agent. *Materials and Design*, 43(2013)112-117
- [8]. C. Klason, J. Kubt and H.E. Strmvall. The efficiency of cellulosic fillers in common thermoplastics part-I, filling without processing aids or coupling agents. *International Journal of Polymeric Material*, 10(1984)159-187.
- [9]. P. Zadorecki and A.J. Michell. Future prospects for wood cellulose as reinforcement in organic polymer composites. *Polymer Composites*, 10(1989)69-77.
- [10]. D. Maldas, B. V. Kokta, R. G. Raj, and C. Daneault. Improvement of the mechanical properties of the sawdust wood fibre-polystyrene composites by chemical treatment. *Polymer*. 29(1988)1255-1265
- [11]. D. Maldas, B. V. Kokta and C. Daneault. Influence of coupling agents and treatments on the mechanical properties of cellulose fibre-polystyrene composites. *J. Appl. Polym. Sci.*, 37(1989) 751-775.
- [12]. E.A. Abdel Razik, D.M,Ayaad abd A.M.Elbedwehy. Graft copolymerization of acrylonitrile on to Acacia gum by manganese(IV)-nitric acid as redox initiator in aqueous media under visible light. *International J. of Modern Organic Chemistry*, 2(2013)191-206.
- [13]. E.I. A. Sayed, Abdul Razik, Doria S. Badway and E.E.I. Nahas. Graft Copolymerization of Acrylamide onto Corn Starch Using Mohr's Salt/Hydrogen Peroxide Redox System in Aqueous Media under Visible Light. *International J. of Modern Organic Chemistry*, 4(2015)1-17.
- [14]. D.Pathania and R. Sharma. Synthesis and characterization of graft copolymers of methacrylic acid onto gelatinized potato starch using chromic acid initiator in presence of air. *Adv. Mat. Lett.*, 2012, 3(2): 136-142.
- [15]. L.Wang and Y. Xu. Graft Copolymerization Kinetics of Ethyl Acrylate onto Hydroxypropyl Methylcellulose Using Potassium Persulphate as Initiator in Aqueous Medium. *Iranian Polymer Journal*, 2006, 15(6): 467- 475.
- [16]. E.A. Abdel Razik, M.M.Ali, M.Y.Abdel Al and A.A.Sarhan. Homogeneous Photoinduced Graft Copolymerization of Acrylamide onto Abs Copolymers in the Presence of 4-Acetylphenyl as Photosensitizer.: 1. Influence of of Butadiene Content in Abs Copolymers. *Polym.Plast.Technol.Eng.* 35(1996)865-876.
- Influence of Butadiene Content in Abs Copolymers. *Polym.Plast.Technol.Eng.* 35(1996)865-876.
- [17]. Z.Wang and Z.Liu. The optimization of synthesizing graft copolymer of starch with vinyl monomers. *J. of Wuhan Univ. of Technology*, 2006, 21(2): 83-87 .
- [18]. D.Mohan, G. Radhakrishnan, S.Radhakrishnan. S. Rajaduri, K.Rao and G.G. Cameron. Graft copolymerization of acrylamide onto casein: A kinetic study. *J. of Polymer Sci. A* , 1989, 27(6): 2123- 2133
- [19]. D.K. Mishra, J.Traipathy and K.K.Behari. Synthesis of graft copolymer (k-carrageenan-g-N,Ndimethylacrylamide) and studies of metal ion uptake, swelling capacity and flocculation properties. *Carbohydrate Polymers*, 71(2008) 524-534
- [20]. P. Lanthong, R. Nuisin and S. Kiatamjornwong. Graft copolymerization, characterization, and degradation of cassava starch-g-acrylamide/itaconic acid superabsorbents. *Carbohydrate Polymers*, 66(2006) 229-235
- [21]. V.Singh, A.Tewari, S.Pandey and S.K. Singh. Peroxydisulfate initiated synthesis of potato starchgraft-poly(acrylonitrile) under microwave irradiation. *Express Polymer Letters*, 1(2007)51-58
- [22]. V. Stannet 1982. Some challenges in grafting to cellulose and cellulose derivatives in graft copolymerisation lignocellulosic fibers. *Graft copolymerisation of lignocellulosic fibers*. ACS series 187(1982) 3-20.
- [23]. J.C.J. Arthur . *Free radical initiated graft polymerisation of vinyl monomers onto cellulose in graft copolymerization of lignocellulosic fibres*.*Graft copolymerisation of lignocellulosic fibers*, ACS series 187(1982)21-31
- [24]. B.Ranby and L. Gadda. Graft copolymerization of vinyl monomers onto cellulosic fibres. *Am. Chem. Soc. Symp.*, 187(1982)33-43.
- [25]. B. V. Kokta and J. L. Valade. Effect of acrylonitrile on grafting of styrene with the redox system cellulose xanthate-hydrogenperoxide. *TAPPI*, 55(1972) 366-369.

