Mechanical and Thermal Behavior of Cotton Cellulose Graft-Copolymerized Using Hydroxyethyl Methacrylate in Presence of Triethylene Glycol Dimethacrylate

S. R. SHUKLA* and A. R. ATHALYE

Department of Chemical Technology, University of Bombay, Matunga, Bombay 400 019, India

SYNOPSIS

UV-radiation-induced graft-copolymerization of cotton cellulose was carried out with 2-hydroxyethyl methacrylate (HEMA) in the presence of small amounts of triethylene glycol dimethacrylate (TEGDMA) using benzoin ethyl ether (BEE), uranyl nitrate (UN), and ceric ammonium nitrate (CAN) as photoinitiators. The presence of very small amounts of TEGDMA in the HEMA grafting bath led to great enhancement in the graft add-on as compared to that obtained on the sodium hydroxide-preswollen substrate. With increase in the graft add-on, the breaking load of cotton decreased, whereas its thermal stability improved. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

The chemical modification of cotton cellulose via a graft-copolymerization reaction using vinyl monomers has been investigated extensively.[1-3] The graft-copolymerization reaction causes significant changes in the physical and mechanical properties of the backbone polymer. The UV-radiations have been used for graft-copolymerization of cellulosic materials. As UV-radiation is less energetic than are radiation and chemical initiation, it cannot dissociate the strong bonds in the backbone polymer to initiate the free radical formation. It is therefore essential to use the UV sensitizers or photoinitiators of different types[4-7] for the UV-radiation-induced grafting. The benzoin ethers[8] also have been used as photoinitiators for the graft-copolymerization of cellulosic substrates. As the rate of diffusion of a monomer inside the substrate is the governing factor for the grafting reaction, various solvents have been shown to positively enhance the graft add-on.[9,10]

The graft copolymerization of 2-hydroxyethyl methacrylate (HEMA) onto cotton cellulose has been studied using different photoinitiators.[11] We have reported the UV-radiation-induced graft-copolymerization of HEMA onto unswollen and preswollen cotton cellulose using uranyl nitrate, ceric ammonium nitrate, and benzoin ethyl ether as the photoinitiators.[12,13] Davis and Garnett[14] showed the synergistic effect of the addition of various bifunctional monomers during the grafting of usual monofunctional monomers onto cotton.

Natural fibers like cotton degrade on heating and therefore imparting thermal stability to the fiber is highly advantageous. Together, differential thermal analysis and thermogravimetric analysis provide a method for determination of thermal stability of the polymer as a function of time and temperature.[15] Another important characteristic for the use of a textile fiber is the breaking load, a mechanical property dependent on the modification of internal fiber structure that has been frequently reported.[16]

In the present communication, results on graft-copolymerization of cotton cellulose with HEMA containing a small amount of TEGDMA using three different photoinitiators have been reported, indicating the role of a bifunctional monomer. The grafted samples were analyzed for their thermal and mechanical behavior and explanations have been given.

* To whom correspondence should be addressed.

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EXPERIMENTAL

Materials

Substrates

The scoured and bleached 30 s count cotton yarn was used as the cellulose sample. Preswelling of substrate was carried out using 24% (w/w) sodium hydroxide at 20°C for 1 h, followed by thorough washing with water and air-drying.

Chemicals

2-Hydroxyethyl methacrylate (HEMA) supplied by Aldrich Chemical Co. and triethylene glycol dimethacrylate (TEGDMA) supplied by Fluka were used without further purification. Two inorganic photoinitiators, namely, uranyl nitrate (UN) and ceric ammonium nitrate (CAN) and one organic photoinitiator, benzoin ethyl ether (BEE), were used for graft-copolymerization. Methanol and sodium hydroxide of "chemically pure" grade were used.

Graft-copolymerization

The process of UV-radiation-induced graft-copolymerization of cotton with HEMA is similar to that reported earlier.[12] The photoinitiators UN and CAN were water-soluble, whereas BEE was used after dissolving it in a mixture 10 : 90/methanol : water. The parameters of (HEMA) grafting alone, viz., initiator and monomer concentrations, as well as the time and temperature of reactions were first optimized for each initiator.[12,13] Grafting of HEMA was also carried out onto sodium hydroxide-swollen substrate under these conditions. In the present work, the bifunctional monomer, TEGDMA, was added in different amounts to the grafting bath containing HEMA and an initiator under optimized conditions for both the unswollen and swollen substrates. The graft add-on and the graft yield were determined as reported earlier.[12]

Breaking Load

The control and grafted cotton samples of 1 cm length were tested for breaking load on an Instron tensile tester, which recorded load elongation curves. The full scale of the chart was adjusted for a load corresponding to 500 g.

