Synthesis and Characterization of Graft Copolymers of Hydroxypropyl Cellulose with Acrylamide and Some Comonomers

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ABSTRACT: To obtain new polymeric materials for environmental management, we used pine needles from the huge forest of the Western Himalayas as a source of cellulose. Cellulose was derivatized to hydroxypropyl cellulose (HPC), a useful water-soluble cellulose ether. HPC was graft-copolymerized with acrylamide (AAm) with benzoyl peroxide as the initiator. At optimum grafting conditions, five different concentrations of the comonomers glycidyl methacrylate, acrylic acid, 2-hydroxyethyl methacrylate, and acrylonitrile were grafted with AAm. Networks of HPC and AAm were also synthesized by crosslinking reactions with glutaraldehyde as a crosslinker over a range of four different concentrations of crosslinker under acidic conditions. Crosslinked networks of HPC with AAm and a comonomer at one comonomer concentration were also synthesized. Graft copolymers were characterized by Fourier transform infrared spectroscopy, scanning electron microscopy, and swelling behavior. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 91: 545–555, 2004

Key words: monomers; mixing; crosslinking

INTRODUCTION

We recently reported a considerable amount of work on the utilization of pine needles as a cellulose resource base. To incorporate some desirable properties on this backbone, we studied the grafting of 4-vinylpyridine,[1] styrene,[2,3] acrylamide (AAm),[4] and acrylic acid (AAc)[5] and the cografting of styrene and maleic anhydride,[6] styrene and acrylonitrile (AN),[7,8] AAm,[4] and AAc[5] with some methacrylates and AN. We also prepared networks based on cellulosics,[9] and many of the functionalized grafted and crosslinked cellulosics based on native cellulose and its different derivatives have been used as effective metal ion sorbents[10,11] and flocculents.[12] In this article, we report the grafting of AAm and some comonomers onto hydroxypropyl cellulose (HPC) obtained from the cellulose extracted from pine needles. HPC is a useful water-soluble ether of cellulose that finds application in a host of industrial areas. Due to its versatile properties, recently it has attracted the attention of many workers as it is now being modified by grafting with monomers.[13–16] Its graft copolymer with methyl methacrylate is a new effective drug-release material.[17,18] To improve its surface-active properties, for better molecular interactions with low-molecular-weight molecules, and to provide good reinforcing agents in interpenetrating networks, its graft copolymers and crosslinked networks were synthesized with AAm and some comonomers for environmental management technologies. This article reports on the kinetics of the grafting and network formation and the characterization of these novel polymeric materials by Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), and swelling behavior studies in water, which were aimed at the investigation of their structural aspects.

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EXPERIMENTAL

Synthesis of HPC

The synthesis of HPC from 1,2-propylene oxide and alkali cellulose was discussed elsewhere; 1 g of cellulose yielded 1.15 g of HPC, and the molar degrees of substitution as calculated for HPC were 0.42 and 32% soluble in water.[9]

Graft copolymerization

AAm (Aldrich) was purified by recrystallization from its aqueous solution with a minimum quantity of methanol (MeOH) and was kept standing overnight. Optimum grafting conditions were obtained by the application of the grafting reaction scheme given in Table I. At the optimum reaction conditions were worked out for the grafting of AAm onto HPC, AAc

TABLE I
Grafting of AAm onto HPC

No.	[BPO] × 10^2 (mol/L)	[AAm] × 10^2	Solvent (mL)	Temperature (°C)	Time (h)	$P_{\text{add-on}}$
1	1.65	56.27	25.00	60	0.5	28.50
2	1.65	56.27	25.00	60	1.0	34.50
3	1.65	56.27	25.00	60	1.5	42.70
4	1.65	56.27	25.00	60	2.0	40.50
5	1.65	56.27	25.00	60	2.5	35.50
6	0.83	56.27	25.00	60	1.5	31.20
7	1.24	56.27	25.00	60	1.5	38.80
8	2.07	56.27	25.00	60	1.5	41.30
9	2.48	56.27	25.00	60	1.5	41.60
10	2.48	56.27	25.00	50	1.5	37.20
11	2.48	56.27	25.00	70	1.5	47.40
12	2.48	56.27	25.00	80	1.5	37.30
13	2.48	56.27	25.00	90	1.5	37.00
14	2.48	56.27	H_2O	70	1.5	15.00
15	2.48	56.27	Benzene	70	1.5	18.00
16	2.48	56.27	Dioxane	70	1.5	39.50
17	2.48	56.27	MeOH	70	1.5	18.00
18	2.48	14.10	Acetone	70	1.5	10.40
19	2.48	28.20	Acetone	70	1.5	13.20
20	2.48	84.40	Acetone	70	1.5	27.00
21	2.48	112.51	Acetone	70	1.5	44.00
22	12.37	281.37	5.00	70	1.5	42.20
23	4.12	93.79	15.00	70	1.5	44.20
24	1.76	40.20	35.00	70	1.5	47.00
25	1.37	31.26	45.00	70	1.5	46.40

HPC = 1 g; solvent = acetone.

(Merck, Schuchardt, Germany), 2-hydroxyethyl methacrylate (HEMA; Merck), glycidyl methacrylate (GMA; Merck), and AN (S.D. Fine, Mumbai, India) also were grafted over a range of five concentrations. Crosslinked graft copolymers [HPC-*g*-poly(AAm)] were synthesized with a 25% solution of glutaraldehyde (GA; S.D. Fine) at the optimum grafting conditions. The crosslinked graft copolymers of HPC with AAm and comonomers to give HPC-*g*-poly(AAm-*co*-CM), where CM stands for AAc, AN, HEMA, or GMA, were synthesized at a selected concentration of comonomer at an optimum concentration of crosslinker. Polymer yield as a function of monomer or monomer add-ons ($P_{\text{add-on}}$) was expressed as

$$P_{\text{add-on}} = \frac{\text{Weight of the graft copolymer} - \text{weight of backbone polymer}}{\text{Weight of backbone polymer}} \times 100$$

For the networks, only the insolubilized part was recovered, and $P_{\text{add-on}}$ was the expressed weight increase of the weight of HPC taken.

