Thermal Behavior of Some Homogeneously Polymethyl Methacrylate (PMMA)-Grafted High α-Cellulose Products

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ABSTRACT: The graft copolymerization of methyl methacrylate (MMA) onto high α-cellulose was carried out homogeneously in an *N,N*-dimethyl acetamide/lithium chloride solvent system by using benzoyl peroxide as radical initiator. The rate of grafting was evaluated as a function of concentrations of initiator and monomer, reaction time, and temperature. The grafted products were characterized with the help of infrared spectroscopy, whereas the thermal decomposition of optimum PMMA-grafted high α-cellulose was studied using TGA, DTG, and DTA techniques at two heating rates, 10 and 20°C/min, in nitrogen atmosphere in the range of room temperature to 650°C. Three major decomposition steps were identified and the relative thermal stabilities of the PMMA-grafted high α-cellulose products were assessed. The kinetic parameters for the three decomposition steps were estimated with the help of two well-known methods. The thermal stability of the grafted products decreased with the increase of graft yield (GY). Crystallinity or peak intensity of wide-angle X-ray diffraction patterns decreased with the increase of GY. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 3471–3478, 2004

Key words: graft copolymers; degradation; thermogravimetric analysis (TGA); X-ray diffraction (XRD); thermal properties

INTRODUCTION

Homogeneous graft copolymerization of methyl methacrylate (MMA) onto high α-cellulose was carried out under various conditions to synthesize grafted products in the *N,N*-dimethyl acetamide/lithium chloride (DMAc/LiCl) solvent system using benzoyl peroxide (BPO) as radical initiator. In this reaction, graft copolymer and attendant homopolymer were synthesized simultaneously.[1,2] Many workers investigated the thermal decomposition behavior of the grafted cellulose products. However, grafting reactions were carried out in heterogeneous[3–6] and homogeneous reaction conditions and all the reported homogeneous reactions were investigated in solvent systems like dimethyl sulfoxide and paraformaldehyde (DMSO/PF).[7,8,11,12] It was reported that crystallinity, crystal size, and degree of polymerization of cellulose greatly affect the pyrolysis kinetics of high α-cellulose,[9,10,13] attributed to the synthetic polymer chains hindering the crystallization of cellulose chain. The thermal behavior of homogeneously grafted high α-cellulose products in the DMSO/PF solvent system were studied, although the thermal degradation behavior of homogeneously grafted high α-cellulose products in the DMAc/LiCl solvent system has not been reported so far.

The present work was therefore undertaken to study the thermal behavior of homogeneously MMA-grafted high α-cellulose in a DMAc/LiCl solvent system. In our experiments, cellulose samples were grafted with PMMA under six different reaction temperatures ranging from 30 to 80°C, keeping all other reaction conditions constant.

EXPERIMENTAL

Materials

High α-cellulose pulp extracted from *Hibiscus cannabinus,* containing 94.40% α-cellulose and 0.04% ash, was used for this study.[14] The pulp was dried to less than 5% moisture before use. DMAc and LiCl were analytical-grade chemicals from BDH, India and were used as received. MMA was purified by passing it through a column of activated basic alumina to remove any inhibitor.[15] BPO, hydroquinone, and acetone were also analytical-grade chemicals from BDH, India and were used without further purification.

Methods

Grafting

The high α-cellulose was dissolved in the DMAc/LiCl solvent system.[16] All polymerization reactions were

TABLE I
Characteristics of the PMMA Grafted High α-Cellulose Products[a]

Sample code	Total conversion of monomer to polymer, TC (%)	Graft yield, GY (%)	Grafting efficiency, GE (%)	M_v ($\times 10^{-5}$)	Number of graft
F1	5.49	36.33	54.5	2.9	0.24
F2	10.36	40.67	32.1	4.1	0.19
F3	27.61	55	15.88	4.8	0.21
F4	20.31	31	12.23	5.5	0.11
F5	16.62	20.67	10.00	5.7	0.07
F6	13.12	18.00	11.02	6.02	0.06

[a] Conditions of grafting: Grafting time, 5 h; cellulose, 2% (1.85 mmol); MMA, 50 mmol; BPO, 1.24 mmol; reaction temperature ranges from 30 to 80°C for F1–F6 samples, respectively.

