GRAFT COPOLYMERIZATION OF METHYL METHACRYLATE ONTO CELLULOSE BASED WHATMAN FILTER PAPER USING MOHR'S SALT/POTASSIUM PERSULPHATE REDOX SYSTEM IN AQUEOUS MEDIA UNDER VISIBLE LIGHT

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ABSTRACT

The graft copolymerization of methyl methacrylate (MMA) onto Whatman Filter Paper (Wfp) as pure cellulose material using Mohr's salt/potassium persulphate (FAS-KPS) redox system in aqueous media under visible light was extensively investigated. The effects of various reaction parameters such as time of irradiation, as well as the contents of initiators, monomer, cellulose material etc. on the grafting percentage (GP%) and grafting efficiency (GE%) were studied. The λ_{max} and their extinction coefficient values of the used initiators were determined. The initial rate of grafting was found to be 0.57% per min. The products of polymethyl methacrylate grafted cellulose (PMMA-g-Cell) were characterized using FT-IR spectroscopy and thermal analysis techniques such as TGA and DTA. Water absorption and solvent resistance of PMMA-g-Cell copolymers were examined. The mechanism of grafting was suggested.

INTRODUCTION

Modification by graft polymerization provides a means of altering the physical and chemical properties of cellulosic materials and increasing their functions. Graft copolymerization of vinyl monomers on cellulosic

materials has been the important subject of many investigators [Roy, et al., (2009); Malmstrom & Carlmark (2012); Chauhan & Desalination (2003) and Nakamura & Amino (1997)]. Some of the grafted products have potentional applications for sanitary and medical uses, ion exchangers, insulators, packaging material etc. Visible light was used to photo-induce grafting of many vinyl monomers onto different substrates [Maji & Banerjee (1996); Ghosh & Ghosh (1982); Kumar, et al., (1999); Abdel-Razik, et al., (2001); Abdel-Razik, et al., (2005) and Abdel-Razik, et al., (2009)].

A redox initiator system as Mohr's salt/potassium persulphate was used before for grafting various vinyl monomers onto different natural polymers [Abdel-Razik, et al., (2001) and Misra, et al., (1980)]. This study describes the results of the graft copolymerization of MMA onto Whatman filter paper as pure cellulose and using Mohr's salt/potassium persulphate redox system under visible light irradiation.

EXPERIMENTAL AND TECHNIQUES

Materials

Whatman filter paper (Wfp) was the pure cellulose used throughout the investigation. Mohr's salt (BDH) and potassium persulphate (BDH) were used as received. Methyl methacrylate (Merck) was washed with a solution of 5% NaOH, washed with distilled water then dried over calcium chloride. Acetone, distilled water, sodium hydroxide, hydrochloric acid and sodium chloride were used. Hydroquinone (BDH) was used as inhibitor.

Techniques

The determined quantities of small parts of Wfp, MMA and the initiators were added to distilled water in Pyrex tubes. Polymerization experiments were mainly studied under photo-activation with visible light by placing the test tubes between a pair of tube lamps (40 W) for specified time periods. Initially a few polymerization experiments were also done in similar systems in the dark at room temperature. The polymerization process was finally terminated by adding hydroquinone solution (3%). The product was filtered and washed with distilled water. The extraction of polymethyl methacrylate homopolymer was achieved by acetone. The grafted copolymer was dried at 40°C till constant weight. Grafting % and grafting efficiency % were calculated according to the following expressions:

$$\text{Grafting percentage (GP\%)} = \frac{A - B}{B} \times 100$$

$$\text{Grafting efficiency (GE\%)} = \frac{A - B}{C} \times 100$$

Where A, B, C are the weight of graft product, filter paper and monomer respectively.

The water absorption % (WA%) was calculated according to the following relation [9,12].

$$\text{WA\%} = \frac{\text{water absorbed wt}}{0.05} \times 100$$

Where the weight of PMMA-g-cell copolymer was 0.05

The resistance of PMMA-g-cell copolymer toward acids, alkalis and NaCl solution was calculated according to the following relation **[Pathania & Sharma (2012)]**.

$$\text{Sol\%} = \frac{0.05 - \text{wt of copolymer after soaking and drying}}{0.05} \times 100$$

Where 0.05 g was the weight of PMMA-g-cell copolymer

The UV spectra of the used initiators were measured by UV spectrophotometer (Perkin Elmer Lambda 3B) and their λ_{max} in the visible region were determined. The chemical structure of the grafted products was examined by IR spectrophotometer (Perkin Elmer 1430) using KBr to prepare its disks. The thermal analysis of PMMA-g-cell copolymers was determined using thermal analyzers (Shimadzu DTA-50 and Shimadzu TGA-50H) under nitrogen atmosphere.