FTIR, SEM, and swelling studies

FTIR (Nicolet spectrometer Series II, Madison, WI) spectra and SEM (Jeol-6100 scanning microscope, Japan) micrographs of cellulose, the graft copolymers of AAm and its comonomers, and the crosslinked networks were recorded. Swelling studies were carried out by the equilibration method with 0.5 g of polymer network immersed in 50.0 mL of water, kept undisturbed for 24 h. We removed surface water by keeping the polymer in loose folds of filter paper. Percentage swelling (P_s) was calculated by the following expression:

$$P_s = \frac{\text{Weight of the swollen polymer} - \text{weight of dry polymer}}{\text{Weight of dry polymer}} \times 100$$

To study the effect of partial hydrolysis on the polymer structure and properties, 0.5 g of the polymer was immersed in 0.5*N* NaOH, was left undisturbed for 48 h, and was washed with water. FTIR spectroscopy, SEM, and water uptake by these polymers was also studied.

RESULTS AND DISCUSSION

For the homogeneous distribution of monomer and initiator, the grafting of AAm onto HPC was carried out in acetone due to the solubility of benzoyl peroxide (BPO) and the monomer to minimize losses of water-soluble backbone in water. Apart from the abstraction of hydrogen atoms from 2, 3, and 6 —H or

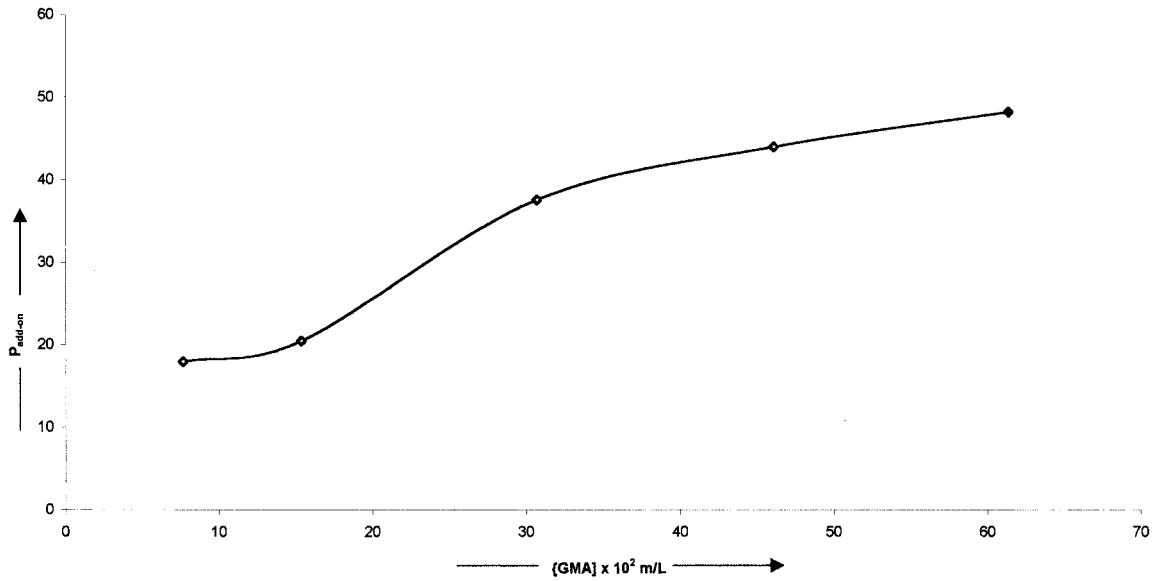

Figure 1 Effect of [GMA] on the grafting of a binary mixture of GMA with AAm onto HPC. HPC = 1 g; [AAm] = 56.27 $\times$ 10^{-2} mol/L; [BPO] = 2.47 $\times$ 10^{-2} mol/L; acetone = 25.0 mL; reaction time = 1.5 h; temperature = 70°C.

—OH from the anhydroglucose unit, the hydroxypropyl units could also provide grafting sites.

Effects of various reaction parameters on the grafting of AAm onto HPC

The effects of various reaction parameters on the graft yield are shown in Table I. The variation in time from 0.50 to 2.5 h afforded maximum $P_{add\text{-}on}$ (40.70) at 1.5 h. From 1.50 to 2.00 h, $P_{add\text{-}on}$ remained almost unaffected (40.50) but decreased (35.50) with a further increase in time to 2.5 h. Thus, an optimum reaction time was established (1.5 h). Variation in [BPO] was studied in a narrow concentration range (0.83 $\times$ 10^{-2} to 2.48 $\times$ 10^{-2} mol/L), and $P_{add\text{-}on}$ increased regularly with increasing [BPO]. At the observed optimum reaction time and initiator concentration, with other conditions of monomer concentration and amount of solvent kept constant, temperature varied in the range 50–90°C. A maximum $P_{add\text{-}on}$ of 47.40 was observed in 25.00 mL of acetone at 70°C. Grafting efficiency followed the order 50 $<$ 60 $<$ 70 $>$ 80 $\sim$ 90°C (Table I). This implied that there existed an optimum temperature to afford a maximum graft yield. [AAm] was varied between 14.10 $\times$ 10^{-2} and 112.51 $\times$ 10^{-2}

