

Graft Copolymers of Xyloglucan and butyl acrylate

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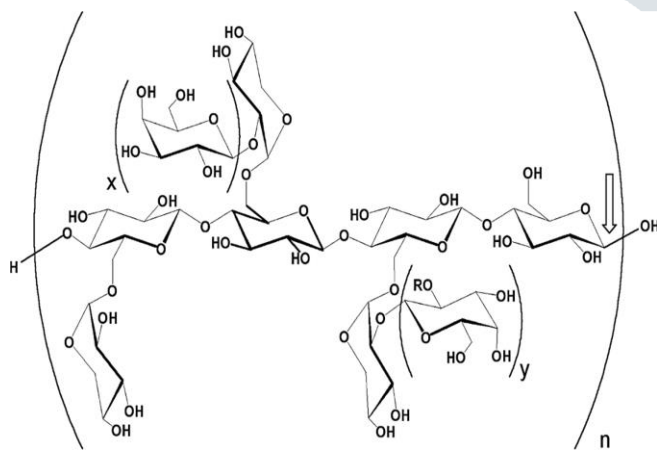
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Abstract—Xyloglucan, a water-soluble food grade polysaccharide, was reported as a substrate for graft copolymerization of Butyl Acrylate (BA). Grafting BA with Xyloglucan (XG) makes a new material with improved thermal stability, shelf life, adhesive properties and an improved sizing agent. XG was isolated from Tamarind seed mucilage by aqueous extraction. Grafting of BA was initiated by ceric ion in aqueous medium under N₂ atmosphere and the progress of the reaction was monitored gravimetrically by varying different reaction parameters. Grafting of BA onto XG was confirmed by FTIR Spectroscopy, Thermal Gravimetric Analysis (TGA). This grafted material might find potential to be used as coatings for non-woven binders and a sizing agent.

Index Terms—Butyl acrylate, FTIR, Thermo Gravimetric Analysis, Xyloglucan.

1. introduction

Polysaccharides are biologically produced (bio-based) materials that have a unique combination of functional properties and environmentally friendly features. Polysaccharides are also polymers and their long chain structures, as in man-made polymers, provide good mechanical properties for applications such as fibers, films, adhesives, melt processable plastics, thickeners, rheology modifiers, hydrogels, drug delivery agents, emulsifiers, etc. They are renewable materials, produced from other biological compounds, and generally are non-toxic and biodegradable. These features make polysaccharide materials that are a natural fit for sustainable development. 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 ¹³C NMR [1]. This branched polysaccharide constitutes about 65 percent of the seed components [2]. 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 a α D-(1, 6) linkage. One D-glucopyranosyl unit is attached to one of the xylopyranosyl units through a β-D-(1, 2) linkage.



The improvement of natural polymers by grafting other monomers has been finding a large interest in the literature [3]- [11] and industry due to combinatorial properties of both natural and synthetic polymers.

Xyloglucan associates tightly with cellulose microfibrils in the primary cell walls of plants or accumulates as a storage polysaccharide in seeds. Because of their tight binding to cellulose, xyloglucans (as tamarind kernel powder) are used commonly as sizing agents for textil [12], [13] and can also be used as wet-end additives in papermaking[14], [15].

In general all the acrylate esters show properties like surface coating, as adhesive/sealant, as textile size, paper size etc. Polybutyl acrylate shows all the above mentioned uses along with an added advantage of being biodegradable. It readily hydrolyses by carboxyesterase to acrylic acid and butanol. It is copolymerized with MMA to give a product with properties of a tougher and slightly softer feel. Sheet form of this material was marketed as asterite earlier [16] Chitosan grafted with BA found application in microencapsulating N, N diethyl-m-toluamide (an insect repellent). The compound was encapsulated *in situ* during the graft copolymerization of butyl acrylate onto chitosan in an aqueous solution. Aqueous emulsions were applied to cotton textiles by spraying. Treated cloth showed high bactericidal activity against *Staphylococcus aureus* [17], [18].

Studies were carried out on the grafting of butyl acrylate (BA) to amylose by the ceric ion method [19].

Starch is grafted with PBA [20], [21] and the material is used as a sizing agent, coating composition etc. The material is a thermoplastic which can be readily molded [22].

The xyloglucan polysaccharide carrying new chemically reactive groups can be bound to different cellulosic surfaces to alter their physicochemical properties. As the cellulose-XG interaction is purely based on hydrogen bonding, a grafted XG should also show the same binding capacity like XG and as the modification is achieved through binding interactions, and not by direct chemical modification of cellulose, the fiber integrity and strength of cellulose is maintained.