RESULTS AND DISCUSSION

Preliminary experiments were carried out in absence and presence of the couple initiator redox system as well as visible light irradiation. The results in **Table 1** showed that the presence of the combined initiator of Mohr's salt/$K_2S_2O_8$ in the presence of visible light irradiation gave the highest value of GP% which was 126% after 3.5hrs but in case of dark and after 24hr, GP% was only 84%. This explains that the energy absorbed by the combined initiator enhances the rate of cleavage of O-O bond in the structure of persulphate molecule, yielding SO_4^{--} as summarized in the following reaction **[Yyu, et al., (2004)]**.

$$S_2O_8^{-2} + hv \longrightarrow 2SO_4^{--} \quad \text{(1)}$$

Table (1): Graft copolymerization of MMA onto Wfp in aqueous medium, filter paper 71 g/l, MMA 1.3 mole/l, initiator system FAS 0.007 mole/l and FAS 0.029 mole/l, KPS 0.05 mole/l.

| Initiator system	Conc.(Mole/l)	condition	GY %	GE%
FAS + KPS	0.007+0.05	Dark (24hr)	84%	32.3%
KPS	0.05	Dark (24hr)	64%	24.6%
FAS	0.007	Dark (24hr)	50%	19.2%
FAS + KPS	0.007+0.05	Visible (210min)	126%	67.1%
KPS	0.05	Visible (210min)	96%	36.9%
FAS	0.007	Visible (210min)	74%	28.5%
FAS	0.029	Visible (210min)	16%	8.5%

SO_4^{--} are highly reactive and may react with organics by electron transfer, hydrogen abstraction or addition mechanisms [**Anipsitakis, et al., (2006)**]. The bond (O-O) energy in potassium persulphate has been estimated to 33.5 Kcal/mole. The UV spectrum of KPS show slight absorption at 377, 398 nm and 425 nm and the extinction coefficient values corresponding to them are 51×10^{-3}, 51×10^{-3} and 49×10^{-3} in l mole^{-1} cm^{-1} respectively, whereas Mohr's salt did not absorb in visible light region **Table 2**.

Table (2): Characterization of $K_2S_2O_8$ and Mohr's salt in the visible light region.

Name	Structure	Max (nm)	$\varepsilon_{coeff.}$ in l mole^{-1} cm^{-1}
potassium persulphate (KPS)	$K_2S_2O_8$	377 398 425	51×10^{-3} 51×10^{-3} 49×10^{-3}
Mohr's salt (FAS)	$FeSO_4.(NH_4)_2SO_4.6H_2O$	---	---

This explains the activity of $K_2S_2O_8$ as a good initiator when used alone and when coupled with Mohr's salt in presence of visible light. The results in **Table 1**, shows that the presence of FAS only at contents 0.007 and 0.029 mole/l respectively, appeared that GP% was 74% and 16% after 3.5hrs, this indicates that the irradiation of cellulosic material in the

presence of air produces hydroperoxides that are decomposed by the reaction

$$ROOH + Fe^{+2} \longrightarrow R\dot{O} + OH^- + Fe^{+3}$$

(2)
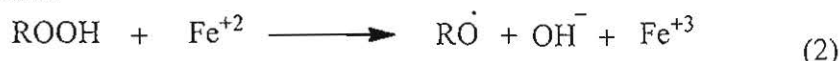
to produce radicals capable of initiating graft copolymerization [lawrence & Verdin (1973)]. Additionally FAS do not absorb in the visible region as shown in Table 2, this confirms the reaction explained in equation 2.