- [26]. V. Hornof, B. V. Kokta, and J. L. Valade. The xantate method of grafting.II. Effect of operating conditions on the grafting of acrylonitrile onto woodpulp. *J. Appl. Polym. Sci.*, 19(1975)545-556
- [27]. V. Hornof, B. V. Kokta, and J. L. Valade. The Xanthate method of grafting.II. Effect of lignin content on the grafting of wood pulp. *J. Appl. Polym. Sci.*, 19(1975)1573-1584
- [28]. V.Hornof, B. V. Kokta, and J. L. Valade. . The Xanthate method of grafting.IV. Grafting of acrylonitrile onto high-yield pulp. *J. Appl. Polym. Sci.*, 20(1976)1543-1554.
- [29]. V. Hornof, B. V. Kokta, and J. L. Valade. . The Xanthate method of graftingVI the copolymer-homopolymer ratio. *J. Appl. Polym. Sci.*, 19(1977) 2991-3002
- [30]. C. Danuealt, B. V. Kokta and D. Maldas. The Xanthate method of grafting XII effect of operating conditions on the grafting of vinyl monomers onto woodpulp *Journal of Applied Polymer Science*, 38(1989)841-848.
- [31]. W.Oraby, H.B. Hopfenberg and V. Stannet. Radiation grafting of vinyl monomers onto woodpulp cellulose partI. *J. Appl. Polym. Science*, 15(1972)2987-2998.
- [32]. E.L. Ellwood, R.C. Gilmore and A.J. Sharma. Dimensional stabilization of wood with vinyl monomers. *Wood Science*. 4(1972)137-141.
- [33]. I.Chun and R. T. Woodhams. Use of processing aids and coupling agents in mica- reinforced polypropylene. *Polymer Composite*, 5(1984)250 -257.
- [34]. G. De Vito, N. anzetta, G. Maglio, M. Malinconico, P. Musto, and R. Palumbo. Functionalisation of an amorphous ethylene-propylene copolymer by free radical initiated grafting of unsaturated molecules. *J. Polym. Sci.*,22(1984)1335-1347.
- [35]. H. Kishi, M.Yoshioka, A. Yamanoi, and N. Shiraishi. Composites of wood and polypropylenes. *Mokuzai Gakkaishi*, 34(1988)133-139.
- [36]. D. Maldas and B.V.Kokta. Influence of polar monomers on the performance of wood fibre reinforced polystyrene composites I evaluation of critical conditions. *International Journal of Polymeric Material*, 14 (1990)165-189.
- [37]. H. Kubota and J.Ogiwara. Decomposition of peroxide on carboxymethyl cellulose and its ability to initiate graft copolymerization. *J Appl Poly sci*, 23(1979) 241-247.
- [38]. C. Danuealt, B. V. Kokta and H. Cheradame. Graft polymerization of vinyl monomers of peroxidized cellulosic fibres. *J of Wood Chemistry and Technology*, 6(1986)269-291.
- [39]. G. Mino and Kaizerman. A new method for preparation of graft copolymers. Polymerisation initiated by ceric ion redox system. *Journal of Polymer Science*. 31(1958)242-243
- [40]. F Ide. Graft and block copolymer by synthetics and natural macro molecules. *Macromol.chem.*, 65(1962) 322-341.
- [41]. R.Y.M. Huang and P. Chandramouli. Structure and properties of cellulose graft copolymerII cellulose styrene graft copolymer synthesized by ceric ion method. *J App Poly Sci.*, 12(1968) 2549-2562.
- [42]. R. Mehrotra and B. Ranby. Graft copolymerization onto starch I complexes of Mn<sup>3+</sup> ions as a initiator *Journal of Applied Polymer Sci.*, 21(1977)1647-1654.
- [43]. J.J.Lingane and R. Karplus. *New method for determination of manganese*. ACS Legacy Archives (1946)191-194.
- [44]. H.B.Altaf and O.Y.Mansour. *Polymeric materials encyclopedia*, CRC Press, Boca Raton (1996).

## BIOGRAPHIES



Dr. Pankaj Aggarwal, Scientist F at Institute of Wood Science & Technology (IWST), Malleswaram Bangalore. IWST is an institute under Indian Council of Forestry Research & Education, which is an autonomous council of Ministry of Environment, Forest and Climate Changes, Government of India. He works on wood polymer composites- an advanced material. Dr Aggarwal has around 43 papers into his credit.