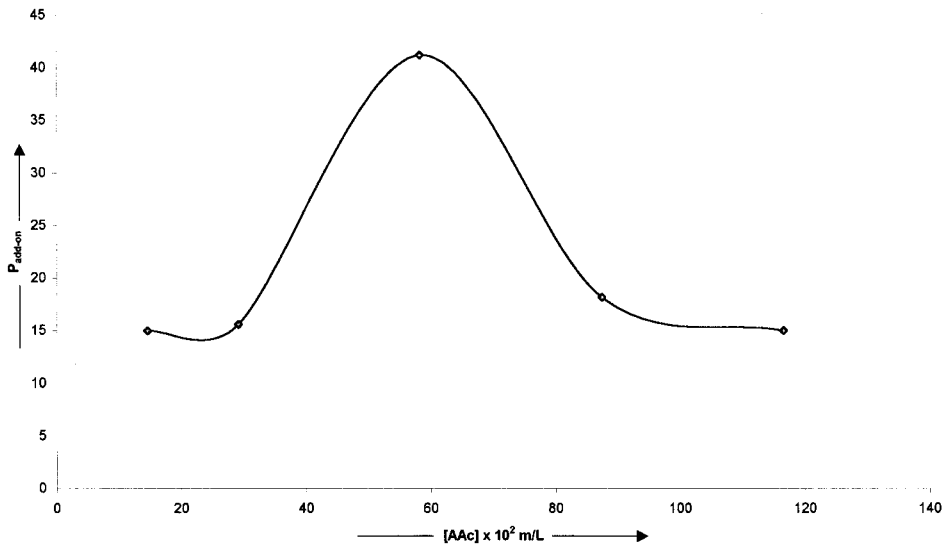

Figure 2 Effect of [AAc] on the grafting of a binary mixture of AAc with AAm onto HPC. HPC = 1 g; [AAm] = 56.27 $\times$ 10^{-2} mol/L; [BPO] = 2.47 $\times$ 10^{-2} mol/L; acetone = 25.0 mL; reaction time = 1.5 h; temperature = 70°C.

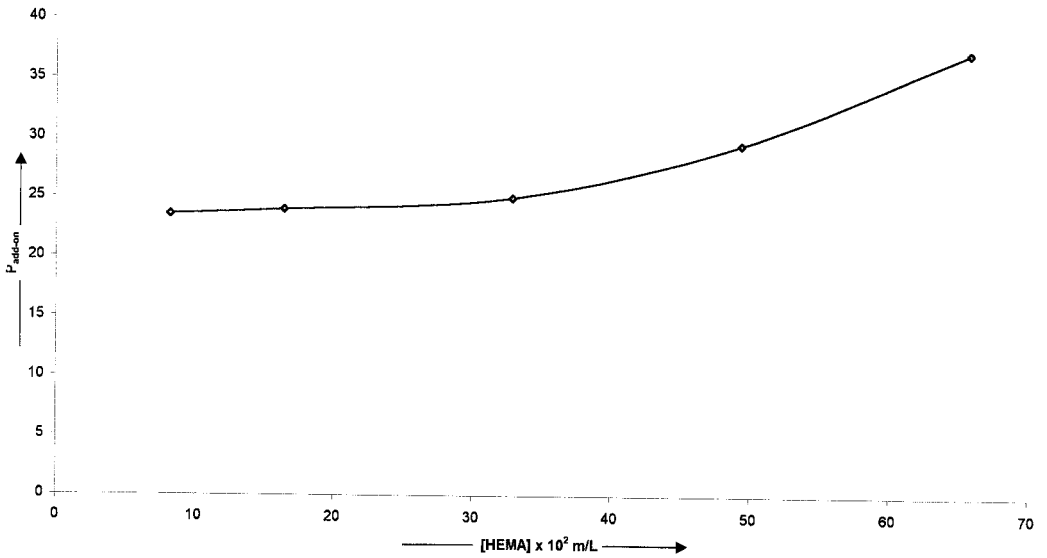

Figure 3 Effect of [HEMA] on the grafting of a binary mixture of HEMA with AAm onto HPC. HPC = 1 g; [AAm] = 56.27 $\times$ 10^{-2} mol/L; [BPO] = 2.47 $\times$ 10^{-2} mol/L; acetone = 25.0 mL; reaction time = 1.5 h; temperature = 70°C.

mol/L. The graft yield increased initially with increasing monomer concentration, followed by a regular decrease as at higher initiator and monomer concentrations, the number of reactions initiated increased significantly, and as a result of enhanced mutual termination of the growing polymeric radicals, more homopolymer was formed. A maximum $P_{add\text{-}on}$ of 47.40 was observed at 56.27 $\times$ 10^{-2} mol/L of the monomer (Table I).

The effect of the nature of the solvent was studied at the optimum reaction time temperature, and initiator and monomer concentrations with 25.00 mL of benzene, MeOH, dioxane, and water (Table I). A change in the nature of the solvent had a significant effect on the graft yields in the following order: water (15.00) < MeOH (18.00) = benzene (18.00) < dioxane (39.50). It was evident that all of these solvents afforded a lesser graft yield than acetone. The low $P_{add\text{-}on}$ observed in water may have been due to a loss of graft copolymer in the separation process. It appeared that the solubility of the initiator in the reaction medium was a more important factor for the promotion of graft