XG is an inexpensive, natural polymer that may be modified with petroleum-based monomers to form useful copolymers. XG is also hydro degradable and biodegradable, which make copolymers of XG and synthetic monomers environmentally friendly. So it was thought that if XG is grafted with BA, the resulting material will show potential applications for sizing materials for recycled paper processing, disposable plates, and biodegradable plastics. The product will also have

properties of both the sizing agents like good thermal stability, along with the cost effective and biodegradability as an added advantage. These copolymers may be used for many different applications because the mechanical properties may be varied by changing the monomer grafted or a combination of monomers added.

2. Materials and methods

2.1 Materials

Xyloglucan was obtained from Rama Gums Gujarat India Limited. The monomer Butyl acrylate was washed three times with a 10% sodium hydroxide solution, washed three times with distilled water, dried over calcium chloride, and freshly distilled under vacuum. The fraction boiling at 72°C/54 mm Hg was collected [23]. Ceric ammonium nitrate, hydroquinone and nitric acid (S.D. Fine-Chem Ltd, India) were used as received without further purification. Xyloglucan was prepared following methods by [12], [24] on a laboratory scale. To 20g of tamarind kernel powder, 200ml of cold distilled water was added and slurry was prepared. The slurry was poured into 800ml of boiling distilled water. The solution was boiled for 20 minutes 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 minutes. 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 to 60°C under vacuum.

2.2 Preparation of Xyloglucan-g-PBA

Xyloglucan-g-PBA was synthesized by grafting butyl acrylate onto purified xyloglucan by radical polymerization method in aqueous system using ceric ion/nitric acid redox initiator [19], [25]. 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 minutes. Then the required amount of BA was added into the solution through the stopper by hypodermic syringe with constant stirring using magnetic stirrer. The solution was stirred for 30 minutes while being bubbled with nitrogen. The required amount of ceric ion solution (in 1N HNO₃) was injected through the stopper by hypodermic syringe. The nitrogen flushing was continued for another 20 minutes; 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 continuously; the reaction was continued for various time intervals and then terminated by injecting 0.5 mL of saturated aqueous hydroquinone solution.

The solution was filtered; the polymer precipitated by methanol was washed with acetone, and the precipitate then dried under vacuum at 40 C. The homo-PBA was separated with soxhlet extraction of the precipitate with THF and toluene. The PBA content of the graft copolymers was determined by acid hydrolysis with 1N HCl. 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 and efficiency were calculated by the following equations:

$$\% \text{ Grafting} = \frac{\text{weight of Polymer grafted}}{\text{weight of pure mucilage}} \times 100 \quad (1)$$

$$\% \text{ Efficiency} = \frac{\text{weight of polymer grafted}}{\text{weight of polymer grafted} + \text{weight of homopolymer formed}} \times 100 \quad (2)$$

The grafting was confirmed by FTIR spectra recorded on a Perkin-Elmer Model 599 B (KBr pellets). Grafted and pure samples were characterized by 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.

3. Result and discussion

The detailed mechanism proposed for the synthesis of XG-g-PBA is same as described elsewhere for other polysaccharide based grafted copolymers of acrylamide [26].

3.1 Characterization of Graft Copolymers Infra Red (IR) Spectrum

The FTIR spectra of pure XG and XG-g-PBA (PG=88.9%) are shown in Figs.1(a) and (b) respectively. The wide band observed at 3431.17 cm⁻¹ can be attributed to the O-H stretching of 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.

In the grafted sample of Xg-g-PBA, the characteristic absorption at 1740.54 cm⁻¹ of C=O and the absorption band at 1159.37 cm⁻¹ for C-O stretching in XG-g-PBA spectrum (Fig.1 (b)) indicates grafting of PBA with XG. The O-H stretching frequency in the grafted product is broader as compared in the pure polysaccharide. This is due to unequal hydrogen bonding in the grafted product again attributing to the fact that grafting has occurred.

Thermal gravimetric analysis

The percentage of grafting ratio gives information about the extent of a synthetic polymer grafted onto the backbone

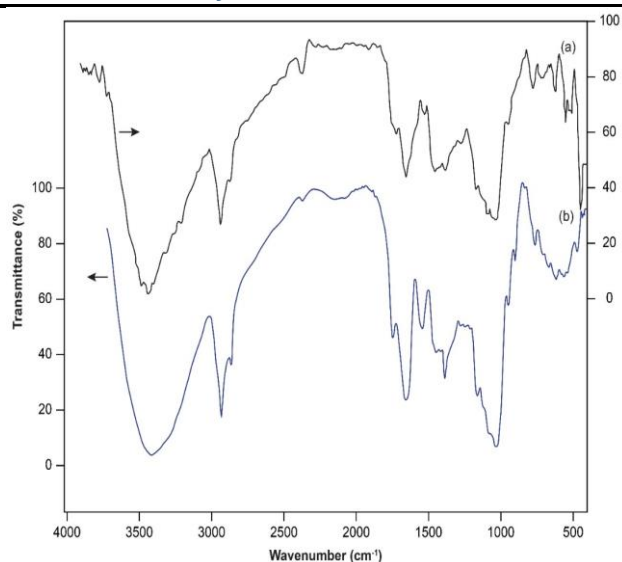


Fig. 1 (a) FTIR spectra of XG ;(b) FTIR spectra of XG-g-PBA

polymer and hence it is a preferred parameter to study thermal stability of the grafted polymer. The thermal stability of graft copolymer can be compared at the onset temperature of decomposition and the percentage of weight loss for different stages of the decomposition.

