Mechanical and Thermal Behavior of Cotton Cellulose Grafted with Hydroxyethyl Methacrylate Using Photoinitiation

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SYNOPSIS

The textile properties of tensile strength and thermal decomposition of cotton cellulose grafted by photoinitiation technique using 2-hydroxyethyl methacrylate monomer were studied. The photoinitiators, namely, uranyl nitrate (UN) and ceric ammonium nitrate (CAN), were used during grafting of unswollen and swollen cotton samples. The tensile strength decreased with increase in graft add-on, whereas, the thermal stability was imparted to the grafted cotton according to the level of graft add-on.

INTRODUCTION

The use of UV radiations for graft copolymerization of cellulosic materials using vinyl monomers has been extensively studied by many workers.[1,2] In order to impart different properties to the backbone polymer, grafting is supposed to be the most suitable technique. The UV radiation is quite weak and, therefore, can dissociate only the weakest bonds in the backbone polymer, thus making it necessary to use the photoinitiator. A number of photoinitiators have been reported in the literature.[3-5] Further, even with the use of photoinitiators, the graft levels are not sufficiently high in many cases, which necessitates the improvement in the accessibility of substrates by methods such as preswelling of the substrate prior to grafting.[6]

Since natural fibers such as cotton decompose when heated and totally degrade losing all textile characteristics, imparting the thermal stability is highly advantageous.

Differential thermal analysis provides a very good method for the rapid detection and measurement of the physicochemical changes that a polymer undergoes when subjected to heating, whereas, thermogravimetric analysis provides a method for the determination of mass change in the polymer as a function of time and temperature.[7] Another important characteristic from the point of view of the use as a textile fiber is tenacity, a mechanical property that depends on the crystallinity and the nature of bonds inside the fiber. The effect of grafting polyester with acrylamide on tenacity and thermal properties of the fiber has been studied by Gaceva-Bogoeva et al.[8] Mohammed and Mousa[9] reported a decrease in tensile strength with increase in methyl methacrylate graft content onto cellulose backbone.

We have reported[6] the results on the textile properties, such as moisture regain and dyeability, of the photoinduced graft copolymerized cotton cellulose with hydroxyethyl methacrylate under optimized conditions. Here, we report the further results on the tensile behavior and the thermal stability of cotton cellulose grafted with 2-hydroxyethyl methacrylate using UV radiation.

EXPERIMENTAL

Materials

Substrate

The 30-count cotton yarn was used as cellulose sample after purification by standard method.[10] It had the following specifications: iodometric carboxyl value, 0.56 meq. of COOH / 100 g of cellulose; copper

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number, 0.034; cuprammonium fluidity, 3.71 p^{-1}. The swollen samples of cotton were prepared by using 24% (w/w) sodium hydroxide and 70% (w/w) zinc chloride at 20°C for 1 h each, followed by water washing and drying in air at room temperature.

Chemicals

2-Hydroxyethyl methacrylate (HEMA) supplied by Aldrich Chemical Company, Inc., was vacuum distilled to make it free from the inhibitors. Uranyl nitrate (UN) and ceric ammonium nitrate (CAN), supplied by LOBA-CHEMIE Indoaustranal Co., India, were the two photoinitiators used. The sodium hydroxide and zinc chloride used for swelling were of laboratory reagent grade.

Graft Copolymerization

The process of graft copolymerization using UV radiation of 360-nm wavelength obtained from a Philips HPW 125 W mercury lamp has been reported in our earlier communication.[6]

Determination of Tenacity

The breaking load for control and grafted cotton samples was determined on an Instron tensile tester. The load elongation curves of 1-cm yarn samples were recorded with a chart speed of 50 mm/min. The full scale of the recorder was adjusted for a load corresponding to 500 g.