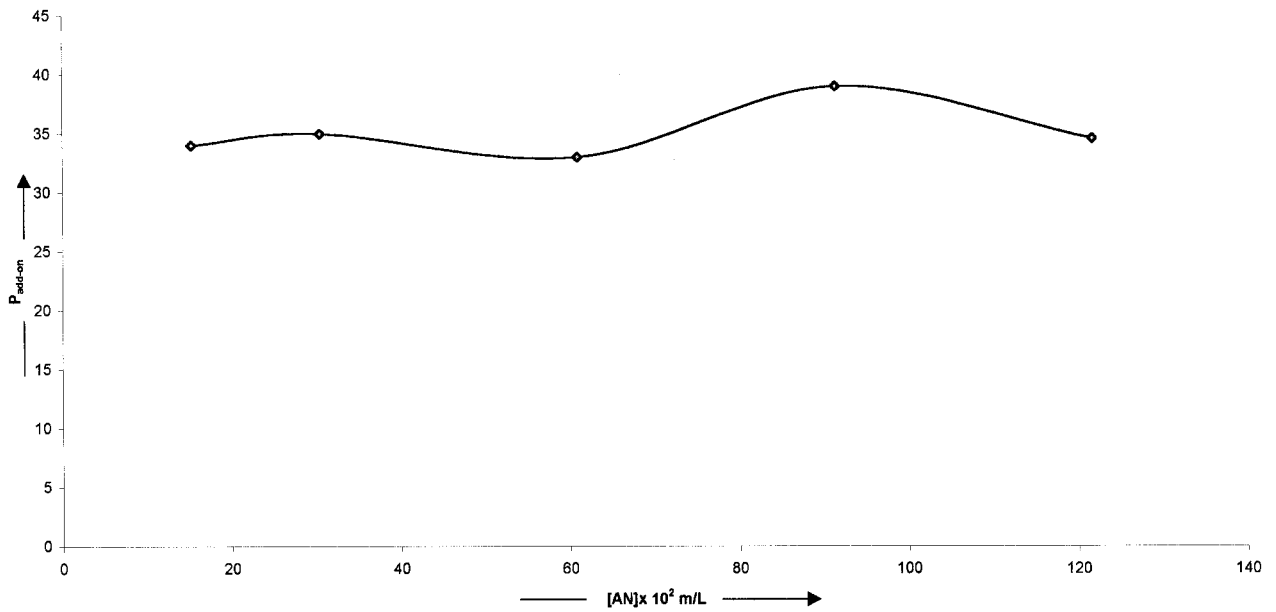

Figure 4 Effect of [AN] on the grafting of a binary mixture of AN with AAm onto HPC. HPC = 1 g; [AAm] = 56.27 $\times$ 10^{-2} mol/L; [BPO] = 2.47 $\times$ 10^{-2} mol/L; acetone = 25.0 mL; reaction time = 1.5 h; temperature = 70°C.

TABLE II
Effect of Crosslinking on the Grafting of AAm onto HPC

No.	[GA] × 10^2 (mol/L)	[HCl] × 10^2 (mol/L)	$P_{add\text{-}on}$
1	32.121	196.146	—
2	62.532	190.377	—
3	90.857	184.938	28.1
4	177.777	179.801	67.7

HPC = 1 g; [AAm] = 1.406 × 10^2 mol, [BPO] = 8.25 × 10^4 mol; solvent system = 5.00 mL acetone + 10.00 mL water; reaction time = 2.5 h; reaction temperature = 100°C.

TABLE IV
Swelling Behavior of Crosslinked HPC-*g*-Poly(AAm)

No.	[GA] × 10^2 (mol/L)	$P_{add\text{-}on}$	P_s	$P_{s(h)}$
1	32.121	—	465.00	500.00
2	62.352	—	625.00	665.00
3	90.857	28.10	238.00	258.00
4	177.777	67.70	228.00	274.00

HPC = 1 g; [AAm] = 1.406 × 10^2 mol; [BPO] = 8.25 × 10^4 mol; solvent system = 5.00 mL acetone + 10.00 mL water; reaction time = 2.5 h; reaction temperature = 100°C; swelling time = 24 h; hydrolysis time = 48.00 h in 0.5*N* NaOH.

yields; hence, appreciable changes in the graft yield were observed with the variation of solvent. Initially, $P_{add\text{-}on}$ increased with a variation in the amount of acetone from 5.00 to 25.00 mL (10.40, 13.20, and 47.40) but decreased on further progressive addition to 45.00 mL (27.00 and 44.20). The dilution of a reaction system generally leads to a decrease in $P_{add\text{-}on}$, as the accessibility of the growing monomeric species to the backbone polymer is diminished, affecting overall polymerization processes adversely. However, in this case, chain-transfer reactions also played an important role.

Grafting of binary monomer mixtures

Changing only the comonomer concentration, we grafted binary monomer mixtures of AAm with AAc, GMA, HEMA, and AN onto HPC at the optimum reaction conditions evaluated and discussed earlier for the grafting of AAm only (Figs. 1–4). $P_{add\text{-}on}$ increased regularly with increasing concentration of GMA (7.65 × 10^{-2} to 61.40 × 10^{-2} mol/L; Fig. 1). [AAc] was varied from 14.55 × 10^{-2} to 116.50 ×10^{-2} mol/L, and initially, $P_{add\text{-}on}$ increased with increasing [AAc] up to 58.20 × 10^{-2} mol/L and then decreased sharply to 18.20 and 15.00, corresponding to 87.4 ×10^{-2} and 116.40 × 10^{-2} mol/L of AAc (Fig. 2). A maximum $P_{add\text{-}on}$ (41.20) was obtained at an AAc concentration of 58.20 × 10^{-2} mol/L. For the grafting of a binary mixture of AAm and HEMA, $P_{add\text{-}on}$ remained nearly constant initially when concentration of HEMA was varied from 8.20 × 10^{-2} to 32.887 × 10^{-2} mol/L (24.60, 24.00, 25.00, and 29.50). However, a further increase in the comonomer concentration (65.775 × 10^{-2} mol/L) resulted in a slight hike in $P_{add\text{-}on}$ to 37.30 (Fig. 3). Almost similar trends were observed when AN was used as the comonomer, where $P_{add\text{-}on}$ remained nearly constant as [AN] was varied from 15.20 × 10^{-2} to 121.60 × 10^{-2} mol/L, with respective $P_{add\text{-}on}$ values of 34.00, 35.00, 33.00, 39.00, and 34.60 (Fig. 4).

Kinetics of the crosslinker on grafting

The crosslinking reactions of HPC and AAm were in an aqueous medium (10.0 mL) at optimum concentrations of BPO and AAm with 32.121 × 10^{-2} to 177.78 × 10^{-2} mol/L GA as crosslinker and with the concentration of HCl kept constant (0.12 mol/L). Insolubilized HPC-*cl*-poly(AAm) networks were separated, and total polymer network yields ($P_{add\text{-}on}$ over original weight of HPC) of 28.10 and 67.70 (Table II) were obtained only at the higher concentrations of the crosslinker. Crosslinked HPC-*cl*-poly(AAm-*co*-CM) was synthesized at a selected comonomer concentration, and the polymer yields ($P_{add\text{-}on}$) for different

TABLE III
Effect of Crosslinking on the Grafting of Binary Mixtures of AAm onto HPC

No.	[M] × 10^2 (mol/L)	[GA] × 10^2 (mol/L)	[HCl] × 10^2 (mol/L)	$P_{add\text{-}on}$
1	10.515 GMA	116.164	177.338	43.00
2	112.086 AAc	108.717	165.970	148.30
3	63.245 HEMA	108.717	165.970	118.10
4	20.832 AN	116.164	177.338	43.00

M = monomer. HPC = 1 g; [AAm] = 1.406 × 10^{-2} mol; [BPO] = 8.25 × 10^{-4} mol; solvent system = 5.00 mL acetone + 10.00 mL water; reaction time = 2.5 h; reaction temperature = 100°C.