carried out in a nitrogen atmosphere.[9,10] A three-neck 250-mL round-bottom flask, fitted with stirrer in a temperature-controlled water bath, was used for the reactions. To the reaction flask containing 50 mL (6.17 mmol) cellulose solution (2% of 61.7 mmol) and 15 mL of BPO of varying concentrations from 1 to 4%, (0.62–2.48 mmol) were added. Purified nitrogen was bubbled through the reaction mixture for 30 min at 20°C. Varying amounts of monomer in the range of 2.2–5.3 mL (20–50 mmol) were added and the polymerization reactions were carried out at different temperatures between 30 and 80°C for 1–5 h. The reaction was terminated by the addition of hydroquinone.[17] The polymerization mixture was poured into cold distilled water with vigorous stirring. The crude grafted products were Soxhlet extracted with acetone for 24 h to remove any adherent homopolymer. The extracted cellulose-grafted products were then dried to a constant weight and kept in a desiccator over P_2O_5.

The graft yield (GY), total conversion of monomer to polymer (TC), grafting efficiency (GE), and number of graft per cellulose chain were calculated on the basis of oven-dried weight of the cellulose from the increase in weight after grafting by using the following relations.[18]

$$GY\ (\%) = \frac{C - A}{A} \times 100$$

$$TC\ (\%) = \frac{B - A}{D} \times 100$$

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

Number of grafts per cellulose chain

$$= \frac{\text{Molecular weight of cellulose}}{\text{Molecular weight of grafted PMMA}} \times \frac{GY}{100}$$

where A is the weight in grams of the original cellulose taken for the reaction; B is the weight in grams of

the grafted cellulose; C is the weight in grams of the grafted products after extraction; and D is the weight in grams of the monomer charged.

The molecular weight (M_v) of α-cellulose was calculated viscosimetrically by using Ubbelohde dilution viscometer (Cannon–Ubbelohde, State College, PA) at 30°C by measuring intrinsic viscosity $[\eta]$ (in $cm^3\ g^{-1}$) of cellulose solution as 19×10^4 by using the DMSO/PF solvent system.[19]

Cellulose grafted with PMMA was hydrolyzed with 72% H_2SO_4 to isolate PMMA.[17] The intrinsic viscosities $[\eta]$ (in $cm^3\ g^{-1}$) of isolated graft polymers were measured at 25°C, taking acetone as a solvent to estimate the viscosity-average molecular weight by using the following Mark–Houwink–Sakurada equation[17]:

$$[\eta]_{acetone} = 5.3 \times 10^{-3}/M^{0.73}$$

IR studies

IR spectra of grafted and ungrafted cellulose samples were recorded on a Perkin–Elmer spectrometer (Model 580 B, Perkin Elmer Cetus Instruments, Norwalk, CT) using the KBr disk technique, in the range 4000–400 cm^{-1}, with a resolution of 2 cm^{-1}, using five scans per sample.

Thermal analysis

Thermogravimetry (TG) and differential thermogravimetry (DTG) were carried out using a Shimazdu Model 30 thermal analyzer, (Shimadzu, Kyoto, Japan). The weight of the grafted products ranged from 10 to 15 mg. α-Alumina was used as a reference material and the temperature ranged from 30 to 650°C at heating rates of 10 and 20°C min^{-1} for all the products in nitrogen atmosphere.

X-ray diffraction analysis

X-ray diffraction data were collected using an X-ray diffractometer (Type JDX-11P3A, JEOL, Tokyo, Japan)
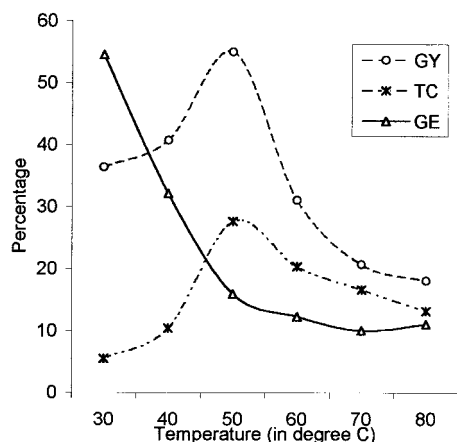
Figure 1 Effect of polymerization temperature on grafting of MMA with BPO. Grafting time, 5 h; cellulose, 2% (1.85 mmol); MMA, 50 mmol; BPO, 1.24 mmol.

with pulse-height analyzer and scintillation counter with scintillator NaI (TI) single crystal.

