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Characterization and evaluation of methyl methacrylate-acetylated *Saccharum spontaneum* L. graft copolymers prepared under microwave

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ABSTRACT

Hybridization of the natural polymers with synthetic polymers is of great interest because of its application to biomedical and biodegradable materials. Synthesis of graft copolymers of methyl methacrylate (MMA) onto acetylated *Saccharum spontaneum* L. fiber using ferrous ammonium sulphate–potassium per sulphate (FAS–KPS) redox initiator under the influence of microwave radiation (MWR) was carried-out. Different reaction parameters such as time, initiator molar ratio, monomer concentration, microwave power, pH and solvent were optimized to get maximum graft yield (72.2%). On grafting, percentage crystallinity decreases rapidly with reduction in its stiffness and hardness. The graft copolymers thus formed were characterized by FTIR, SEM, XRD, TGA, DTA and DTG techniques. Moreover, graft copolymers have been found to be more moisture resistant and also showed higher chemical and thermal resistance.

1. Introduction

Hybridization of the natural polymers with synthetic polymers is of great interest because of its application to biomedical and biodegradable materials. Grafting involves attachment of polymer chains, usually monomer, to the back-bone polymer. It is one of the methods to increase the compatibility between synthetic polymers and cellulose. It has been observed that monomers with polar groups favor the absorption of microwave radiations and modification of fibrous proteins and cellulose through graft copolymerization has been reported (Chauhan, Guleria, Misra, & Kaur, 2000). MWR technique reduces the extent of physico-chemical stresses to which the fibers are exposed during the conventional techniques. It has been reported that properties of fibers treated under MWR are same or even better than those of fibers modified through other conventional techniques (Kaith & Susheel, 2008). Recently grafting of butylacrylate, acrylic acid and acrylonitrile onto starch, acrylamide onto LDPE (low density polyethylene) films (Gupta, Anjum, & Gupta, 2000) and butyl methacrylate onto wool fibers (Gabriel et al., 1998), has been studied using redox initiators under microwave irradiation. Methyl methacrylate has been reported to polymerize under microwave irradiation using very low concentration of initiator (Zhenping, Xiulin, Mingchen, Chen, & Zhang, 2003). Grafting of acrylamide (Singh, Tiwari, Tripathi, & Sanghi, 2004a) and acrylonitrile (Singh, Tiwari, Tripathi, & Sanghi, 2004c) onto chitosan and acrylonitrile onto Guar gum (Singh, Tiwari, Tripathi, & Sanghi, 2004b) under microwave conditions, in very short reaction time and in absence of any redox initiator or catalyst has been reported. Polyacrylamide was graft copolymerized onto chitosan using MWR and maximum grafting 169% was observed in 1.16 min, under optimum reaction conditions (Singh, Tiwari, Tripathi, & Sanghi, 2006).

Grafting under MWR has advantages in terms of time consumption and cost effectiveness. In the present study MMA has been graft copolymerized onto acetylated *S. spontaneum* under the influence of MWR and evaluation of its different physical, chemical and thermal properties have been carried-out.

2. Experimental

2.1. Materials

2.1.1. Purification of materials

Acetylated *S. spontaneum* L. fiber was purified by soxhlet refluxing in acetone for 72 h (Kaith, Singha, & Gupta, 2003). MMA (s. d. fine) was purified by washing with 5% NaOH and subsequent drying over anhydrous Na_2SO_4 followed by distillation. FAS (s. d. fine) was recrystallized from hot water and KPS (s. d. fine) was used as received.

2.2. Microwave equipment

Microwave equipment (LG, Model No. MG-3937C, 1200W) was used for all experiments. The average bulk temperature at the end of the reaction was measured by inserting thermometer in the

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reaction mixture and was found to be less than 100 °C as all the reactions were performed in aqueous medium.

2.3. Methods

2.3.1. Acetylation of S. spontaneum L. fiber

Acetylation of *S. spontaneum* L. fiber was carried-out as per the standard method (Furniss, Hannaford, Smith, & Tatchell, 2004).

2.3.2. Graft copolymerization

Activation of acetylated *S. spontaneum* L. fiber (0.5 g) was done at room temperature by immersing in 25 ml of distilled water for 24 h prior to carrying-out graft copolymerization. A definite molar ratio of FAS–KPS was added to the reaction flask. A known amount of monomer was added drop by drop with continuous stirring to the reaction mixture and the reaction was carried-out under the influence of MWR for a definite time interval. Homopolymer was extracted with acetone and the graft copolymer thus obtained was dried at 50 °C till a constant weight was attained. Percentage polymer loading (%PL), percentage graft yield (%GY), percentage graft efficiency (%GE) and percentage homopolymer (%HM) formed (Table 1) were calculated as (Princi et al., 2005):

$$\text{Percent polymer Loading} \quad (\%\text{PL}) = \frac{(W_2 - W_1)}{W_1} \times 100$$

where W_1 and W_2 are the initial and final weights of the sample, respectively, (before homopolymer extraction).

$$\text{Percent graft yield} \quad (\%\text{GY}) = \frac{(W_3 - W_1)}{W_1} \times 100$$

The quantity of the grafted polymer is evaluated as the weight increase of the sample (W_3) after extraction of the homopolymer.

$$\text{Percent graft efficiency} \quad (\%\text{GE}) = \frac{(W_3 - W_1)}{(W_2 - W_1)} \times 100$$

Percent graft efficiency is the ratio between the quantity of grafted monomer and the total polymerized monomer.

$$\text{Percent homopolymer} \quad (\%\text{HM}) = 100 - (\%\text{GE})$$

2.4. Infrared spectroscopy (IR)

IR spectra were recorded with a Perkin-Elmer Fourier transform-infrared (FT-IR) spectrophotometer using KBr pellets.