Thermal Analysis

The thermogravimetric analysis (TGA) and the differential thermal analysis (DTA) were carried out using a Stanton Redcroft thermal analyser, STA 780. It simultaneously records weight vs. time or temperature for TGA and temperature vs. time curves for DTA. The sample was cut to approximately 1–2 mm length and a 20 ± 5-mg sample was taken for each analysis. The analysis was carried out from room temperature (30°C) to 500°C at a heating rate of 10°C/min and with a chart speed of 200 mm/h.

RESULTS AND DISCUSSION

Effect on Mechanical Property

The optimized conditions of the graft copolymerization reactions of HEMA onto cotton cellulose using UV radiation have been reported in our earlier communication.[6] These are 0.20% (w/v) UN at 50°C and 0.25% (w/v) CAN at 40°C, the time of reaction being optimized at 3 h for both the initiators. The graft add-on increased with increase in HEMA concentration, which further enhanced on swelling the substrate.

Table I gives the results on tensile behavior of the cotton yarn on grafting with HEMA. These results indicate that the breaking load of 197 g for the ungrafted cotton decreased steadily with increasing amount of HEMA graft add-on. At a maximum graft add-on of 56.22% in the case of UN-initiated grafting, the breaking load decreased to 136 g, giving a loss of 30.96% in the tenacity. Preliminary experiments of irradiating the substrate for 4 h with UV radiation did not show any loss in tenacity, making it clear that the graft add-on has a detrimental effect on the tensile behavior of the fiber substrate.

Table I Effect of Grafting of HEMA on Tenacity of Cotton

HEMA Concentration, % (w/v)	Cotton Sample	Graft Add-on (%)		Breaking Load (g)		
		UN[a] Initiation	CAN[b] Initiation	Ungrafted	UN[a] Initiation	CAN[b] Initiation
1	Unswollen	13.40	11.80	197	183	184
	NaOH swollen	27.35	24.30	183	164	168
	$ZnCl_2$ swollen	24.10	23.12	188	168	170
2	Unswollen	37.22	29.06	197	174	176
	NaOH swollen	49.74	44.74	183	145	152
	$ZnCl_2$ swollen	46.80	42.26	188	152	156
3	Unswollen	50.98	42.12	197	159	160
	NaOH swollen	56.22	51.56	183	136	144
	$ZnCl_2$ swollen	54.45	50.32	188	140	146

[a] UN initiation: 0.20% (w/v) UN, 50°C, 3 h.
[b] CAN initiation: 0.25% (w/v) CAN, 40°C, 3 h.