RESULTS AND DISCUSSION

A series of PMMA-grafted high α-cellulose products in DMAc/LiCl solvent system were prepared in fixed monomer and initiator concentrations and time of reaction in different reaction temperatures. The samples prepared at temperatures of 30, 40, 50, 60, 70, and 80°C were coded as F1, F2, F3, F4, F5, and F6, respectively. The characteristics of the products are listed in Table I. Figure 1 shows the effect of reaction temperature on graft copolymerization. The GY and TC were in-

creased with the increase of reaction temperature up to 50°C and then decreased gradually, whereas the GE decreased with the increase of temperature.

IR studies

Figure 2 shows the IR spectra of the ungrafted regenerated high α-cellulose [Fig. 2(a)] and PMMA-grafted high α-cellulose product [Fig. 2(b)]. The IR spectra of the true grafted PMMA [Fig. 2(b)] showed a characteristic band at 1740 cm^{-1}, which is peculiar to the carbonyl group.[20] The band at 3020 cm^{-1} indicated a methyl stretching vibration, which is further confirmed by the presence of bands at 1455 and 1390 cm^{-1} for methyl bending vibrations. The above bands were absent in the spectra of ungrafted regenerated high α-cellulose. The presence of these characteristic bands in the grafted cellulose indicated that MMA was co-polymerized in the cellulose backbone.

Thermogravimetric analysis

The thermogram curves of the different grafted products F1–F6 are shown in Figures 3(a)–(c) and 4(a)–(c) at two different heating rates, 10 and 20°C min^{-1}, respectively. The thermal analysis data at these two different heating rates are summarized in Tables II and III.

All the TG curves of the MMA-grafted cellulose samples are shown in Figures 3(a) and 4(a) for heating rates of 10 and 20°C min^{-1}, respectively. From the figures, it is evident that the thermal degradation of the samples involved three different steps in both of the heating rates.[21] In all the TG curves [Fig. 3(a)], except those for F3
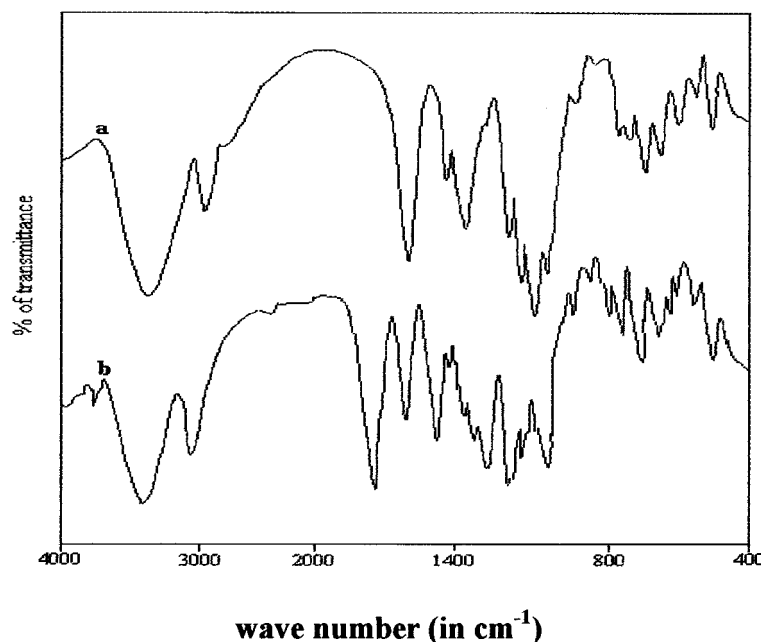

wave number (in cm^{-1})

