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Graft copolymers of xyloglucan and methyl methacrylate

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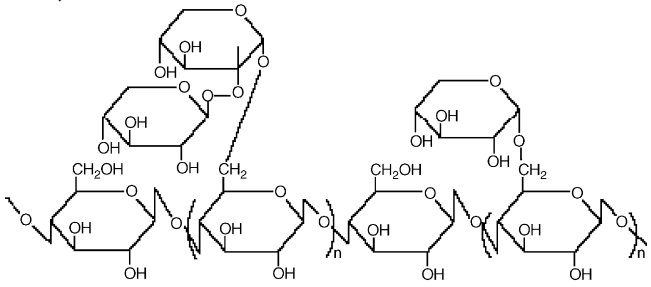
ABSTRACT

Xyloglucan, a water-soluble food grade polysaccharide, was reported as a substrate for graft copolymerization of methyl methacrylate (MMA). Grafting PMMA (polymethyl methacrylate) with xyloglucan (XG) makes a new material with improved thermal stability and shelf life without affecting its hydrophilicity. XG was isolated from tamarind seed mucilage by aqueous extraction. Grafting of MMA was initiated by ceric ion in aqueous medium under N_2 atmosphere and the progress of the reaction was monitored gravimetrically by varying different reaction parameters. Grafting of MMA onto XG was confirmed by FTIR spectroscopy, NMR spectroscopy, differential scanning calorimetric (DSC) studies, thermal gravimetric analysis (TGA) studies and scanning electron micrographs (SEMs). This material might find potential to be used in drug delivery systems.

1. Introduction

Xyloglucan (Mishra & Malhotra, 2009; Rao, Ghosh, & Krishna, 1946; Sano et al., 1996) highly substituted starch like polysaccharide, shares most of its properties with it, so often named amyloid. The properties which draw most of the attention to this particular polysaccharide to work on include high viscosity, broad pH tolerance and mucoadhesivity, non-carcinogenicity, biocompatibility and high drug holding capacity (Burgalassi, Panichi, Saettone, Jacobsen, & Rassing, 1996; Gidley et al., 1991; Kulkarni, Dwivedi, Sarin, & Singh, 1997; Sumathi & Ray, 2002). This has led to its application in food and pharmaceutical industries as stabilizer, thickener, gelling agent and binder and as excipient in hydrophilic drug delivery system (Alebiowu, Khanna, & Singh, 2006; Avachat, Dash, & Shrotriya, 2011; Bangale, Shinde, Umalkar, & Rajesh, 2011; Bhadoriya, Ganeshpurkar, Narwaria, Rai, & Jain, 2011; De-Smet, Floor-Schreudering, Bouvy, & Wensing, 2008; Herrero, Cifuentes, & Ibañez, 2006; Kuchel et al., 2005; Mi et al., 2005; Mishra & Khandare, 2011; Phanikumar, Battu, & Lova Raju, 2011; Rasala et al., 2011; Singh, Karel, & Musyuni, 2010; Tungland & Meyer, 2002). Xyloglucan is a galactoxyloglucan isolated from seed kernel of *Tamarindus indica*. The structure possesses D-galactose, D-xylose and D-glucose subunits and is confirmed by ^{13}C NMR (Gerard, 1980). It is neutral and hydrophilic having main chain of β-D-(1, 4) linked glucopyranosyl units and that a side chain consisting of single D-xylopyranosyl units through an α-D-(1, 6) linkage. One D-glucopyranosyl unit is attached to one of the xylopyranosyl units through a β-D-(1, 2) linkage. It possesses mucomimetic, mucoadhesive and pseudoplastic properties. Its 'mucin-like' molecular structure is similar to corneal and conjunctival mucin 1 (MUC1), a transmembrane glycoprotein thought to play an essential role in protecting and wetting the corneal surface and may explain its increased retention on the eye surface (Burgalassi, Chetoni, Panichi, Boldrini, & Saettone, 2000; Mannucci, Fregona, & di-Gennaro, 2000; Rolando & Valente, 2007; Sahoo, Sahoo, Nanda, Tripathy, & Nayak, 2010).