TABLE V
Swelling Behavior of Crosslinked HPC-*g*-poly(AAm-*co*-CM)

No.	[M] × 10^2 (mol/L)	[GA] × 10^2 (mol/L)	$P_{add\text{-}on}$	P_s	$P_{s(h)}$
1	10.515 GMA	116.164	43.00	168.40	170.00
2	112.086 AAc	108.717	148.30	183.60	803.00
3	63.245 HEMA	108.717	118.10	180.00	324.00
4	20.832 AN	116.164	43.00	157.40	235.00

M = monomer. HPC = 1 g; [AAm] = 1.406 × 10^{-2} mol; [BPO] = 8.25 × 10^{-4} mol; solvent system = 5.00 mL acetone + 10.00 mL water; reaction time = 2.5 h; reaction temperature = 100°C; swelling time = 24 h; hydrolysis time = 48.00 h in 0.5*N* NaOH.

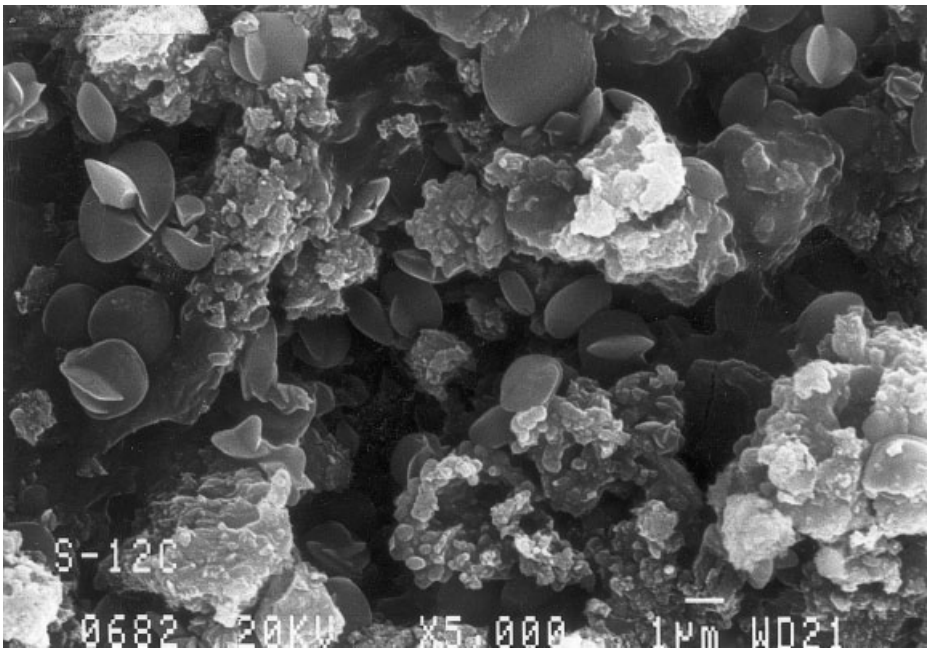

Figure 5 SEM of HPC-*g*-poly(AAm) (magnification = 5000×).

comonomer networks (GMA = 43.0, AAc = 148.3, HEMA = 118.1, and AN = 43.0) are given in Table III. These results were a reflection of the monomer concentrations used in the crosslinking reactions; thus, lower values of $P_{\text{add-on}}$ in the cases of GMA and AN were a reflection of concentrations of the comonomers, as these were added in lower amounts than the other two.

Characterization of cellulose and its graft copolymers

Swelling behavior of HPC and its graft copolymers

Swelling studies of crosslinked HPC-*g*-poly(AAm) and HPC-*g*-poly(AAm-*co*-CM) were carried out in water at room temperature. Swelling or liquid uptake depended on the structure of the polymer matrix and

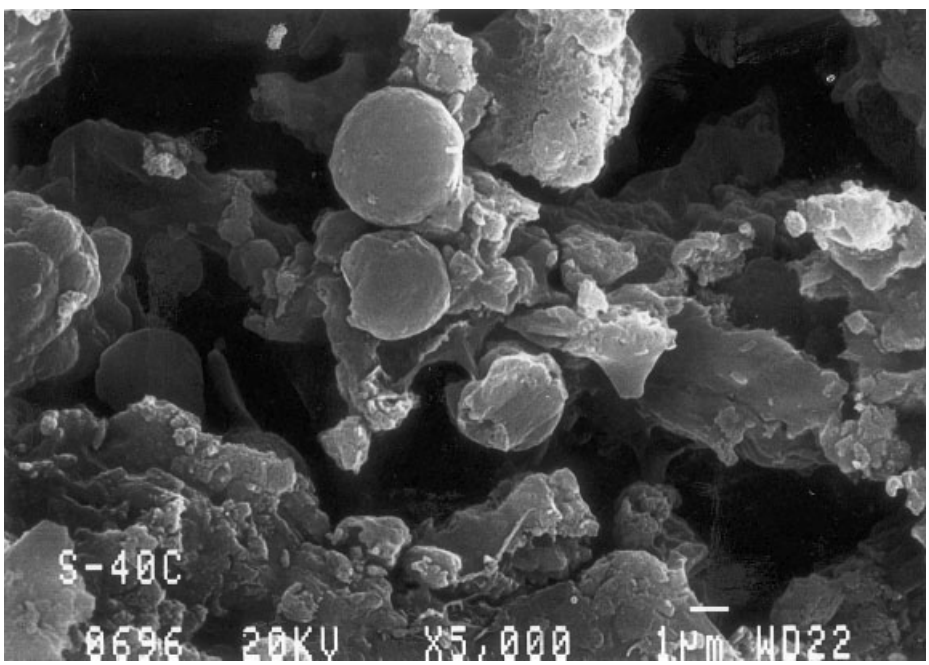

Figure 6 SEM of HPC-*g*-poly(AAm-*co*-HEMA) (magnification = 5000×).