Figure 2 IR spectra of (a) regenerated high α-cellulose; (b) PMMA grafted high α-cellulose.
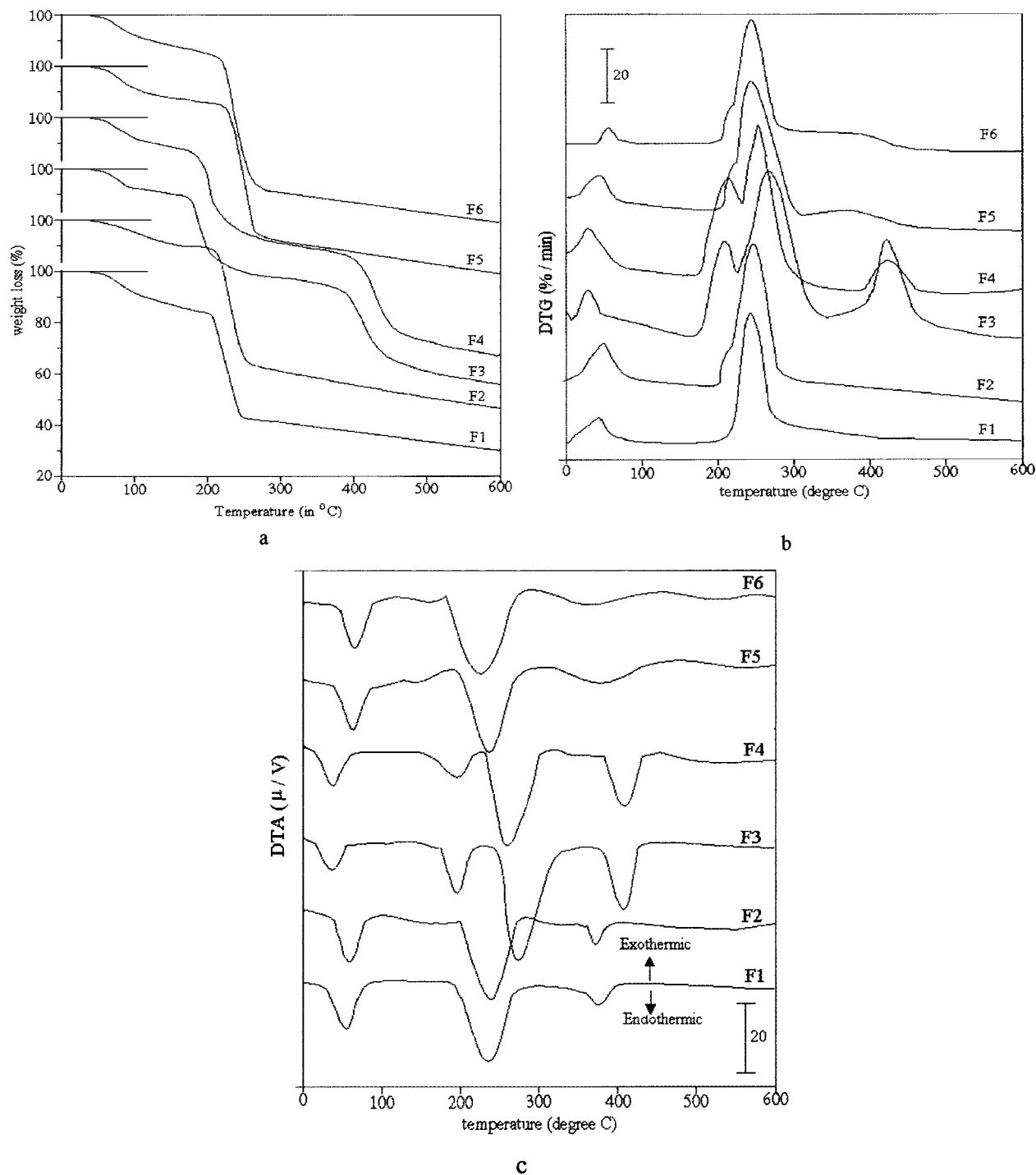
Figure 3 Thermograms of the PMMA-grafted high α-cellulose products in reaction temperatures from 30 to 80°C for samples F1–F6 at a heating rate 10°C min⁻¹. (a) TG curves; (b) derivative thermogravimetric (DTG) curves; and (c) differential thermal analysis (DTA) curves.