Structure of xyloglucan (Mishra, Clark, Vij, & Daswal, 2007)

The improvement of natural polymers by grafting other monomers has been finding a large interest in the literature (Adhikary, Tiwari, & Singh, 2007; Bhattacharya & Mishra, 2004; Fares, 2003; Ghosh, Jha, & Pal, 2011; Goyal, Kumar, & Sharma, 2008; Kaith, Jindal, Jana, & Maiti, 2009; Kumar, Singh, & Ahuja, 2009; Mishra & Bajpai, 2005; Mishra, Rajani, & Gupta, 2003; Mishra et al., 2007; Mishra, Mukul, Sen, & Jha, 2011;Jing, Xiao & Da Biao, 2010;

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Shu et al., 2010; Singh, Tiwari, Tripathi, & Sanghi, 2004) and industry due to combinatorial properties of both natural and synthetic polymers. This ageing free starch (xyloglucan) is used in the repair of corneal wounds and in the integrin-substrate recognition system (Burgalassi, Raimondi, et al., 2000; Saettone et al., 1997). Previous work on cultured conjunctival cells has shown that XG is well tolerated, and exerts a protective action against toxic effects induced by timolol, merthiolate and fluoroquinolones, possibly on account of its mucin-like structure (Raimondi et al., 2000).

Various non-degradable polymers like PMMA have been utilized for antibiotic delivery purposes. Antibiotic loaded PMMA, is used as a non-degradable antibiotic delivery system (Mohanty, Kumar, & Murthy, 2003; Stone et al., 2006). The antibiotic loaded bone-cement based on PMMA has been used to prevent bone infection in total or joint arthroplasty (Cavalu, Simon, Gollerb, & Akin, 2011; He, Trotignon, Loty, Tcharkhtchi, & Verdu, 2002; Kelm, Bohrer, Schmitt, & Anagnostakos, 2009; Randelli et al., 2010). XG, which is known for its biodegradability, can be copolymerized with PMMA and the properties of the graft copolymer can be tuned properly by adjusting concentration of the reactants. This study is undertaken in order to produce a water soluble material, based on XG and PMMA, having potential to be used in drug delivery system.

2. Materials and methods

2.1. Materials

Tamarind seed powder was obtained from Dabur India Limited. The monomer methyl methacrylate (S.D. Fine-Chem Ltd., India) was washed with 2% NaOH solution and distilled water several times to remove inhibitor and alkali respectively till all the alkali was removed. Ceric ammonium nitrate, hydroquinone and nitric acid (S.D. Fine-Chem Ltd, India) were used as received.

Xyloglucan was processed by following method by Rao and Srivastav (1973) on a laboratory scale. To 20 g of tamarind kernel powder, 200 ml of cold distilled water was added and slurry was prepared. The slurry was poured into 800 ml of boiling distilled water. The solution was boiled for 20 min under stirring condition in a water bath. The resulting thin clear solution was kept overnight so that most of the proteins and fibers settled out. The solution was then centrifuged at 5000 rpm for 20 min. The supernatant was separated and poured into twice the volume of absolute ethanol by continuous stirring. The precipitate was washed with absolute ethanol, diethyl ether and petroleum ether and then dried at 50–60 °C under vacuum.

2.2. Preparation of xyloglucan-g-PMMA

Xyloglucan-g-PMMA was synthesized by grafting methyl methacrylate onto purified xyloglucan by radical polymerization method in aqueous system using ceric ion/nitric acid redox initiator (Goyal, Kumar, & Sharma, 2009; Mishra, Rajani, Agarwal, & Dubey, 2002; Mishra, Clark, & Pal, 2008; Wan et al., 2011). The reaction was carried out under a constant light source. The following procedure has been adopted in carrying out the reactions. One gram of xyloglucan was dissolved in distilled water (200 mL) in an Erlenmeyer flask. The flask was then sealed with septum stopper and nitrogen gas was flushed into the solution through hypodermic needle for 20 min. Then the required amount of MMA was added into the solution through the stopper by hypodermic syringe with constant stirring using magnetic stirrer. The solution was stirred for 30 min while being bubbled with nitrogen. The required amount of ceric ion solution (in 1 N HNO_3) was injected through the stopper by hypodermic syringe. The nitrogen flushing was continued for another 20 min; then the needles were taken out, and the flask was further sealed with Teflon tape. The reaction temperature was maintained at requisite temperature. The reaction mixture was stirred occasionally; the reaction was continued for various time intervals and then terminated by injecting 0.5 mL of saturated aqueous hydroquinone solution. The reaction product was precipitated in excess of isopropanol and filtered through sintered glass filter. The precipitate was again slurried in acetone followed by filtration and finally the precipitate was dried in vacuum oven at 40 °C. The resulting product was soxhlet extracted with benzene for 72 h to extract the homopolymer, i.e., poly methylmethacrylate. The remaining product was again purified by soxhlet extraction with methanol until a constant weight was obtained. Reaction optimization was done by varying reaction parameters. Percentage grafting (PG) and efficiency (%GE) were calculated by the following equations