Thermal Behavior

The differential thermal analysis (DTA) and the thermogravimetric analysis (TGA) were carried out in nitrogen atmosphere using Stanton Redcroft thermal analyzer STA 780. The cotton samples were cut to 1–2 mm length and 20 ± 5 mg was taken for each analysis. The analysis was carried out from room temperature (30°C) to 500°C at a heating rate of 100°C/min and with a chart speed of 200 mm/h.

RESULTS AND DISCUSSION

Optimization of HEMA Grafting Parameters

For optimizing the conditions of grafting, the concentration of each photoinitiator was first determined for maximum graft add-on by varying it between 0.1 and 4.0% (w/v). The time of reaction was then varied from 1 to 6 h and a period of 3 h was found to give maximum grafting. This was followed by optimizing the temperature of the reaction in the range of 30–60°C. Finally, the HEMA concentration was varied up to 6.0% (w/v). With the increase in HEMA concentration, the graft add-on increased, which, ultimately, leveled off. In these studies, UN appeared to be the most efficient photoinitiator, giving the highest graft add-on values as compared to those obtained by using CAN or BEE, at each concentration of HEMA. These optimized conditions are given in Table I.

The maximum graft yield was obtained at 2.0% (w/v) HEMA in the case of UN and CAN, whereas, in the case of BEE photoinitiator, it was at 4.0% (w/v) HEMA, suggesting, thereby, that the utilization of HEMA is better at these particular concentrations as compared to that at any other concentration of HEMA used. Beyond these concentrations of HEMA, although the graft add-on values increased further, there is correspondingly higher homopolymer formation also, which has the effect of lowering the graft yield.

Table I Optimized Conditions of HEMA Grafting onto Cotton

	Photoinitiator		
Grafting Parameter	UN	CAN	BEE
Initiator concentration (% [w/v])	0.20	0.25	0.30
Time (h)	3	3	3
Temperature (°C)	50	40	50
Monomer concentration (% [w/v])	2	2	4
Maximum graft yield (%)	18.61	14.53	8.85
Maximum graft add-on (%)	31.22	29.06	35.42

Table II Effect of Swelling on Grafting of HEMA onto Cotton Cellulose

HEMA Concentration, [% (w/v)]	Cotton Sample	Graft Add-on Without TEGDMA			Graft Add-on With TEGDMA		
		UN	CAN	BEE	UN	CAN	BEE
1.0	Unswollen	13.40	11.80	5.94	24.64	21.92	6.42
	NaOH-swollen	27.35	24.30	9.56	35.29	24.98	9.08
2.0	Unswollen	37.22	29.06	9.30	61.92	40.51	23.23
	NaOH-swollen	49.74	44.74	13.23	66.36	48.83	27.72
3.0	Unswollen	50.98	42.12	16.68	68.68	58.04	39.46
	NaOH-swollen	56.22	51.56	23.02	75.25	65.70	46.52
4.0	Unswollen	—	—	35.42	—	—	63.72
	NaOH-swollen	—	—	40.83	—	—	68.02

UN initiation: 0.20% (w/v) UN, 50°C, 3 h; CAN initiation: 0.25% (w/v) CAN, 40°C, 3 h; BEE initiation: 0.30% (w/v) BEE, 50°C, 3 h.

Effect of Preswelling

Since increase in HEMA concentration beyond a certain limit decreased the graft yield, preswollen substrate was used for graft-copolymerization using HEMA. Table II gives the results on grafting of HEMA onto sodium hydroxide-swollen cotton, and it can be seen that due to swelling the graft add-on