and F4, there is a decrease by maximum of 15% weight loss in the first stage at around 70–110°C. The second stage, which is the major thermal decomposition stage, where loss of maximum weight of the sample by 41% or less occurred at around 200–280°C and in the final stage at around 280–600°C, the samples lost a maximum of 30% of weight. In samples F3 and F4, however, the

thermal decomposition was found to proceed in four different stages. In all four stages, weight losses of 6.9, 39.6, 21.3, and 6.2% for F3 and 8.1, 36.9, 21.5, and 5.5% for F4 were observed in the initial, second, third, and fourth decomposition stages, respectively, at temperatures around 56–150, 150–250, 250–410, and 410–600°C. In the initial stage, evaporation of water at around 100°C
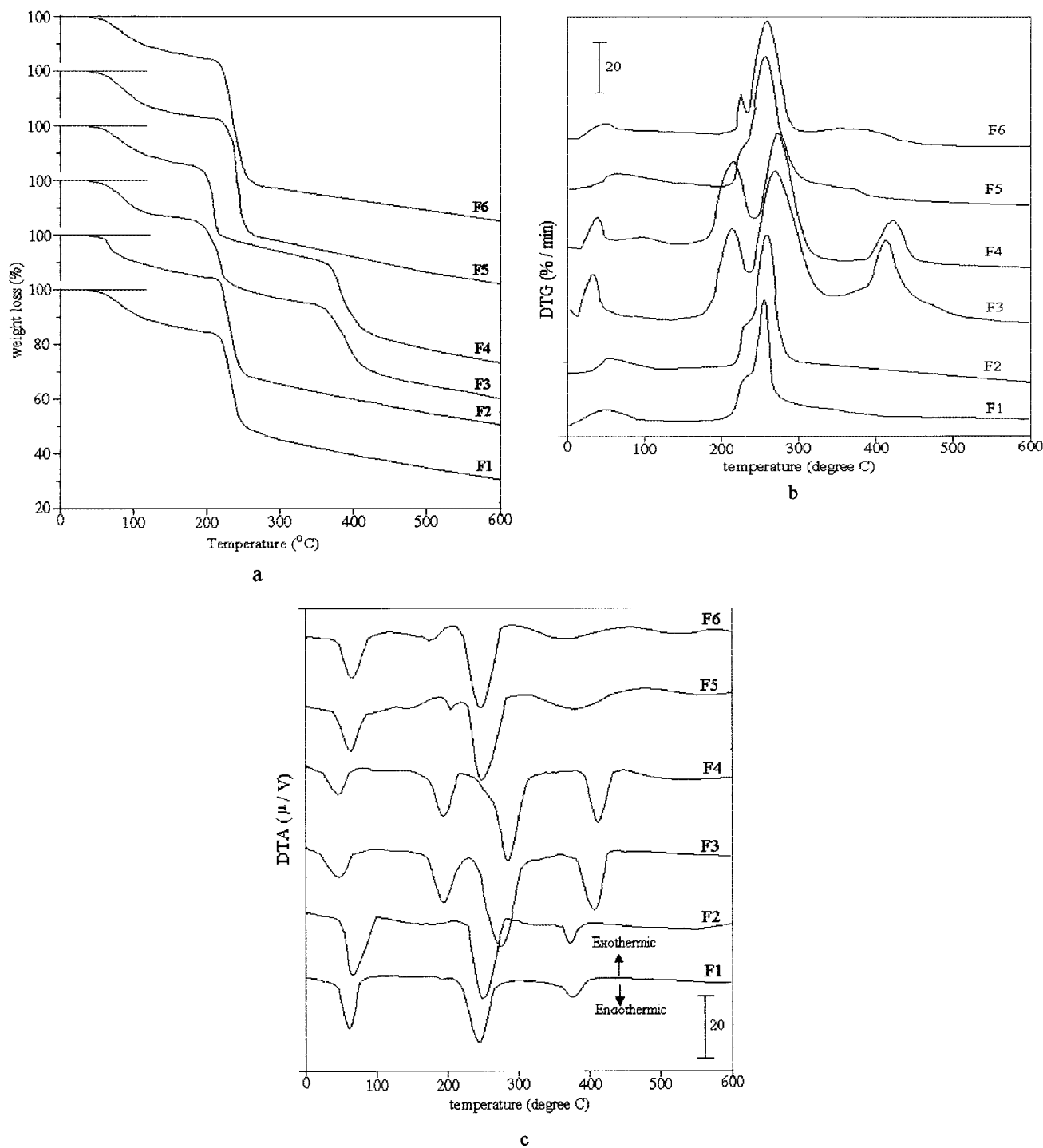
Figure 4 Thermograms of the PMMA-grafted high α-cellulose products in reaction temperatures from 30 to 80°C for samples F1–F6 at a heating rate 20°C min^{-1}. (a) TG curves; (b) derivative thermogravimetric (DTG) curves; and (c) differential thermal analysis (DTA) curves.