$$\%\,\text{grafting} = \frac{\text{weight of polymer grafted}}{\text{weight of pure mucilage}} \times 100$$

$$\%\,\text{efficiency} = \frac{\text{weight of polymer grafted}}{\text{weight of polymer grafted} + \text{weight of homopolymer formed}} \times 100$$

3. Methods of characterization of copolymer

The grafting was confirmed by FTIR and NMR (^{1}H) spectra recorded on a Perkin-Elmer Model 599 B (KBr pellets) and Jeol JNM LA 400 Lambda spectrophotometer using D_2O as a solvent and TMS as an internal reference, respectively. Grafted and pure XG samples were characterized by DSC and TGA (METTLER TA4000 SYSTEM) to compare their thermal stability. Scanning electron micrographs were taken on JEOL, JSM-840 SEM to investigate and compare surface morphology.

4. Results and discussion

Substantially pure graft copolymers are formed through ceric ion initiated polymerization as it produces free radicals exclusively on polymer substrate to be grafted. To obtain a better reproducibility in the results, the reaction was carried out under a constant light source because the oxidative capability of the Ce(IV) ions increases considerably under light (Vazquez, Goni, Guruchanga, Valero, & Guzman, 1992). The length of the grafted polymer chains is proportional to the concentration of ceric ions at a fixed monomer concentration. With higher concentration of ceric ions, the number of free radical sites will be more and consequently the length of grafted chains will be shorter. With lower ceric ion concentration, the grafted chain length should be larger. The detailed mechanism proposed for the synthesis of XG-g-PMMA is same as described elsewhere for other polysaccharide based grafted copolymers of acrylamide (Mishra et al., 2002).

4.1. Evidences of grafting

4.1.1. Infra red (IR) spectra of XG and XG-g-PMMA

The FTIR spectra of pure XG and XG-g-PMMA (PG = 77.4) are shown in Fig. 1. The wide band observed at 3431.17 cm^{-1} can be attributed to the O–H stretching of the xyloglucan and its width was ascribed to the formation of inter and intramolecular hydrogen bonds. The band at 2924.84 cm^{-1} was attributed to the asymmetric stretching of C–H, while the band at 1645.31 cm^{-1} was ascribed to adsorbed water and the bands at 1445.23 cm^{-1} to the angular deformation of C–H. The C–O stretching frequency occurs at 1030.89 cm^{-1}. The characteristic absorption at 1744.3 cm^{-1} of C=O and the absorption band at 1076 cm^{-1} for C–O stretching in XG-g-PMMA spectrum indicates grafting of PMMA with XG. The O–H stretching frequency in the grafted product is broader as compared in the ungrafted polysaccharide. This is due to unequal hydrogen