INFLUENCE OF IRRADIATION TIME

The data shown in **Fig. 1**, indicate that GP% and GE% increase with time, increase in the range of time used. The initial rate of grafting was determined to be 0.57%/min [**Maji & Banerjee (1996); Abdel-Razik, et al., (2001) and Abdel-Razik, et al., (2005)**]. Similar observations have been reported [**Ghosh & Ghosh (1982) and Hirose & Hatakeyama (1982)**]. The combined initiator used is very efficient for grafting methyl methacrylate onto cellulose based filter paper.
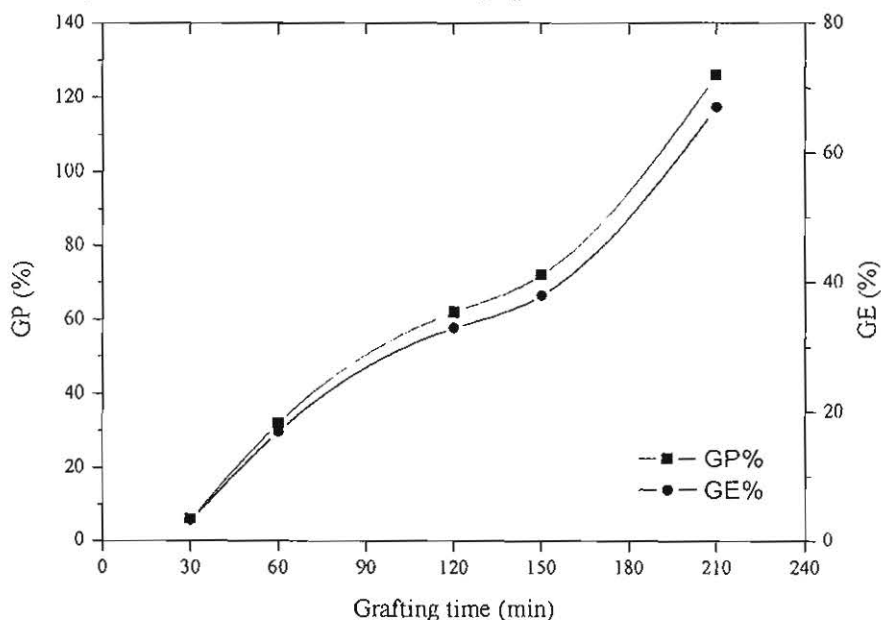
Fig.(1): Influence of time on the photo-induced grafting of MMA onto Wfp in presence of FAS/KPS as initiator in aqueous medium: Wfp 71 g/l, MMA 1.3 mole/l, initiator system FAS 0.007 mole/l, KPS 0.05 mole/l.

INFLUENCE OF MONOMER CONTENT

The effect of monomer content (0.7 to 4 mole/l) on GP% and GE% is shown in **Fig. 2**. Percent grafting (GP %) tends to pass through a maximum at about 2.7 mole/l. it was observed that by increasing monomer content, GE% values follow a decreasing trend. It is accepted that the grafting reaction mainly depend on the ratio between the monomer and initiator content [**Abdel-Razik, et al., (1996) and Nishoka & Kosai (1981)**].
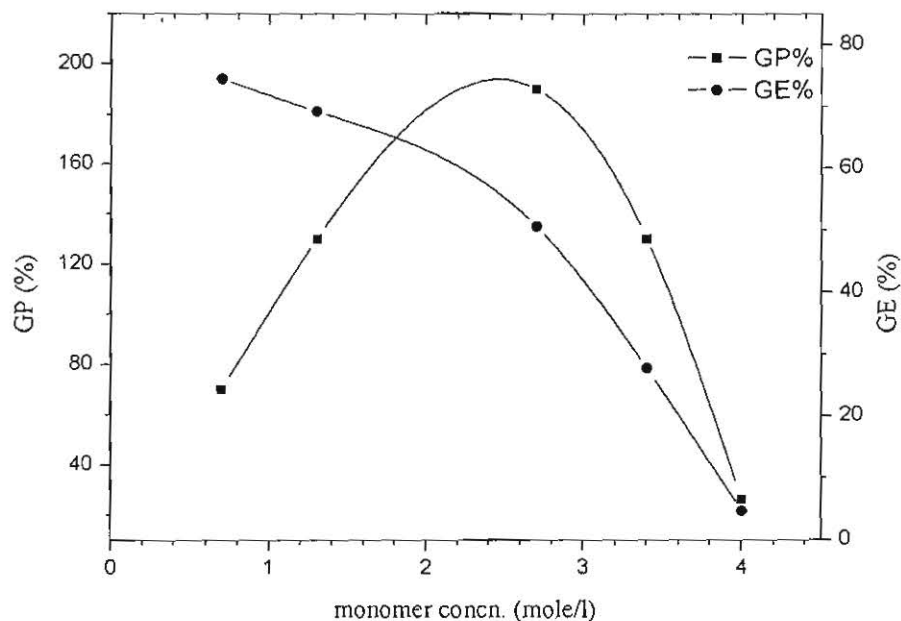

Fig.(2): Influence of MMA content on the photo-induced grafting of MMA onto Wfp in presence of FAS/KPS as initiator in aqueous medium: Wfp 71 g/l, FAS 0.007 mole/l, KPS 0.05 mole/l and time 210min.

INFLUENCE OF CELLULOSE BASED FILTER PAPER CONTENT

It was reported that the grafting percentage decreases with increasing polymer content [19, 20]. The results obtained in **Fig. 3** show that GP% values decrease whereas GE% values increase by increasing filter paper content. At lower filter paper content the formation of cellulose