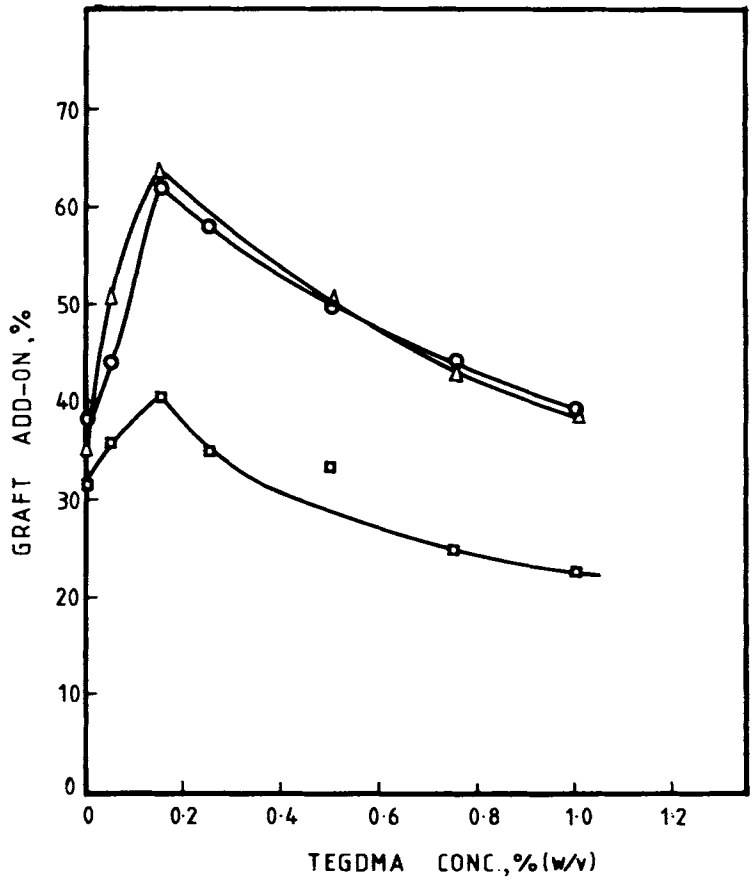

Figure 1 Effect of TEGDMA concentration on HEMA graft add-on: (○) UN photoinitiator; (□) CAN photoinitiator; (△) BEE photoinitiator.

values were higher at each concentration of HEMA used. This was attributed mainly to the higher accessibility and greater reactivity of the swollen substrate. However, the effect of swelling became less pronounced at higher concentrations of HEMA due to the easy availability of the monomer for graft-copolymerization reaction.

Effect of Bifunctional Monomer

Addition of a bifunctional monomer divinyl benzene has been reported to increase the styrene graft level.[17,18] With a view to enhance the (HEMA) graft add-on further, therefore, the bifunctional monomer TEGDMA was added in the HEMA grafting bath under the above-optimized conditions of time, temperature, and the photoinitiator concentrations.

The effect of adding TEGDMA in small amounts to the bath containing 2.0% (w/v) HEMA for UN and CAN and 4.0% (w/v) HEMA for BEE photoinitiation on the graft add-on is shown in Figure 1. It may be observed that, as the concentration of TEGDMA is increased up to only 0.15% (w/v), the graft add-on increased substantially. After this concentration of TEGDMA, however, the graft add-on decreased progressively. This was attributed to the fact that the bifunctional monomer, up to a certain concentration, forms cross-links between the grafted chains of HEMA onto cotton. With further increase in its concentration, however, the TEGDMA homopolymer formation predominates. Also, in the presence of TEGDMA, branching of the growing polyHEMA chains can occur, which takes place when one end of TEGDMA is attached to the growing chain, whereas the other end is unsaturated and free to initiate a new chain growth via scavenging reactions. The newly formed polyHEMA chain may eventually terminate by reacting with the neighboring polyHEMA chain or cross-link with an immobilized TEGDMA radical. The grafting, thus, enhances mainly through the branching of the grafted chains. It is worth noting here that TEGDMA alone could not produce any grafting onto cotton up to a concentration of 1.0% (w/v) and it