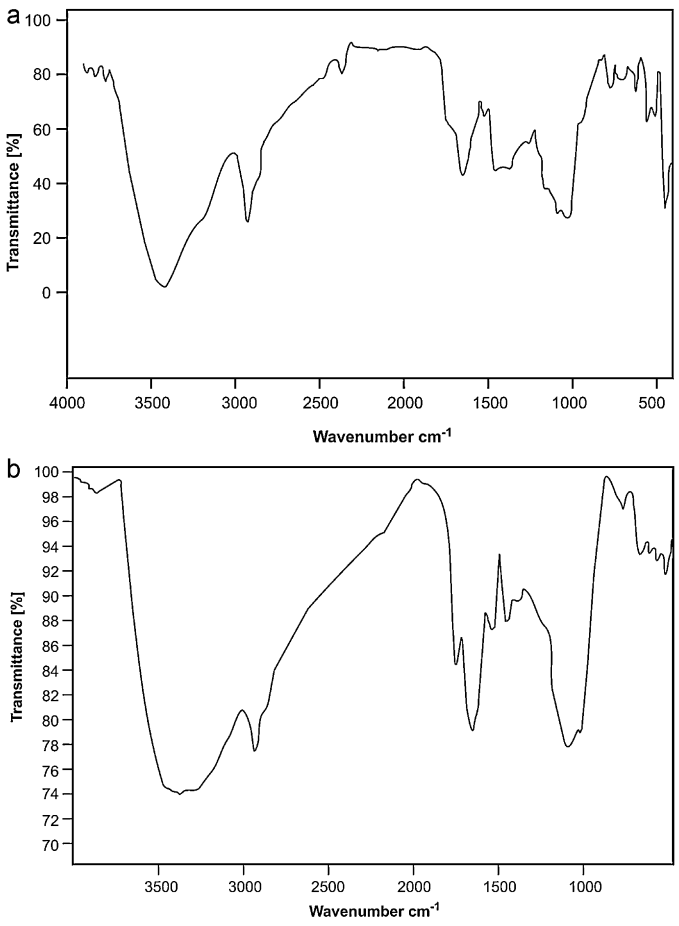

Fig. 1. FTIR spectra of (a) XG and (b) XG-g-PMMA.

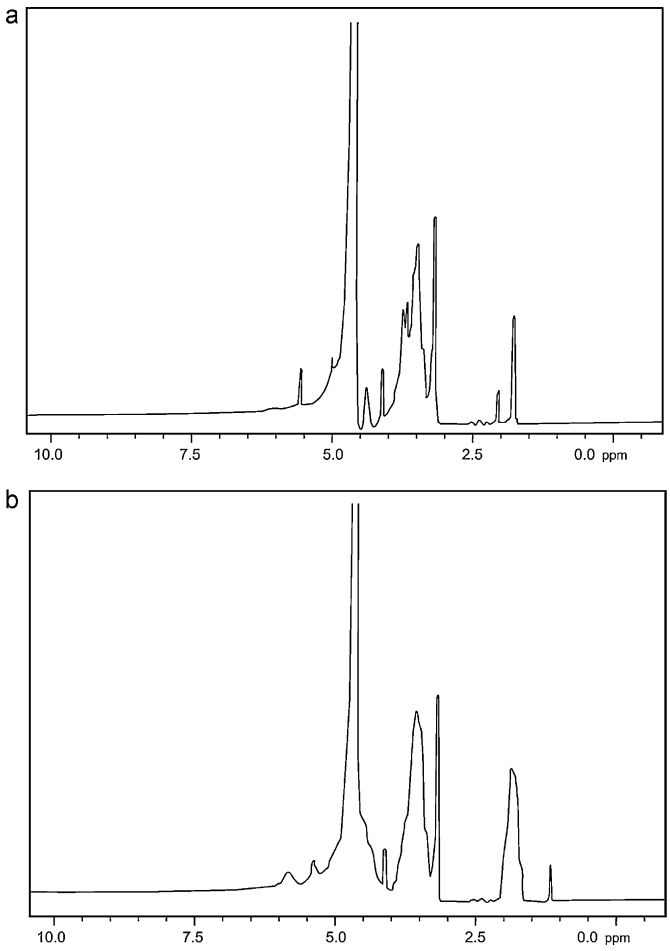

Fig. 2. NMR spectra of (a) XG and (b) XG-g-PMMA.

bonding in the grafted product again attributing to the fact that grafting has occurred.

4.1.2. Nuclear magnetic resonance (NMR) spectra of XG and XG-g-PMMA

The NMR spectra of XG and XG-g-PMMA (PG = 77.4) are shown in Fig. 2. The delta values of Xyloglucan and grafted products indicate that the bonding between polysaccharide and MMA has occurred, again attributing to the fact that grafting has taken place. To simplify the large number of peaks obtained, attention is given to the peaks of the characteristic xyloglucan peaks for anomeric hydrogens of three different residues found, i.e. galactose, xylose and glucose. At 5.6 ppm the peak for 2-ogalactosylxylose residues is seen, 5 ppm for terminal xylose residue and 4.6 ppm for all of the glucose and galacose residues. As hydrogen bonding involves electron cloud transfer from hydrogen atom to a neighbouring electronegative atom (in this case, ester group's oxygen atom of methyl methacrylate $-COOCH_3$), the hydrogen atoms in xyloglucan experience a net deshielding effect due to grafting. In the grafted product, the peaks for galactose and terminal xylose units are deshielded, having the values at 5.7 ppm and 5.3 ppm, whereas no deshielding is seen in the case of glucose units. This shows the fact that the methyl methacrylate is unable to graft to the backbone of the xyloglucan due to stearic hinderance caused by the side chains, but is easily grafted to its side chains, i.e. terminal xylose units and the galactose residue. In the case of PMMA, the methoxy protons appear at 3.6 ppm, methyl protons at 0.9–1.01 ppm and methylene protons between 1.6 and 1.9 ppm. In the grafted product, methoxy protons and methylene protons are overlapped by the peaks of xyloglucan. A slight but not very appreciable deshielding is observed in the case of methyl protons of PMMA.