macro-radical greatly increases leading to the observed increase in GE%. Additionally, the decrease observed in GP% by further increase of Wfp content may be due to the decrease in the monomer to cellulosic material ratio [**Abdel-Razik, et al., (1996); Abdel-Razik, (1990) and Hornof, et al., (1975)**].
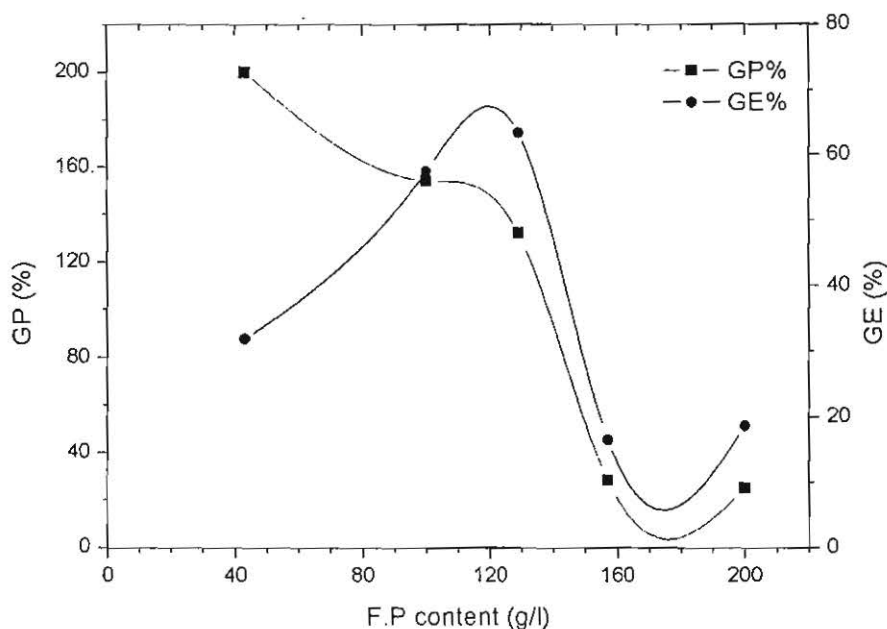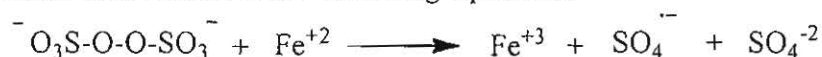

Fig.(3): Influence of cellulose based filter paper content on the photo-induced grafting of MMA onto Wfp in presence of FAS/KPS as initiator in aqueous medium: FAS 0.007 mole/l, KPS 0.05 mole/l, MMA 2.7 mole/l and time 210min.
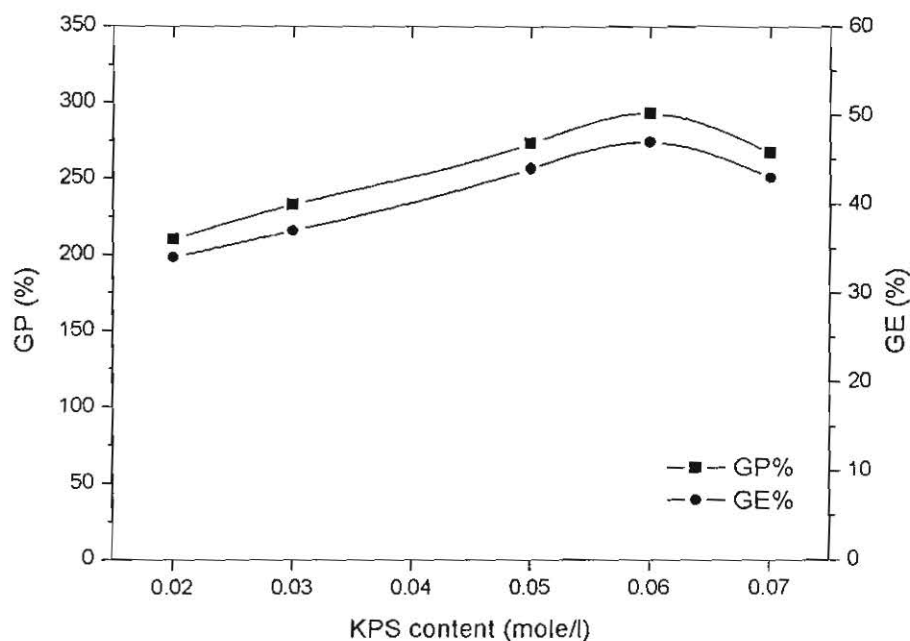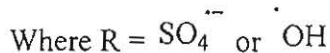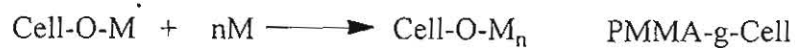
INFLUENCE OF $K_2S_2O_8$ CONTENT

The results showing the variation of KPS content indicate that the GP% and GE% increase with increasing KPS content and then slightly decrease **Fig. 4**. The increasing trend may be due to the formation of more grafting sites on the cellulosic backbone with increasing the amount of KPS while the content of FAS was kept at 0.007mole/l and under visible light irradiation. The formation of different free radicals may be explained on the basis of the following equations:

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

$$SO_4^{\cdot-} + H_2O \longrightarrow HSO_4^- + \cdot OH$$

The produced free radical as $SO_4^{\cdot-}$ and $\cdot OH$ may attack the cellulosic materials giving cellulosic macroradicals which initiate the graft copolymerization as follows:

$$Cell\text{-}OH + \overset{\cdot}{R} \longrightarrow Cell\text{-}\overset{\cdot}{O} + R\text{-}H$$

$$Cell\text{-}\overset{\cdot}{O} + M \longrightarrow Cell\text{-}O\text{-}\overset{\cdot}{M}$$

$$Cell\text{-}O\text{-}\overset{\cdot}{M} + nM \longrightarrow Cell\text{-}O\text{-}M_n \qquad PMMA\text{-}g\text{-}Cell$$
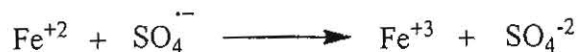
$$Where\ R = SO_4^{\cdot-}\ or\ \cdot OH$$

Fig.(4): Influence of KPS content on the photo-induced grafting of MMA onto Wfp in presence of FAS/KPS as initiator in aqueous medium: Wfp 43g/l, FAS 0.007 mole/l, MMA 2.7 mole/l and time 210min.

INFLUENCE OF MOHR'S SALT CONTENT

The variation of FAS content and keeping the content of KPS constant at 0.06mole/l on the photo-induced graft copolymerization of

MMA onto cellulosic material was examined **Fig. 5**. It was found that the GP% values decrease by increase of FAS content. This trend may be attributed to the consumption of the sulphate ion radical ($\overset{..}{SO_4}^{-}$) by Fe^{+2} ions present in the system [**Bataille, et al., (1992)**] as in the following equation:

$$Fe^{+2} + \overset{..}{SO_4}^{-} \longrightarrow Fe^{+3} + SO_4^{-2}$$

Similar observations were also reported [**Abdel-Razik et al., (2001); Abdel-Razik et al., (2009) and Hornof, et al., (1975)**].
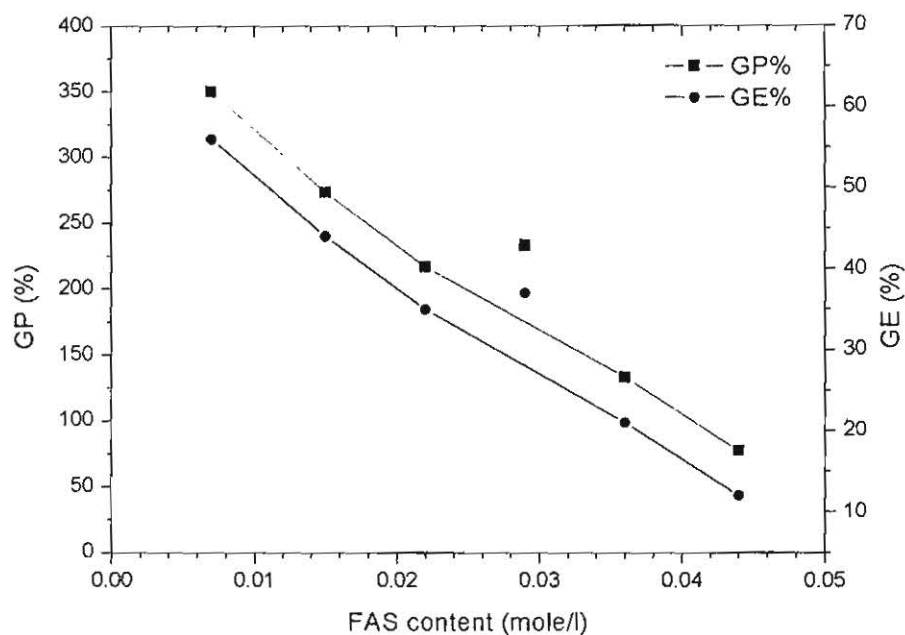

Fig.(5): Influence of FAS content on the photo-induced grafting of MMA onto Wfp in presence of FAS/KPS as initiator in aqueous medium: Wfp 43g/l, KPS 0.06 mole/l, MMA 2.7 mole/l and time 210min.

WATER ABSORPTION MEASUREMENTS

It was known that cellulose has high hydrophilicity because it contains many hydroxyl groups in each glucose unit in its structure. But after grafting cellulose by MMA a significant decrease of water absorption is observed when compared with original cellulose material

Table 3. Thus, the grafting and entering polymethyl methacrylate hydrophobic grafted chains decreases the hydrophilic character.

Table (3): Water absorption measurements: 0.05 gm of Wfp in 10 ml water for 24 hr, Weight of wet Wfp after soaking.