There are two main degradation steps in the case of XG. Till 200°C, there is a 16.18% weight loss which is mainly due to water evaporation. The second step assigned to cleavage of the XG's side chains of galactose and xylose subunits and then ultimately the main chain which is β 1, 4 linked glucose subunit. The temperature at which the maximum weight loss occurred is 296.88°C and almost 50% of the polymer is retained at the temperature of 400°C, after which there is a continuous degradation. In the case of XG-g-PBA, one step degradation is seen with the onset of degradation at 278.96°C. Only 7% weight loss is seen till this temperature. Till 400°C about 40% of the grafted sample is retained. Lesser polar nature of PBA in the XG matrix creates a lower density of the grafted product resulting in decrease of thermal stability.

4. Influence of Reaction Parameters

4.1 Effect of Monomer Concentration

The effect of monomer concentration on percentage grafting (PG) is shown in Table-1. The best PG was obtained for 0.14 moles of PBA in 300 ml of the solution. The increase of PG till 0.14 moles was expected with increase in PBA concentration due to the availability of PBA monomer with respect to polysaccharide macroradicals, leading to larger possibility of grafting. When more than 0.14 moles of BA was taken in the reaction medium the formation of homopolymers i.e. PBA hindered the rate of penetration of monomer molecules to the polysaccharide free radicals, resulting in decrease in PG.

4.2 Effect of Initiator (CAN) Concentration

The effect of initiator concentration (CAN) on percentage of grafting is shown in Table-1. On increasing the concentration

Sample no.	[BA] mol/L (x1)	Ce(IV) $\times 10^3$ mol/L (x2)	PG (y ₁)	%GE (y ₂)	Time (hours) (x3)	Temp. °C (x4)
1	0.09	0.5	34.3	53.29	4.5	40
2	0.11	0.5	36.3	56.73	4.5	40
3	0.14	0.5	42.6	68.24	4.5	40
4	0.16	0.5	38.7	62.63	4.5	40
5	0.09	0.75	41.5	65.78	4.5	40
6	0.11	0.75	62.4	69.89	4.5	40
7	0.14	0.75	68.1	72.14	4.5	40
8	0.16	0.75	61.2	71.68	4.5	40
9	0.09	1.0	75.6	81.54	4.5	40
10	0.11	1.0	77.2	83.48	4.5	40
11	0.14	1.0	88.9	97.79	4.5	40
12	0.16	1.0	83.1	90.56	4.5	40
13	0.09	1.5	64.8	76.96	4.5	40
14	0.11	1.5	67.2	79.28	4.5	40
15	0.14	1.5	78.6	84.11	4.5	40
16	0.16	1.5	72.7	81.92	4.5	40
17	0.14	1.0	82.3	79.28	4.5	30
18	0.14	1.0	79.8	83.37	4.5	50
19	0.14	1.0	65.5	80.86	4.5	60
20	0.14	1.0	83.9	91.51	3	40
21	0.14	1.0	85.2	94.67	4	40
22	0.14	1.0	86.3	97.45	5	40
23	0.14	1.0	87.4	97.33	24	40

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

(PE: Percent Grafting; %GE: Graft Efficiency)

of initiator i.e., CAN from 0.5×10^3 moles/L to 1.0×10^3 moles/L, PG increased due to increase in the number of free radicals on polysaccharide chain. With further increase in CAN concentration, up to 1.5×10^3 moles, 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 [27].

4.3 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 4.5 hours and after that the values became almost constant. This agrees with the earlier observation with free radical initiated polymerization [28].

4.4 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 30 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 [5] but decreased PG observed with increase in temperature beyond 40°C might be attributed to faster rate of termination and more homopolymerization at higher temperature.

5. Conclusions

Grafting of PBA with xyloglucan, a natural polysaccharide, offer a new polymeric material with properties that can be exploited industrially. Grafting of PBA on XG makes a material with improved thermal stability in the lower temperature range and shelf life. Grafting introduces more reactive sites on XG without making any change in the basic structure of the polysaccharide. Grafting has been done successfully by using CAN/HNO₃ redox initiator system. The optimum monomer and initiator concentrations were 0.14 M and 1.0x10³ Moles/L, respectively. The maximum percent grafting (88.9%) was achieved at 40°C after 4.5 hours. Grafting was studied by IR spectroscopy and thermal gravimetric analysis. This material might find potential to be used in sizing materials, coating compositions and in the formation of adhesive materials.

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