from the pairs of ungrafted hydroxyl groups took place. In the main degradation steps (i.e., second and third stages of active decomposition), the removal of CO, CO_2, hydrocarbons, and such was accomplished. The final process at around 400°C corresponded to the decomposition of PMMA fraction. The weight losses were found more at the second and third stages of active decompo-

sition than were found at the initial and final stages. A similar trend was also observed for the samples heated at 20°C min^{-1} [Fig 4(a)].

The DTG curves are shown in Figures 3(b) and 4(b) for heating rates 10 and 20°C min^{-1}, respectively. Figure 3(b) illustrates more clearly the differences in thermal decomposition behavior of the samples F1, F2,

TABLE II
Weight Loss Percentage of PMMA-Grafted High α-Cellulose Products[a]

Sample	10°C min⁻¹			20°C min⁻¹		
	I	II	III	I	II	III
F1	14.6 (40–220)	38.7 (220–280)	17 (280–600)	10.9 (40–225)	37.3 (225–290)	10.2 (290–600)
F2	13.4 (40–210)	36.9 (210–275)	16.3 (275–600)	10.5 (40–225)	38.4 (225–295)	11.2 (295–600)
F3[b]	6.9 (50–170)	39.6 (170–250)	21.3 (250–410)	7.4 (50–180)	37.8 (180–265)	19.5 (265–415)
F4[b]	8.1 (50–180)	36.9 (180–270)	21.5 (270–415)	9.4 (50–185)	38 (185–280)	18.5 (280–420)
F5	13.6 (50–210)	36.3 (210–270)	16.5 (270–600)	10 (40–210)	38 (210–275)	16 (275–600)
F6	10.6 (40–200)	39.4 (200–280)	16.5 (280–600)	9 (30–210)	38 (210–285)	16 (285–600)

[a] I, II, and III: Pre, second, and final stages; temperature range (°C) in parentheses.
[b] 4th stage of weight loss of these samples is not included in the table.

F5, and F6 with two peaks at around 80 and 250°C. However, samples F3 and F4 showed four peaks at around 60, 210, 280, and 400°C. The DTG peak temperatures are used as a measure of thermal stability.[11] The DTG peaks of the F3 and F4 samples showed the first two peaks at lower temperatures compared to that of the rest of the four samples, suggesting that F3 and F4 were least stable. However, the DTG peaks of F3 were found at the lowest temperature. With the increase of percentage of GY, the DTG peaks of PMMA-grafted products shifted to low temperatures, indicating that higher GY products are thermally less stable. However, two more prominent peaks at around 280 and 415°C were also observed, which might arise as a result of the decomposition of grafted MMA fraction, given that these samples contained high amounts of grafted PMMA (Table I). The DTG curve of samples at 20°C min⁻¹ heating rates [Fig 4(b)] also exhibited similar characteristic curves, although the peaks were observed at a slightly higher temperature.

Figures 3(c) and 4(c) show the differential thermal analysis (DTA) curves of the PMMA-grafted high α-cellulose samples. In the case of samples F1, F2, F5, and F6 two endothermic peaks were observed, whereas F3 and F4 were associated with four clear endothermic peaks. The DTA peaks [Fig. 3(c)] of samples F1, F2, F5, and F6 were observed at around 65–85

and 245–260°C and for F3 at 63, 207, 273, and 403°C. The peak temperature for sample F4 was found to increase slightly compared to that of F3. However, at heating rate 20°C min⁻¹, the peaks were observed at around 64–75 and 256–261°C for F1, F2, F5, and F6 and at 79–85, 215–230, 277–295, and 410–425°C for F3 and F4. In samples F3 and F4, the first two DTA peaks shifted to lower temperature, indicating that these are thermally less stable.