4.1.3. Thermal analysis of XG and XG-g-PMMA

DSC plots of XG and XG-g-PMMA grafted product (PG = 77.4) are shown in Fig. 3. The value for ΔH in case of XG is found to be 258.5 J/g while XG-g-PMMA has ΔH of 265.8 J/g. An endothermic peak is observed at 132.5 in XG-g-PMMA and another exothermic peak above 227 °C may be due to the crosslinking of the polymer. A slight increase in ΔH is supportive of PMMA grafting on XG. The TGA curve of XG and XG-g-PMMA are shown in Fig. 4. The grafted polymer is clearly indicative of its higher thermal stability as it mainly begins to degrade at around 200 °C while the curve of pure polymer drifts continuously. Char yield of XG at 400 °C is ~50% while almost 60% of XG-g-PMMA is retained at that temperature. Thus it can be interpreted that a new improved material which is thermally more stable than the xyloglucan, is formed.

4.1.4. Scanning electron microscope studies

SEMs of XG and XG-g-PMMA are shown in Fig. 5. The structural changes on the surface of xyloglucan were introduced by grafting. The ridges on the pure sample have reduced and a homogeneous plane surface of the grafted sample indicates that grafting has occurred.

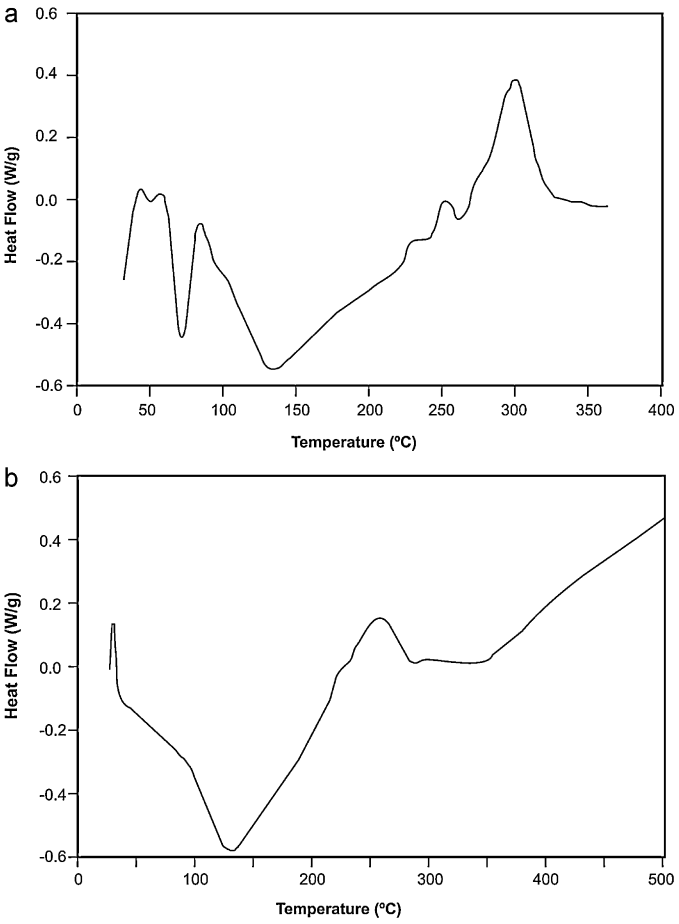

Fig. 3. DSC scans of (a) XG and (b) XG-g-PMMA.