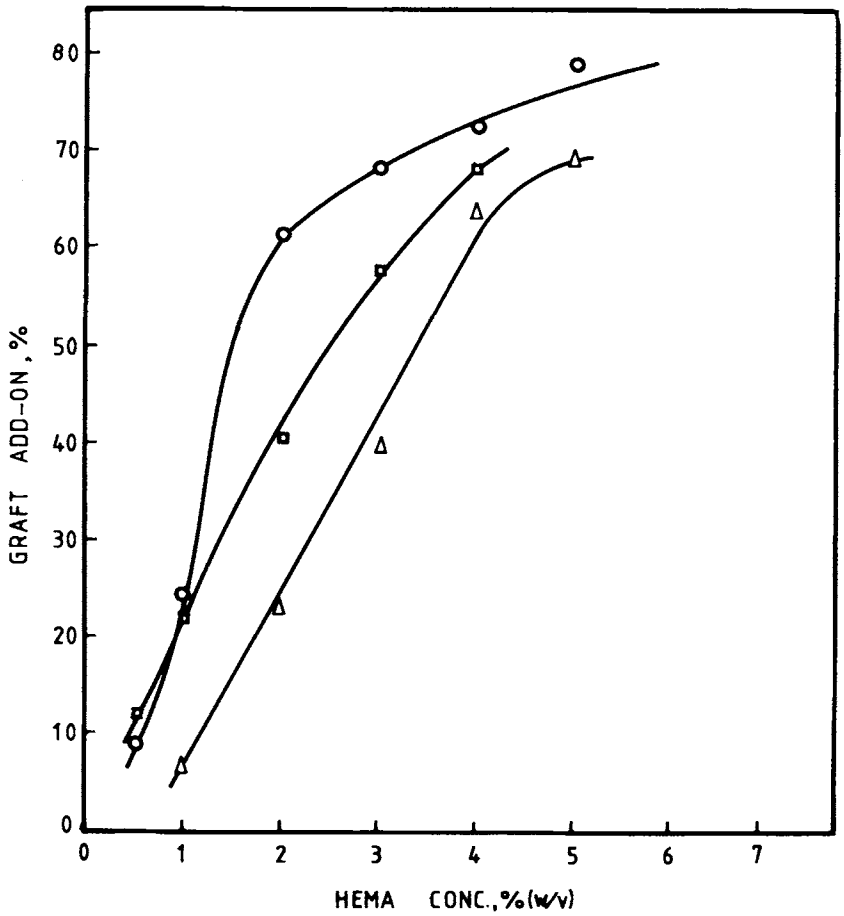

Figure 2 Effect of HEMA concentration, in presence of TEGDMA, on graft add-on: (○) UN photoinitiator; (□) CAN photoinitiator; (△) BEE photoinitiator.

formed only homopolymer in the bath. This may be attributed to its bulky nature, which hinders its penetration inside the substrate.

When the concentration of HEMA in the grafting bath was varied from 1.0% (w/v) to 5.0% (w/v), keeping TEGDMA concentration at 0.15% (w/v), the graft add-on values increased with increasing concentration of HEMA, as shown in Figure 2.

The infrared spectra of the grafted samples are shown in Figure 3 along with those of the ungrafted cotton. An additional peak was observed at 1700 cm^{-1} in the samples grafted with HEMA alone as well as in the presence of TEGDMA, confirming the introduction of ester carbonyl groups in the fiber structure. Since both the monomers have identical functional groups, all the samples showed similar IR spectra.

Effect on Breaking Load

Table III shows the results on breaking load of the cotton yarn grafted with HEMA in the presence of TEGDMA. These results indicate that the breaking load of cotton decreased steadily with the increasing amount of graft add-on. At a maximum graft add-on of 63.72%, for the unswollen substrate using BEE photoinitiator, the breaking load decreased by 22.84%. Initial experiments on irradiating the ungrafted substrate for 3 h with UV-radiation without photoinitiator did not show any loss in the breaking load, making it clear that it is the graft add-on that has the detrimental effect on the tensile behavior of the substrate. The negative influence of the HEMA graft add-on on tensile strength of cotton cellulose may be attributed to the grafted side chains that act as a dead load on the backbone cellulosic chains as far as the tensile properties are concerned. The strength per unit fiber thickness, thus, decreases with the increasing graft add-on.

In the case of swollen cotton under unstretched conditions, there is a decrease in the orientation of cellulosic chain molecules that loosens the fiber structure to some extent, thereby decreasing the tensile strength. As the swelling of substrate enhanced the graft add-on, further decrease in the tensile strength was observed, corresponding only to the level of graft add-on.

Effect on Thermal Properties

The differential thermal analysis (DTA) curves of the ungrafted and HEMA-grafted cotton cellulose in the presence of TEGDMA are shown in Figure 4. In the DTA curve of the control cotton, an en-