Careful study of Tables II and III shows that stability of the highest PMMA-grafted high α-cellulose samples are thermally least stable.

X-ray diffraction studies

Figure 5 indicates the X-ray diffraction patterns of grafted products and cellulose. The curves b, c, and d represent diffraction patterns of PMMA-grafted high α-cellulose samples F1, F3, and F6, respectively, whereas curve a is for regenerated high α-cellulose. The peak intensity of the samples decreased with the increase in percentage of GY, suggesting a decrease in crystallinity. Thermal stability of cellulose mainly depends on crystallinity.[10,13,22] The diffraction pattern of sample F3 [Fig. 5(c)] suggested it to be the least crystalline and as such it is thermally least stable.

TABLE III
Active Decomposition Temperatures (°C) of PMMA-Grafted High α-Cellulose Products[a]

Sample	10°C min⁻¹				20°C min⁻¹			
	I	II	III	IV	I	II	III	IV
F1	65 (endo)	238 (endo)	—	—	68 (endo)	256 (endo)	—	—
F2	70 (endo)	244 (endo)	—	—	75 (endo)	261 (endo)	—	—
F3	56 (endo)	205 (endo)	273 (endo)	407 (endo)	60 (endo)	210 (endo)	275 (endo)	410 (endo)
F4	60 (endo)	207 (endo)	279 (endo)	415 (endo)	62 (endo)	215 (endo)	283 (endo)	415 (endo)
F5	63 (endo)	240 (endo)	—	—	70 (endo)	260 (endo)	—	—
F6	60 (endo)	234 (endo)	—	—	64 (endo)	253 (endo)	—	—

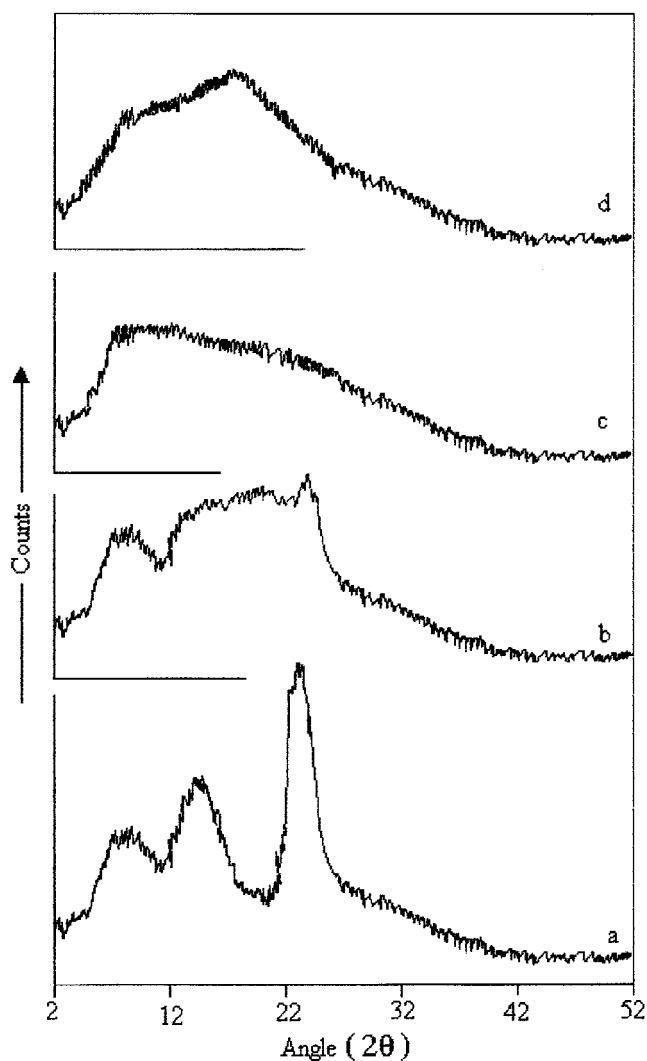[a] I, II, and III: Pre, second, and final stages.

Figure 5 X-ray diffraction pattern of the (a) ungrafted cellulose; MMA grafted high α-cellulose products (b) F1, (c) F3, and (d) F6.