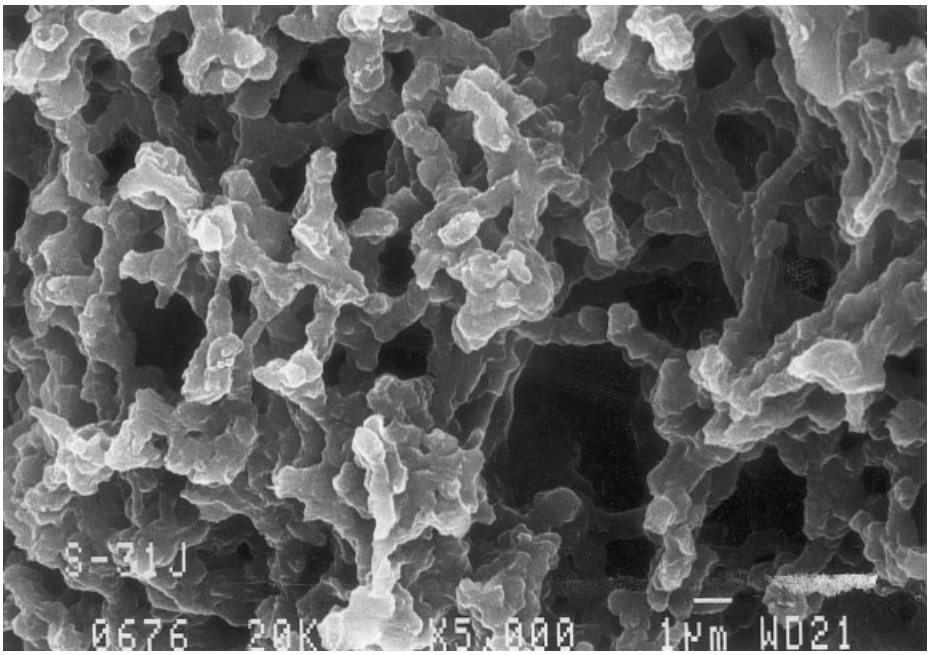

Figure 7 SEM of HPC-*cl*-poly(AAm-*co*-HEMA) (magnification = 5000×).

the extent of crosslinking, and tailored combinations of hydrophilic and hydrophobic moieties on the graft copolymers should have also affected them. Hydrophilic parts tend to interact with water to the maximum. Because AAm is a hydrophilic monomer, it should have increased the water retention characteristics of the graft copolymer. All four samples of HPC-*cl*-poly(AAm) synthesized at different crosslinker concentrations (32.12×10^{-2} to 177.77×10^{-2} mol/L) were subjected to swelling studies. The corresponding P_s values were 465.00, 625.00, 238.00, and 228.00, respectively (Table IV). Lower grafting levels and lower crosslinker concentrations resulted in more water retention than slightly higher levels. A high degree of crosslinking resulted in a closer binding of chains and created voids among the backbone chains. Crosslinked HPC-*cl*-poly(AAm-*co*-CM), synthesized at those concentrations of comonomers used for the crosslinking of cell-*g*-poly(AAm-*co*-CM), were subjected to swelling studies. The following P_s values of the crosslinked copolymers were observed: GMA = 168.40, AAc = 183.6, HEMA = 180.0, and AN = 157.00 (Table V).

All of the crosslinked graft copolymers of HPC-*cl*-poly(AAm) and HPC-*g*-poly(AAm-*co*-CM) were subjected to basic hydrolysis by immersion in 0.5*M* NaOH

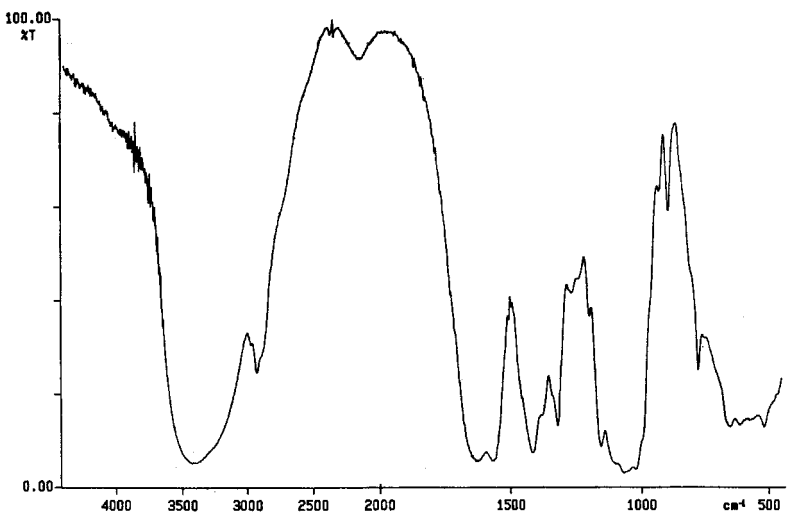

Figure 8 FTIR spectrum of HPC.

TABLE VI
Analysis of the FTIR Spectra of HPC and Its Graft Copolymers

HPC C—O—C stretching (cm^{-1})	% Absorbance (A)	AAm C═O stretching (cm^{-1})	% Absorbance (B)	C═O or CN stretching (CM; cm^{-1})	% Absorbance (C)	$P_{add\text{-}on}$ (gravimetric)	Monomer absorbance ratio		
							(B.71.08)/(B.71.08 + A.205)	(C.CM)/(C.CM + A.71.08)	(C/B) × (M/71.08)
1068.9	96.84	—	—	—	—	—	—	—	—
1065.8	76.90	1637.0	84.18	—		18.00	0.2949		—
1063.8	85.40	1654.5	92.50	—	—	47.40	0.2927	—	—
1060.7	88.43	1660.0	68.25	1732.9[a]	75.87	18.00	0.2277	0.6895	2.22
1069.0	70.37	1667.7	86.60	1737.0[a]	75.72	48.20	0.3198	0.6359	1.75
1062.4	78.44	1638.0	88.05	1730.0[b]	72.00	15.00	0.3001	0.4532	0.83
1062.5	88.70	1654.5	95.97	1725.0[b]	87.15	41.20	0.2925	0.4793	0.92
1064.5	71.90	1654.2	81.86	1725.0[c]	60.00	24.60	0.3026	0.5730	1.34
1062.6	82.21	1654.2	89.27	1712.5[c]	82.00	37.30	0.2932	0.6271	1.68
1065.7	60.70	1654.3	78.07	2250.0[d]	3.50	34.00	0.3295	0.0323	0.033
1067.5	36.56	1670.6	77.27	2225.7[d]	42.5	39.00	0.4488	0.2908	0.41
1035.1[e]	92.52	1664.0	78.38	—	—	0.00	0.2445	—	—
1035.2[e]	80.30	1664.1	80.17	—	—	0.00	0.2761	—	—
1070.7[e]	85.72	1664.2	95.59	1719.5[a]	89.04	43.00	0.2988	0.6504	1.88
1020.7[e]	82.66	1655.8	91.42	1720.0[b]	90.95	148.3	0.2970	0.5021	1.01
1074.2[e]	92.80	1670.3	96.10	1719.1[c]	96.84	118.8	0.2835	0.6485	1.84
1068.2[e]	89.84	1669.9	93.69	2241.8[d]	15.67	43.00	0.2861	0.1108	0.124
1062.7[f]	96.84	1654.4	90.21	—		0.00	0.2625	—	—
1065.9[f]	96.50	1670.1	95.22	—		0.00	0.2549	—	—
1065.4	87.34	1669.5	96.84	1725.0[a]	90.72	43.00	0.2976	0.6517	1.87
1076.5	82.38	1655.7	94.44	1719.5[c]	91.45	118.8	0.3046	0.6393	1.77
1062.8[f]	96.24	1654.4	96.83	2245.8[d]	18.25	43.00	0.2777	0.1223	0.14