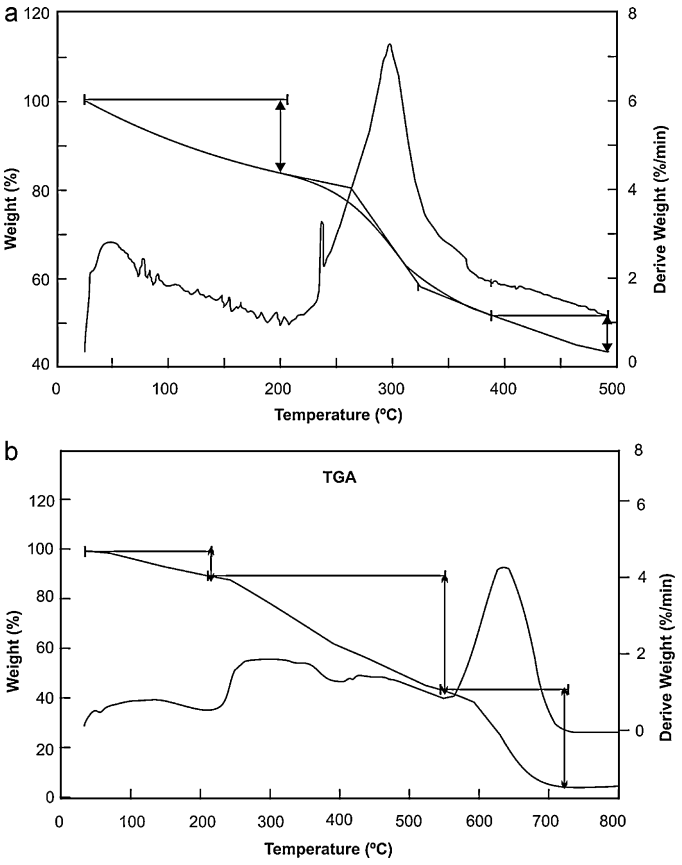

Fig. 4. TGA scans of (a) XG and (b) XG-g-PMMA.

4.2. Influence of reaction parameters

4.2.1. Effect of monomer concentration

The effect of monomer concentration on percentage grafting (PG) is shown in Table 1. The best PG was obtained for 0.02 mol of MMA in 150 ml of the solution. The increase of PG till 0.02 mol was expected with increase in MMA concentration due to the availability of MMA monomer with respect to polysaccharide macroradicals, leading to larger possibility of grafting. When more than 0.02 mol of MMA was taken in the reaction medium the formation of homopolymers i.e. PMMA hindered the rate of penetration of monomer molecules to the polysaccharide free radicals, resulting in decrease in PG.

Table 1
Effect of reaction parameters on PG and %GE.

Sample no.	Moles of MMA	Moles of Ce(IV) ($\times 10^{-3}$)	PG	%GE	Time (h)	Temperature (°C)
1	0.01	0.50	75.2	84.76	2	30
2	0.01	1.00	77.4	89.54	2	30
3	0.01	1.50	80.3	87.34	2	30
4	0.01	2.00	74.8	78.78	2	30
5	0.02	0.50	55.3	72.89	2	30
6	0.02	1.00	80.6	91.27	2	30
7	0.02	1.50	84.7	94.78	2	30
8	0.02	2.00	78.9	88.53	2	30
9	0.025	0.50	62.4	72.28	2	30
10	0.025	1.00	66.1	78.26	2	30
11	0.025	1.50	82.2	90.51	2	30
12	0.025	2.00	80.8	86.11	2	30
13	0.02	1.50	47.9	79.82	2	20
14	0.02	1.50	78.3	92.72	2	40
15	0.02	1.50	69.2	94.19	2	50
16	0.02	1.50	54.6	86.65	1	30
17	0.02	1.50	68.5	93.32	3	30
18	0.02	1.50	70.1	93.45	24	30

4.2.2. Effect of initiator (CAN) concentration

The effect of initiator concentration (CAN) on percentage of grafting is shown in Table 1. On increasing the concentration of initiator i.e., CAN from 0.5×10^{-3} mol to 1.5×10^{-3} mol, PG increased due to increase in the number of free radicals on polysaccharide chain. With further increase in CAN concentration, up to 2.0×10^{-3} mol, PG decreased. The falling of PG at higher CAN concentration is a well-known phenomenon and ascribed to the increasing participation of the ceric ion in the termination of the growing grafted chains.

4.2.3. Effect of time

The effect of time on %GE and PG is shown in Table 1. The percentage grafting as well as grafting efficiency increased with increase in the reaction time up to 2 h and after that the values became almost constant. This agrees with the earlier observation with free radical initiated polymerization (Fares, 2003).