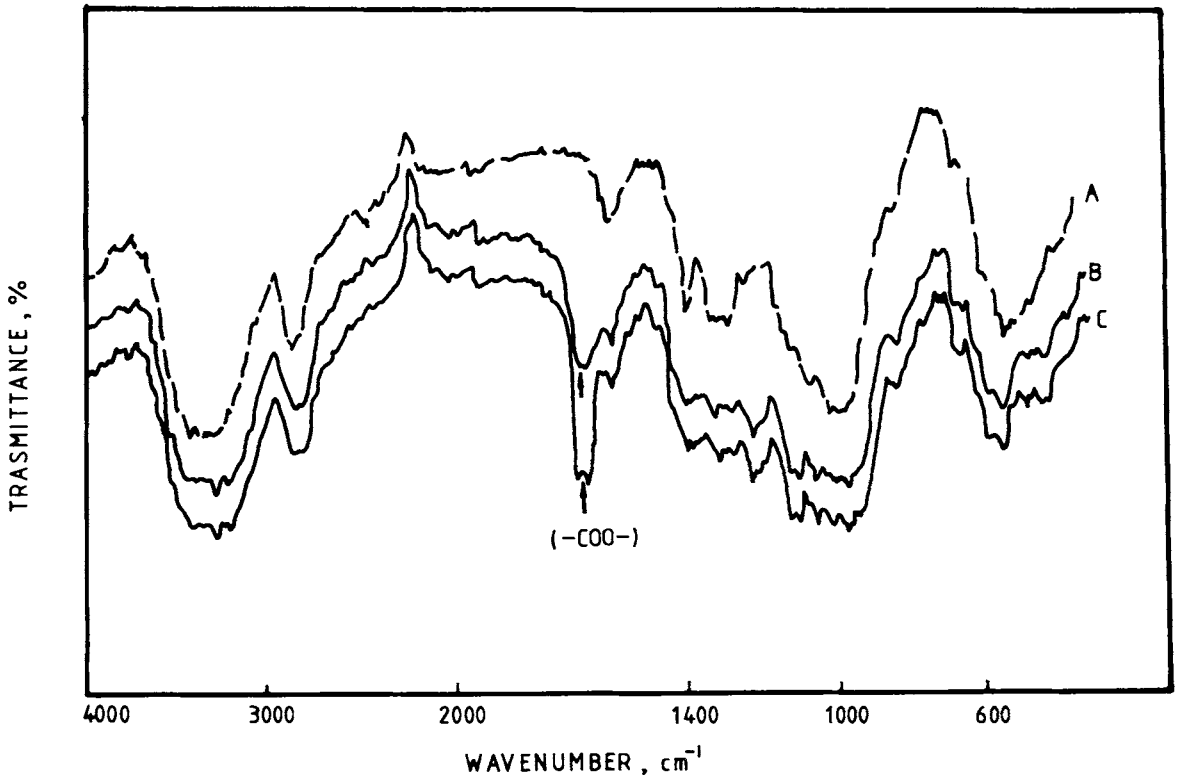

Figure 3 Infrared spectra of cotton samples: (A) ungrafted cotton; (B) HEMA-grafted cotton; (C) HEMA–TEGDMA-grafted cotton.

Table III Effect of Grafting of HEMA in Presence of TEGDMA on Breaking Load of Cotton Using BEE Photoinitiator

HEMA Concentration (% [w/v])	Cotton Sample	Graft Add-on (%)	Breaking Load (%)	Loss in Breaking Load (%)
0.0	Unswollen	0.00	197	—
	NaOH-swollen	0.00	186	—
2.0	Unswollen	23.23	177	10.15
	NaOH-swollen	27.27	170	8.60
3.0	Unswollen	41.12	161	18.27
	NaOH-swollen	46.52	156	16.12
4.0	Unswollen	63.72	152	22.84
	NaOH-swollen	68.02	136	26.88

dotherm is observed at 110°C due to the moisture desorption followed by an exothermic process starting at about 260°C caused by the oxidative attack at the carbonyl groups and at the C—H bonds of the substrate. The major endothermic reaction was observed to start at 290°C with a peak at 350°C, reflecting the thermal depolymerization of cellulose.

The DTA curve of the HEMA-grafted cotton sample is similar in nature to that of ungrafted sample. However, the endothermic peak corresponding to the temperature of decomposition of cellulose was shifted toward higher temperature with the increase in graft add-on. Thus, an endothermic peak observed at 350°C for the ungrafted sample [Fig. 4(A)]