A = % absorbance of C—O—C stretching; B = % absorbance of C═O stretching of AAm; C = % absorbance of C═O of GMA, HEMA, and C≡N stretching of AN; M = monomer.

[a] GMA.
[b] AAc.
[c] HEMA.
[d] AN.
[e] Crosslinked sample.
[f] Hydrolyzed sample.

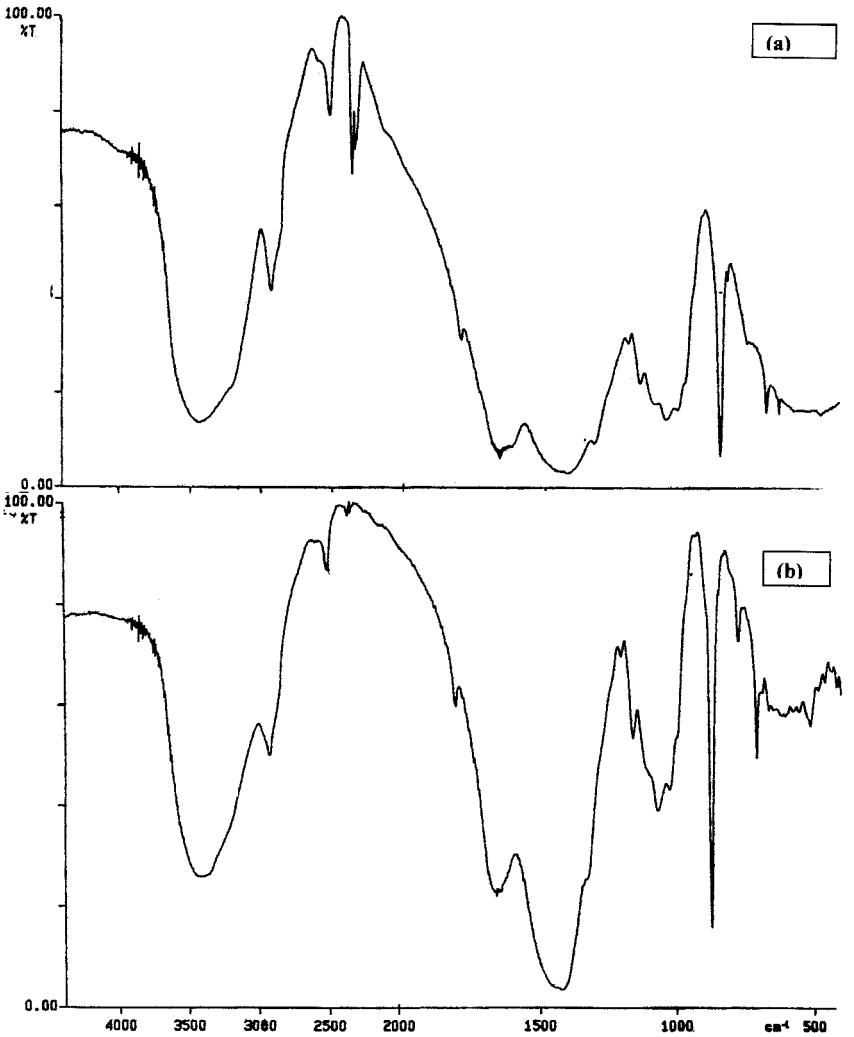

Figure 9 FTIR spectra of (a) HPC-*g*-poly(AAm) and (b) HPC-*g*-poly(AAm-*co*-AN).

for 48 h. As shown in Tables IV and V, it became clear that the percentage swelling of the hydrolyzed crosslinked samples [$P_{s(h)}$] was more than that for unhydrolyzed samples. The results were along expected lines, as hydrolysis results in the postfunctionalization of groups such as amide and CN lead to better water-interacting groups and may also lead to the rupture of some crosslinks to create bigger voids in the network structure. Hence, these changes, overall, manifested into improved water uptake by the networks.

SEM of HPC and its graft copolymers

Scanning electron micrographs of HPC, its different graft copolymers, and the networks, recorded at various resolutions, are presented in Figures 5–8. SEM of HPC-*g*-poly(AAm) (Fig. 5) provided evidence that grafting occurred. In the graft copolymers, poly(AAm) was visible in the form of globules and as a coating on the backbone in the SEM of HPC-*g*-poly(AAm). The formation of these globules was attributed to the coiling of graft chains as a result of the interplay of the lyophobic and lyophilic natures of the reaction medium with the graft chains and monomer molecules. At a higher density of aggregation of such granules, they may coalesce to appear as a coating. Somewhat similar structural aspects were observed in the SEM of HPC-*g*-poly(AAm-*co*-HEMA) with some low-density crosslinks (Fig. 6). The networks of HPC-*g*-poly(AAm-*co*-HEMA) synthesized in the presence of the crosslinker assumed honeycomb- or foam-like structures (Fig. 7). Active methylene groups possessed by the crosslinker may have provided additional active sites for grafting, and highly interwoven grafted chains under such conditions are expected to result in a compartmentalized honeycomb-like structure.