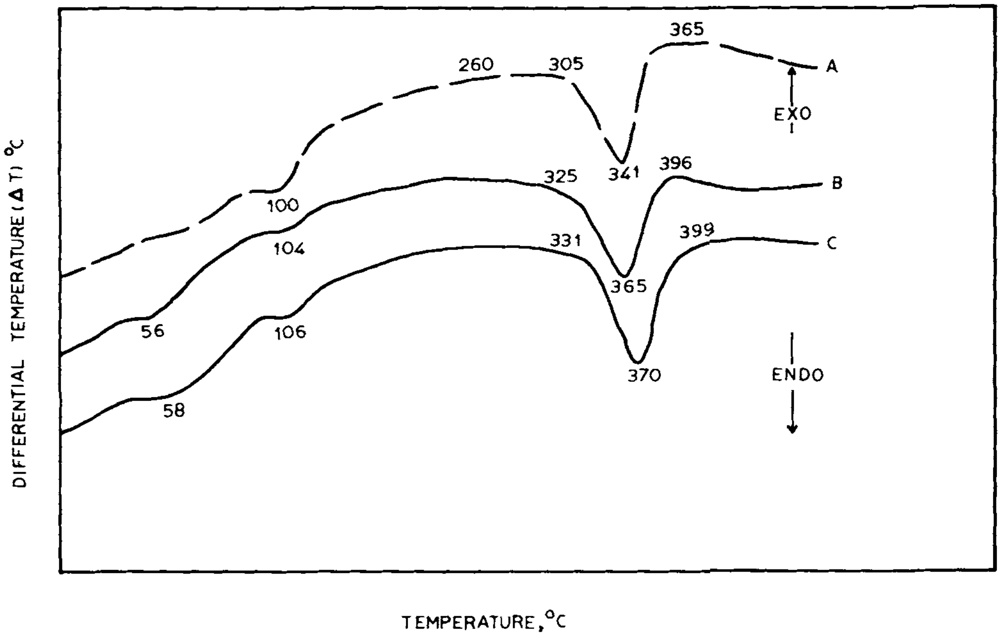

Figure 1 DTA curves of cotton grafted with HEMA at different graft levels: (a) ungrafted cotton, (b) 37.22% HEMA graft, (c) 54.42% HEMA graft.

The decrease in tensile strength of cotton cellulose on grafting with HEMA may be attributed to the likely increase in the extent of hydrogen bonding between the —OH groups of cellulose and those of the grafted chains. It may also be due to the dead load of grafted side chains onto the backbone polymer. In addition, these grafted side chains of bulky HEMA groups may disrupt the original close packing of the aligned cellulose chains in the fiber structure, causing disorientation leading to the decrease in tensile strength.

In the case of swollen cotton under unstretched conditions, there is a deterioration in the orientation of the cellulosic chain molecules that loosens the fiber structure to some extent and therefore decreases the tensile strength. As the swelling enhances the graft add-on, there is further decrease in the tensile strength corresponding only to the level of graft add-on, when they are subjected to the grafting reaction.

Effect on Thermal Properties

The differential thermal analysis (DTA) curves of the ungrafted and grafted cotton cellulose have been shown in Figure 1. In the DTA curve of control cotton [Fig. 1(a)], an endotherm is observed at 100°C due to moisture desorption followed by an exothermic process starting at about 260°C due to the oxidative attack at the carbonyl groups and C–H bonds of the substrate. The major endothermic reaction was observed to start at 305°C with a peak at 341°C reflecting the thermal depolymerization of cellulose. The DTA curve of HEMA-grafted cotton sample is similar in nature to that of an ungrafted sample. However, the endothermic peak corresponding to

Table II Temperature of Decomposition at Different Weight Losses of Cotton Grafted with HEMA

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	280	290	295	310	320	335	340	386	412
HEMA grafted	13.40	333	350	360	365	375	380	398	419	435
	37.22	326	360	368	380	390	395	400	428	452
	54.42	315	341	365	375	387	402	410	440	470

the temperature of decomposition of cellulose was shifted toward higher temperature with the increase in graft add-on. Thus, an endothermic peak observed at 341°C for the ungrafted sample shifted toward higher temperature and was located at 365°C for 37.22% HEMA graft add-on and at 370°C for a sample containing 54.42% graft add-on [Fig. 1(b) and 1(c), respectively]. The endothermic peak corresponding to moisture desorption at around 100–110°C was retained for all the grafted samples, indicating insignificant changes in moisture regain characteristic of the control cotton on grafting with HEMA. The same has been shown by the moisture regain values reported in the earlier communication.[6] An endothermic peak appearing at around 56–58°C for HEMA-grafted cotton was attributed to the glass transition temperature of poly-HEMA, which is known to be around the same temperature.[11]

The results on the TGA carried out by determining the decomposition temperature (T_D) at different weight losses of control cotton and cotton grafted with HEMA are given in Table II. The data indicates 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. Also, the thermal decomposition of grafted cotton starts at a relatively higher temperature as compared to that for the ungrafted sample, and the thermal stability increases with increase in graft add-on. Thus, for a weight loss of 70%, the decomposition temperature for ungrafted cotton is 340°C, whereas, the decomposition of the HEMA-grafted cotton cellulose for the graft levels of 13.40, 37.22, and 54.32% are 398, 400, and 410°C, respectively.

In conclusion, it may be stated that in the case of HEMA grafting onto cotton cellulose, a significant level of graft add-on can be achieved without a great loss in tensile strength. As regards the thermal properties, the fiber decomposition temperature increases substantially with increasing graft add-on, thus imparting greater thermal stability.

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