GP%	Wt. of wet fiber	Water absorbed	WA%
0 % [pure filter paper]	0.075	0.025	50 %
233 %	0.07	0.02	40 %
273%	0.06	0.01	20 %
293 %	0.055	0.005	10 %

CHEMICAL RESISTANCE MEASUREMENTS

The data presented in **Table 4** show that the resistance character of cellulose material and PMMA-g-Cell copolymer in some selected solvents was found to decrease in the following order 1N NaCl $\leq$ 1N HCl >1N NaOH. The results also show that the solubility % slightly decreases by grafting.

Table (4): Chemical resistance measurements: Soaking of 0.05 gm of Wfp in 10 ml solvent for 24 hr then dry till constant weight.

solvent	Wt. of pure filter paper after drying	Sol.%	Wt. of grafted fiber [GP%=350%] after drying	Sol.%
1N NaOH	0.03	40%	0.03	40%
1N HCL	0.025	50%	0.025	50%
1N NaCL	0.025	50%	0.03	40%

EVIDENCE OF GRAFTING

IR spectroscopy

IR spectrum of Wfp cellulose showed a broad peak at 3415 cm^{-1} due to bonded OH group and at 2902, 1641 and 1059 cm^{-1}, relating to CH_2, C-C and C-O stretching, respectively (**Fig. 6a**), whereas an additional peak at 1731 cm^{-1} in case of IR spectrum of PMMA-g-Cell has been observed

due to C=O of poly-MMA grafted chains **(Fig. 6b)**. This suggests that MMA has been grafted onto Wfp cellulose through covalent linkages **[Kaith, et al., (2005) and Eromoselex & Hamagadu (1993)]**.
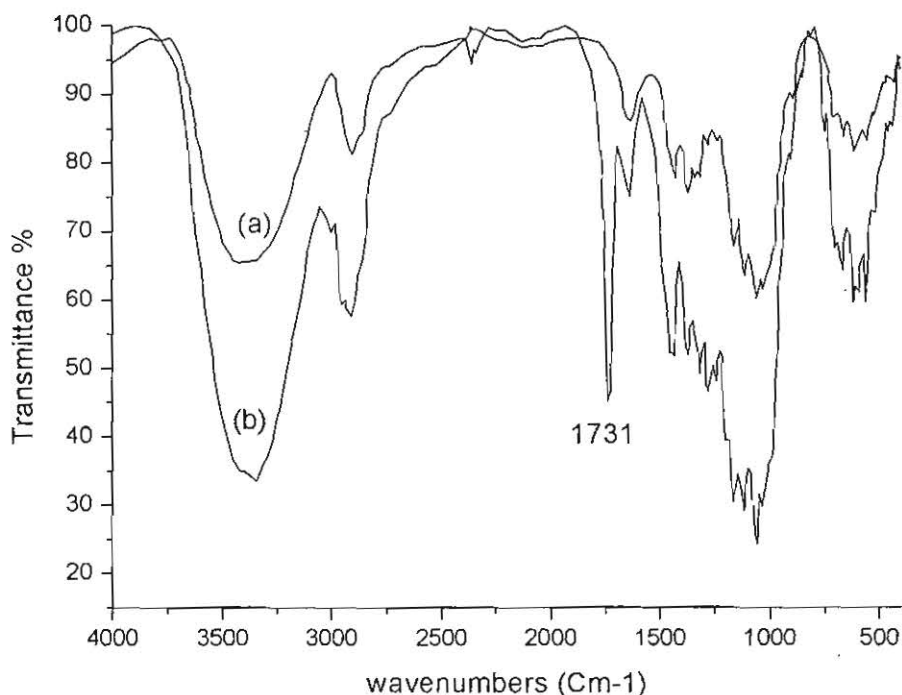

Fig (6): FT-IR spectra of (a) Wfp cellulose, (b) PMMA-g-Cell (GP 126%)

THERMAL ANALYSIS USING TGA AND DTA

The data of TGA presented in **Table 5** shows that the initial decomposition temperature (IDT) and final decomposition temperature (FDT) of Wfp cellulose are 304.34°C and 527.49°C respectively **(Fig. 7)**, while in case of PMMA-g-Cell copolymer (GP 293%), IDT and FDT are 219.43°C and 337.31°C respectively **(Fig. 8)**. It was evident from the data in **Table 5**, that grafting of MMA onto Wfp cellulose decreases the thermal stability. It is explained on the bases that on grafting the crystalline lattice of the cellulose is disturbed and the fibre becomes more amorphous, thereby lower FDTs of graft copolymers obtained **[Kaith & Kalia (2008)]**.

Moreover, in case of Wfp cellulose two stages decomposition has been observed with maximum weight loss occurring between 304.34°C -

410.51°C (64.36%) and between 527.49°C – 615.06°C (10.50%). whereas graft copolymers of PMMA-g-Cell (GP 233% and 293%) showed only single stage decomposition with maximum wt. loss of 69.23% and 63.08% at 322.45°C and 337.31°C respectively. This confirms again that the disturbance in crystal lattice of cellulose has been occurred during the grafting reaction.