FTIR study of HPC and its graft copolymers

HPC showed prominent bands at 3428.6 cm^{-1} (OH stretching), 2928.2 cm^{-1} (C—H stretching), 1069.9 cm^{-1} (C—O—C stretching), and 897.0 cm^{-1} (C—C

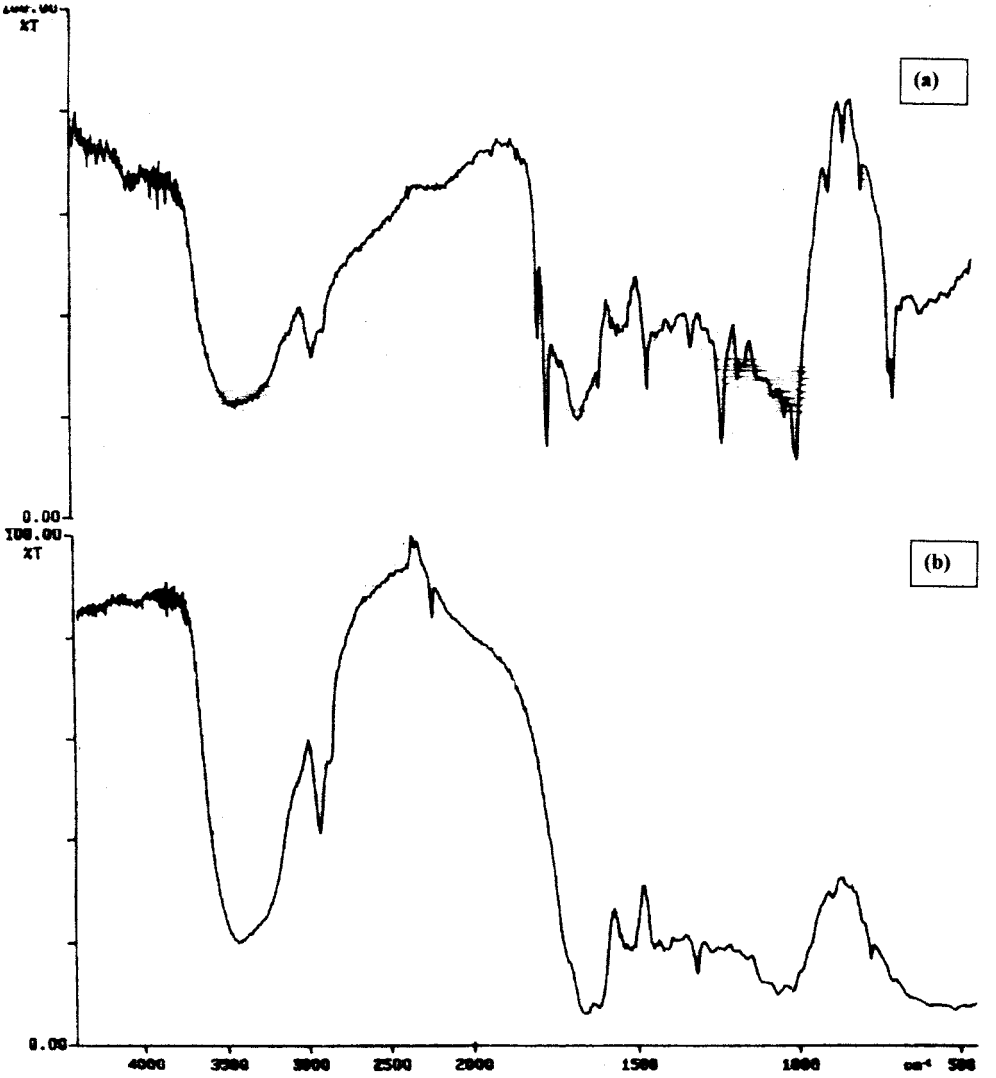

Figure 10 FTIR spectra of (a) crosslinked HPC-*g*-poly(AAm) and (b) crosslinked HPC-*g*-poly(AAm-*co*-AN).

stretching; Fig. 8). The sharp absorption bands due to —OH stretching indicated that cellulose lost association on functionalization. IR bands due to characteristic functions incorporated onto HPC-*g*-poly(AAm) evident at 1654.5 cm^{-1} in the HPC-*g*-poly(AAm), apart from the previously listed bands, (Table VI) provided evidence that poly(AAm) was incorporated onto the cellulose backbone [Fig. 9(a)]. In the FTIR spectra of the graft copolymers of binary mixtures of the monomers, peaks characteristic to the constituent comonomer appeared prominently, apart from the distinguishing peaks of HPC and poly(AAm). Against the most common peak around 1654 cm^{-1} due to >C═O absorption peak of poly(AAm), a shift in this peak was observed to 1670.6 cm^{-1} with 77.27% absorbance as against 42.5% absorbance by the —C≡N. This shift was caused by the inductive effect contribution caused by the cografting of poly(AN) along with poly(AAm) [Fig. 9(b) and Table VI]. A similar shift was observed in the case of the cografting of poly(AAc) and poly(GMA) (Table VI). The FTIR spectra of crosslinked HPC-*cl*-poly(AAm) and HPC-*cl*-poly(AAm-*co*-AN) are shown in Figure 10(a,b). The incorporation of the monomer in the crosslinked network was revealed by the perusal of the appearance of characteristic peaks of different constituents of these networks, and the shift in absorbance of >C═O was also observed in this case.

The ratio of molar absorbances in the region (1654.5 cm^{-1}/1068 cm^{-1}) of the stretching frequency of the >C═O group of amide to the stretching frequency of the cyclic ether of the HEC backbone increased with increasing percentage grafting ($P_{add\text{-}on}$; Table VI). In the FTIR spectra of the graft copolymers of AAm with the comonomers, the ratio of molar absorbances, of the characteristic absorption of comonomer to AAm, was nearly constant. Thus, the incorporation of monomers in the graft copolymers was nearly independent of the varia-

tion in the feed concentration of any of these comonomers at the constant feed concentration of AAm.

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