4.2.4. Effect of reaction temperature

Reaction temperature is an important reaction condition in the graft copolymerization. The effect of temperature on percentage grafting and grafting efficiency is shown in Table 1. PG and %GE both increased on varying the reaction temperature from 20 to 40 °C. The increase in PG with increasing temperature might be due to the increased diffusion rate of monomer and initiator and raised rate of grafting (Shukla & Srivastava, 2003) but decreased PG observed with increase in temperature beyond 40 °C might be attributed to

Table 2
Solubility results for grafted samples.

Sample no.	Moles of MMA	Moles of CAN ($\times 10^{-3}$)	PG	%GE	Solubility result for XG-g-PMMA	Time taken
1	0.01	0.5	75.2	84.76	Soluble in H_2O/D_2O	20 min
2	0.01	1.0	77.4	89.54	Soluble in H_2O/D_2O	35 min
3	0.01	1.5	80.3	87.34	Insoluble in H_2O/D_2O	NA

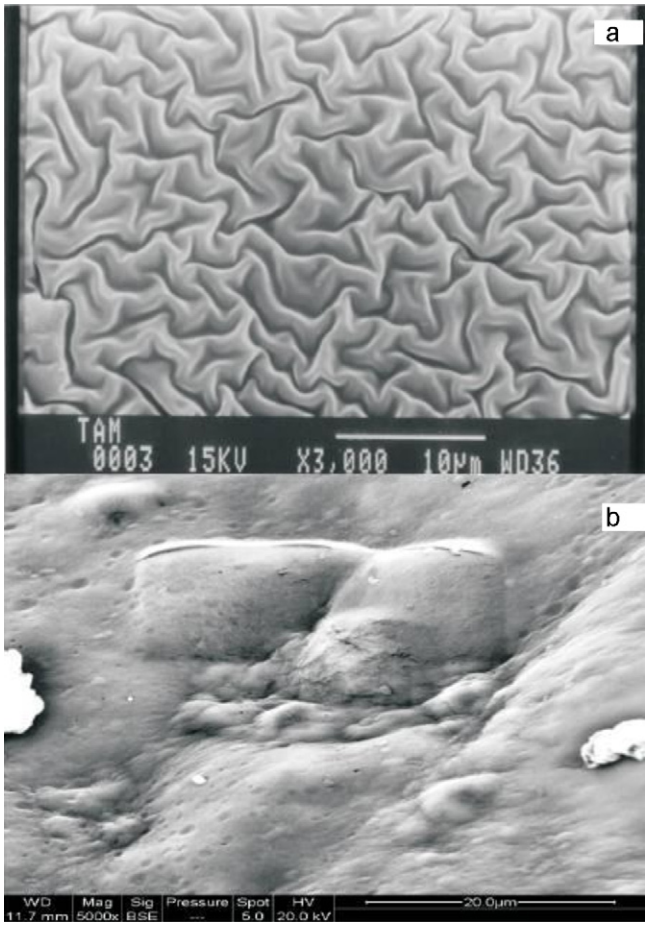

Fig. 5. Scanning electron micrograph of (a) XG and (b) XG-g-PMMA.

faster rate of termination and more homopolymerization at higher temperature.

4.2.5. Effect of reaction parameters on water solubility of XG-g-PMMA

The results of water solubility of XG-g-PMMA are given in Table 2. Grafted samples having up to 77% grafting were water soluble. It appears that as soon as the grafting increases beyond 77%, the corresponding copolymer is water-insoluble.

5. Conclusions

Grafting of PMMA with xyloglucan, a natural polysaccharide, offer a new polymeric material with properties that can be exploited by pharmaceutical industry. Grafting of PMMA on XG makes a material with improved thermal stability and shelf life. Grafting introduces more reactive sites on XG without affecting its hydrophilicity and without making any change in the molecular mobility of its chelating groups. Grafting has been done successfully by using CAN/HNO_3 redox initiator system. The optimum monomer and initiator concentrations were 0.02 M and 1.5×10^{-3} M, respectively. The maximum percent grafting (84.7%) was achieved at 30 °C after 2 h. Grafting was studied by IR and NMR spectroscopy, scanning electron microscopy and differential scanning calorimetric analysis. This material might find potential to be used in drug delivery systems.

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