DTA of Wfp cellulose showed one exothermic peak at 361.57°C (7.9 μV) which shows the breakdown of C-C and C-O bonds of crystalline region [**Kaith & Kalia (2008) and Princi, et al., (2005)**] (**Table 6** and **Fig. 7**). However, in case of PMMA-g-Cell copolymer, an exothermic rise in temperature was examined in the exothermic peaks at 370.66°C (20 μV) and 374.27°C (35 μV) for graft copolymers with (GP 233%, 293%) respectively. It is evident from DTA data in **Table 6** and **Fig. 9**, a broad exothermic peak belongs to Wfp cellulose at 361.57°C (7.9 μV) when compared to the sharp exothermic peak at 374.27°C (35 μV). In case of PMMA-g-Cell (GP 293%) showed only one major exothermic peak appeared in both cases. But higher exothermic temperature was observed in case of graft copolymer. This is considered an evidence of the fact that most of the crystalline portion of the cellulose was disturbed during the grafting process.

Fig. 9 shows the comparison between DTA thermograms of PMMA, PMMA-g-Cell and physical mixture of PMMA and cellulose material (1:1 w/w). It was observed that the exothermic peak of PMMA at 208.82°C (4.2 μV) that was also found in the thermogram of physical mixture at 205.75°C (7.9 μV), is practically disappeared in the thermogram of PMMA-g-Cell copolymer. This trend again confirms the grafting process.

Table(5): TGA data of different polymers.

Sample	GP%	IDT*	FDT**
Wfp cellulose	---	304.34°C	527.49°C
PMMA-g-Cell	233%	225.89°C	322.45°C
PMMA-g-Cell	293%	219.43°C	337.31°C

*: IDT: Initial decomposition temperature.   **: FDT: Final decomposition temperature.

Table(6): DTA data of different polymers.