Kinetic studies

A number of workers[23–28] have analyzed the retrieval of kinetic parameters from weight loss versus temperature data by using different methods.[29–32] In the present work two well-known methods—Coats and Redfern[30] and Horowitz and Metzger.[31]—and were used for retrieving kinetic parameters from dynamic thermogravimetry.

Integral methods of Coats and Redfern

For a first-order reaction process, the general correlation equation used in the Coats–Redfern method is

$$\log_{10}[1 - (1 - \alpha)^{1-n}/T^2(1 - n)]$$
$$= \log_{10}[AR\alpha E_a(1 - 2RT/E)] - E_a/2.3RT$$

where α is the fraction decomposed at temperature T; n is the order of the reaction; A is the frequency factor (in S^{-1}); a is the heating rate (in K min^{-1}); R is the gas constant (in kcal mol^{-1} K^{-1}); T is the temperature (in K), and E_a is the activation energy (in kcal mol^{-1}). A computer program in FORTRAN 77 was used for the least-square analysis with a Gauss–Jordan subroutine and applied to evaluate n and ΔE_a. The data were found to fit well for a first-order reaction and are given in Table IV.

The activation energies for the weight loss degradation stage of all the PMMA-grafted high α-cellulose samples were found to increase with the increase of the GY. The grafted products F3 (55% GY) showed the highest activation energy among all the other products evaluated. The activation energies of sample F3, according to this method, were 28.66, 91.17, and 20.4 kcal mol^{-1} and 21.58, 102.2, and 17.19 kcal mol^{-1} for the heating rates 10 and 20°C/min^{-1}, respectively, at the first three stages of decomposition.

Approximation method of Horowitz and Metzger

For a first-order process, Horowitz and Metzger derived the following relation:

TABLE IV
Activation Energy (E_a) of the PMMA-Grafted Cellulose Samples[a]

Methods	C and R (E_a in kcal mol^{-1})						H and M (E_a in kcal mol^{-1})					
Heating rate	10°C min^{-1}			20°C min^{-1}			10°C min^{-1}			20°C min^{-1}		
Sample	I	II	III	I	II	III	I	II	III	I	II	III
F1	15.07	76.23	9.06	13.17	78.65	11.59	15.63	74.89	—	11.20	76.78	7.71
F2	20.06	84.39	19.53	14.47	98.45	13.17	22.37	83.41	—	12.81	95.54	8.21
F3	28.66	91.17	20.37	21.58	102.2	17.19	29.27	88.53	19.78	20.82	99.25	17.40
F4	27.22	72.87	10.34	12.73	82.51	9.68	20.28	68.94	10.26	10.55	76.36	7.63
F5	23.03	68.2	12.27	10.41	69.32	8.96	19.65	61.09	7.10	9.97	70.83	6.87
F6	16.59	64.46	17.93	9.51	51.94	5.33	17.72	58.86	6.65	8.37	43.26	6.84

[a] C and R: Coats and Redfern method; H and M: Horowitz and Metzger method; I, II, and III: Pre, second, and final stages.

$$\ln \ln[1/(1 - \beta)] = E\theta/RT^2m$$

where $\theta = T - T_m$, and T_m is the temperature at which maximum degradation rate is exhibited. Thus a plot of $\ln \ln[1/(1 - \beta)]$ against θ should give a straight line with a slope of E/RT_m^2. The activation energy is determined from the slope. By using this approximation, the activation energies of all the samples were calculated and are summarized in Table IV.

It was evident that the activation energy, calculated adopting Coats–Redfern method, was more or less higher than that obtained from the Horowitz–Metzger method. The values of activation energies of sample F3 were 29.27, 88.5, and 19.7 kcal mol^{-1} and 20.82, 99.3, and 17.40 kcal mol^{-1} at heating rates of 10 and 20°C min^{-1}, respectively. Here again a similar trend of increase in activation energies with the GY was observed.

CONCLUSIONS

From the above study, it may be concluded that the thermal stability of PMMA-grafted high α-cellulose in a DMAc/LiCl solvent system products decreases as the MMA-grafted yield percentage increases as the crystallinity of the cellulose is reduced on increase in the GY. The reduction in crystallinity of cellulose might be attributable to the homogeneous dissolution of cellulose in appropriate solvent and subsequent graft copolymerzation.

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