2.5. Scanning electron microscopy (SEM)

Scanning electron micrograph (SEM) was obtained using JEOL – JSM – 6100 – scanning electron microscope.

2.6. X-ray diffraction (XRD) studies

X-ray diffraction studies were performed on X-ray diffractometer (X'-Pert-Pra-PAN-Analyzer) under ambient conditions using Cu Kα (1.5418 Å) radiation, N-filter and scintillation counter as detector at 45 kV and 35 mA on rotation between 5° and 40° (2θ-scale) at 1 s step size and increment of 0.01 degree with 0.5 or 1.0 mm of divergent and anti-scattering slit. Crystallinity index (CI) which measured the orientation of the cellulose crystals with respect to fiber axis was determined by using the wide angle X-ray diffraction

Table 1
Evaluation of optimum reaction parameter for grafting of MMA onto acetylated *S. spontaneum*.

Sr. No.	Reaction time (s)	pH	Solvent (ml)	Molar ratio (FAS:KPS)	[MMA] × 10^{-3} (mol/L)	%MW	%PL[a]	%GY[b]	%GE[c]	%HM[d]
1	60	7.0	20	1: 0.500	2.45	80	44.4	21.2	47.7	52.3
2	90	7.0	20	1: 0.500	2.45	80	46.3	26.8	57.8	42.2
3	120	7.0	20	1: 0.500	2.45	80	64.2	43.7	68.0	32.0
4	150	7.0	20	1: 0.500	2.45	80	52.3	36.9	70.5	29.5
5	180	7.0	20	1: 0.500	2.45	80	51.2	26.2	51.1	48.9
6	90	2.0	20	1: 0.500	2.45	80	45.2	18.6	41.1	58.9
7	90	4.0	20	1: 0.500	2.45	80	47.9	27.3	56.9	43.1
8	90	6.0	20	1: 0.500	2.45	80	52.3	35.7	68.8	31.2
9	90	7.0	20	1: 0.500	2.45	80	67.7	46.9	69.2	30.8
10	90	8.0	20	1: 0.500	2.45	80	62.4	34.8	55.7	44.3
11	90	9.0	20	1: 0.500	2.45	80	58.9	21.9	37.1	62.9
12	90	7.0	15	1: 0.500	2.45	80	49.1	19.9	40.5	59.5
13	90	7.0	20	1: 0.500	2.45	80	53.4	38.1	71.3	28.7
14	90	7.0	25	1: 0.500	2.45	80	72.1	49.8	69.0	31.0
15	90	7.0	30	1: 0.500	2.45	80	65.3	38.3	58.3	41.7
16	90	7.0	35	1: 0.500	2.45	80	55.2	27.4	49.6	50.4
17	90	7.0	40	1: 0.500	2.45	80	51.6	22.2	43.3	56.7
18	90	7.0	25	1: 0.125	2.45	80	55.1	19.4	35.2	64.8
19	90	7.0	25	1: 0.250	2.45	80	75.2	52.4	69.6	30.4
20	90	7.0	25	1: 0.375	2.45	80	71.9	45.5	63.2	36.8
21	90	7.0	25	1: 0.500	2.45	80	70.8	34.1	48.1	51.9
22	90	7.0	25	1: 0.625	2.45	80	61.6	26.8	43.5	56.5
23	90	7.0	25	1: 0.250	1.47	80	54.4	15.2	27.9	72.1
24	90	7.0	25	1: 0.250	1.96	80	58.7	34.6	58.9	41.1
25	90	7.0	25	1: 0.250	2.45	80	77.3	62.4	80.7	19.3
26	90	7.0	25	1: 0.250	2.94	80	72.9	49.9	68.4	31.6
27	90	7.0	25	1: 0.250	3.43	80	66.3	35.7	53.8	46.2
28	90	7.0	25	1: 0.250	2.45	60	61.4	45.6	74.3	25.8
29	90	7.0	25	1: 0.250	2.45	70	75.3	64.3	85.3	14.7
30	90	7.0	25	1: 0.250	2.45	80	81.3	72.2	88.2	11.8
31	90	7.0	25	1: 0.250	2.45	90	71.2	47.2	66.2	33.8
32	90	7.0	25	1: 0.250	2.45	100	69.8	42.1	60.3	39.7

[a] Percentage polymer loading.
[b] Percentage graft yield.
[c] Percent graft efficiency.
[d] Percentage homopolymer.