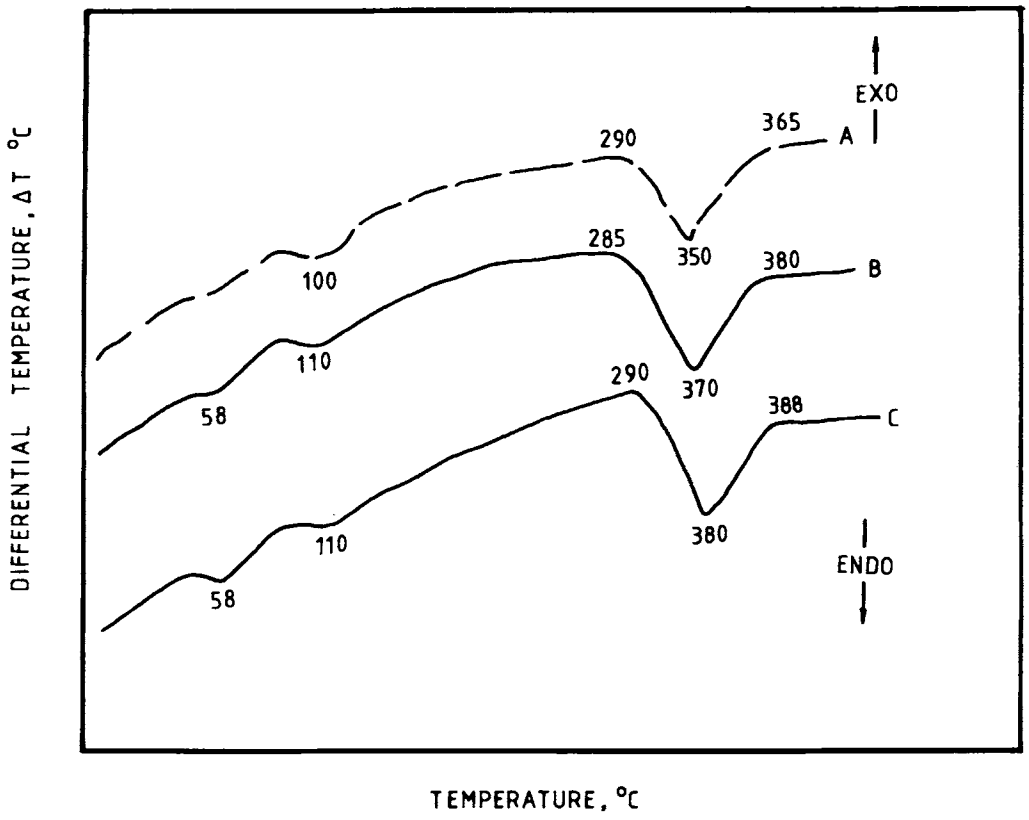

Figure 4 Effect of temperature on differential temperature of grafted cotton: (A) ungrafted cotton; (B) 55.21% HEMA-grafted cotton; (C) 75.21% HEMA–TEGDMA-grafted cotton.

Table IV Temperature of Decomposition at Different Weight Losses of Cotton Grafted with HEMA Using UN Photoinitiator

Cotton Sample	Graft Add-on (%)	Temperature of Decomposition (°C) at Weight Loss of (%)								
		10	20	30	40	50	60	70	80	90
Control	0.00	248	310	325	336	342	355	370	433	460
HEMA-grafted	55.21	237	290	315	331	341	355	365	390	456
HEMA–TEGDMA-grafted	75.21	226	290	315	336	350	360	375	409	484

shifted toward higher temperature and was located at 370°C for a sample grafted with HEMA alone at 55.21% graft add-on [Fig. 4(B)] and at 380°C for a sample grafted with HEMA in the presence of TEGDMA at 75.21% graft add-on [Fig. 4(C)].

The endothermic peak corresponding to moisture desorption at around 100–110°C was retained for all the grafted samples, indicating an insignificant change in moisture regain, a characteristic of the control cotton on grafting with HEMA. The same has been shown by the moisture regain values reported earlier.[12] An endothermic peak appearing at around 56–58°C for HEMA-grafted cotton was attributed to the glass transition temperature of polyHEMA, which is known to be around the same temperature.[19]

The results on the thermogravimetric analysis (TGA) carried out by determining the decomposition temperature (T_D) at different weight losses of control cotton and cotton grafted with HEMA in the absence and presence of TEGDMA are given in Table IV. The data indicate that the thermal stability of HEMA-grafted cotton cellulose increases and the decomposition of the substrate is influenced by the level of graft add-on. Thus, for a weight loss of 50%, the decomposition temperature for ungrafted cotton is 342°C, whereas in the case of cotton grafted at 55.21 and 75.21% graft levels, these temperatures are 341 and 350°C, respectively.

CONCLUSION

In conclusion, the addition of a small amount of bifunctional monomer TEGDMA greatly enhanced the HEMA graft add-on, which is a particularly useful technique in the case of graft-copolymerization reactions using comparatively weak UV-radiations. The properties of the grafted substrates alter to an extent dependent on the level of graft add-on.

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