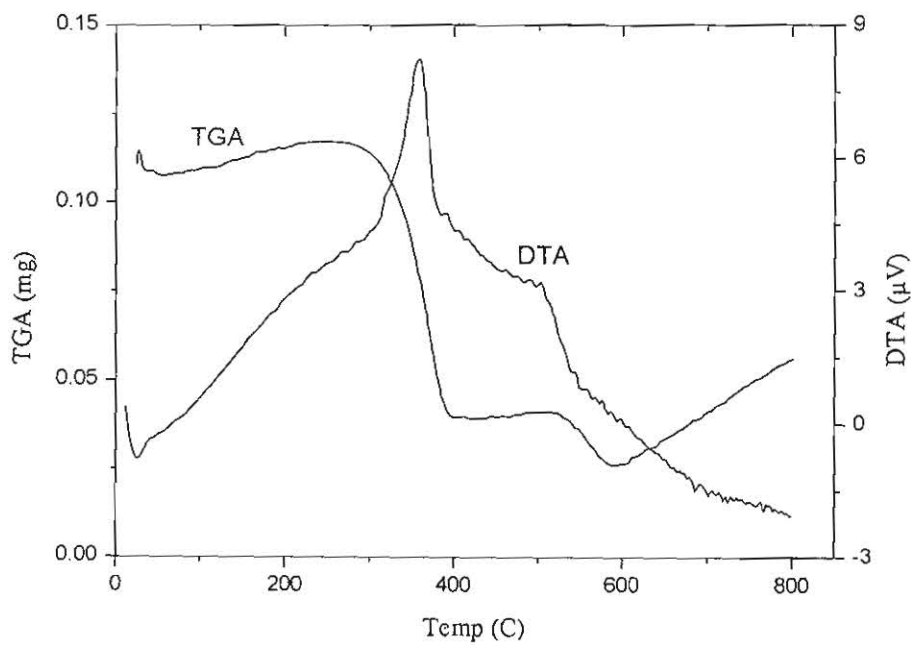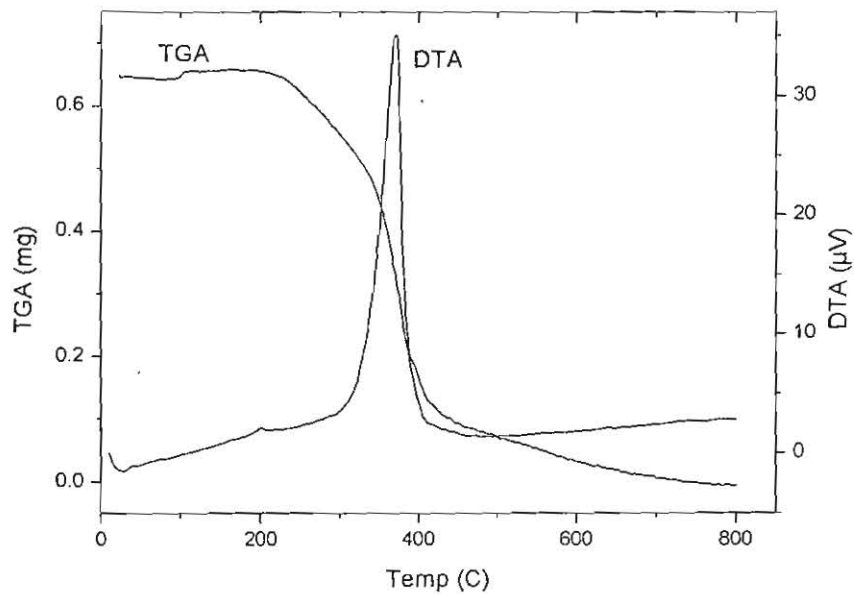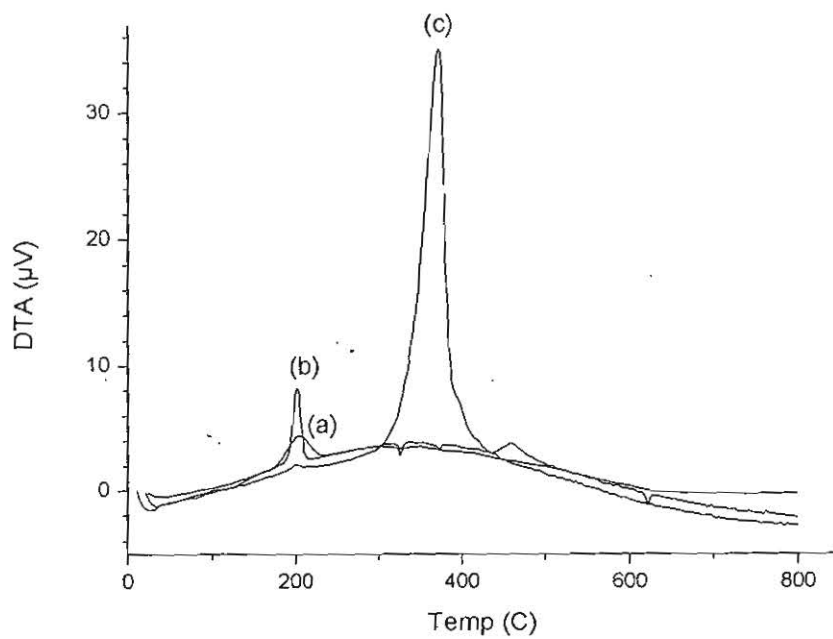| Sample	GP%	Exothermic peaks at temperature(μV)
Wfp cellulose	---	361.57°C (7.9 μV)
PMMA	---	208.82°C (4.2 μV)
PMMA-g-Cell	233%	370.66°C (20 μV)
PMMA-g-Cell	293%	374.27°C (35 μV)
PMMA + Wfp Cell (1:1 w/w)(physical mixture)	---	205.75°C (7.9 μV) 461.82°C (3.5 μV)

Fig (7): TGA/DTA curve of Wfp cellulose.

Fig(8): TGA/DTA curve of PMMA-g-Cell (GP 293%)

Fig(9): DTA curve of (a) PMMA, (b) Wfp+PMMA (1:1 w/w) (physical mixture) and (c) PMMA-g-Cell (GP 293%).

CONCLUSION

In this study, MMA was successfully grafted onto Whatman filter paper by visible light irradiation in air using redox system (FAS-KPS) in aqueous medium leading to hydrophobic surfaces. This method provides an easy procedure to incorporate high percentage of PMMA onto cellulose based Whatman filter paper.

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الملخص العربى

تم دراسة تطعيم الميثيل ميثاكريلات على ورق الترشيح كمصدر للسيلولوز النقي في وجود خليط من ملح الموهر وفوق كبريتات البوتاسيوم في وجود وسط مائي تحت تأثير الضوء المرئي. تم دراسة بعض المتغيرات مثل زمن التعرض للضوء وتركيزات كل من المونومر والحفازات والسيلولوز وحساب النسبة المئوية للتطعيم (%GP) وكفاءة التطعيم (%GE). تم تحليل آلية عمل الحفازات بالأشعة فوق البنفسجية (UV). وجد أن نسبة معدل التفاعل الإبتدائي للتطعيم تساوي ٠،٥٧ في الدقيقة. تم تحليل ناتج التطعيم بالأشعة تحت الحمراء (IR) والتحليل الوزني الحراري (TGA) ، (DTA) لاثبات عملية التطعيم. تم حساب امتصاصية الماء (%WA) ومقاومة السيلولوز قبل وبعد التطعيم للمذيبات. اقترحت آليات لعمليات التطعيم.