Photoinduced Graft Copolymerization of 2-Hydroxyethyl Methacrylate on Cotton Cellulose in the Presence of Triethyleneglycol Dimethacrylate

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SYNOPSIS

The addition of a bifunctional monomer, triethylene glycol dimethacrylate (TEGDMA), to a grafting system containing 2-hydroxyethyl methacrylate (HEMA) and benzoin ethyl ether photoinitiator substantially increased the graft add-on of the unswollen and sodium hydroxide–swollen cotton cellulose. Grafting caused changes in the properties of the substrate such as moisture regain, the water of imbibition, and the dyeability with a direct and a reactive dye in accordance with the graft level. The observations have been explained in relation to structural changes in the grafted cotton. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Graft-copolymerization reactions impart different properties to the backbone polymer. Using ultraviolet radiation for graft-copolymerization reactions, the grafting of various vinyl monomers onto cellulosic materials has been extensively studied.[1,2] The low-energy, UV radiation-induced grafting offers advantages such as reduced degradation of the backbone polymer and control over the grafting reaction, although high graft levels can be difficult to achieve.

The graft copolymerization of 2-hydroxyethyl methacrylate (HEMA) onto cotton has been studied using different photoinitiators.[3,4] Da Silva et al.[5] studied the photoinitiated grafting of acrylamide and HEMA onto cellulosic substrate from acetone/water solutions using isopropyl thioxanthane as the photoinitiator. Various organic solvents have been found to accelerate the diffusion of monomer inside the substrate to enhance the radiation-induced grafting.[6,7] Preswelling of cellulose has shown improvements in the graft levels.[4,8] Since grafting with HEMA has been reported to anchor enzymes for the immobilization purpose,[9,10] high graft add-on levels are useful in providing an increased number of such sites. Very little work has been reported on the use of bifunctional monomers during grafting of cotton with monofunctional vinyl monomers.[11] Small amounts of divinyl benzene have been shown to enhance the graft level of styrene on cotton.[12–14]

This article reports the effect of adding triethylene glycol dimethacrylate during the grafting of HEMA onto cotton cellulose, both in unswollen and sodium hydroxide-swollen forms, using the photoinitiator benzoin ethyl ether. Moisture regain, the water of imbibition, and the dyeability with direct and reactive dyes of the grafted samples were analyzed from the point of view of understanding the changes taking place in the fiber structure on enhanced grafting.

EXPERIMENTAL

Materials

Substrates

Scoured and bleached 30 count cotton yarn was used as the cellulose source. The swollen samples of cotton were prepared by using 24% (w/w) sodium hydroxide at 20°C for 1 h, followed by thorough washing with water and then drying at room temperature.

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Chemicals

2-Hydroxyethyl methacrylate (HEMA) supplied by Aldrich Chemical Co. was vacuum-distilled to make it free from inhibitors. Triethylene glycol dimethacrylate (TEGDMA) supplied by Fluka was used without further purification. Benzoin ethyl ether (BEE) supplied by Fluka was used as the photoinitiator. Methanol and sodium hydroxide of "chemically pure" grade were used.

Dyes

A direct dye, C.I. Direct Blue 86, and a reactive dye, C.I. Reactive Red 31, were used for dyeing the substrates.

Methods

Graft Copolymerization

The photoinduced HEMA graft copolymerization onto cotton cellulose using the BEE photoinitiator was carried out by the method reported earlier.[15] The parameters of grafting were optimized by varying them so as to obtain maximum possible graft add-on along with maximum graft yield. Thus, 0.3% (w/v) BEE, 3 h, and 50°C were found to be the optimum conditions. Grafting was also carried out using sodium hydroxide-swollen cotton as well as by incorporating 0.15% (w/v) TEGDMA into the grafting bath. After grafting, the samples were extracted free of homopolymer and air-dried and then the graft add-on and the graft yield were determined.[4]

Moisture Regain

The moisture regain of control and grafted cotton yarns was determined by the oven-drying method.[16]

Water of Imbibition

Finely cut cotton samples (0.3 g) were thoroughly soaked in distilled water for 2 h at 30°C. Loosely held water was driven out by centrifuging the sample, in a previously weighed centrifuging tube, at 2000 rpm for 15 min. The tube along with the sample was weighed accurately followed by drying at 110°C until a constant weight.[17]

Dyeing with a Direct Dye

The grafted cotton samples were dyed with C.I. Direct Blue 86 at boil for 2% shade, using 20% (owf) Glauber's salt as the exhausting agent. The dye bath exhaustion values were calculated from the amount of dye remaining in the bath after completion of dyeing in 1 h, as estimated by optical density measurements of the solution.

Dyeing with a Reactive Dye

Dyeing with C.I. Reactive Red 31 was carried out at 70–80°C for 2% shade, using 20 g/L Glauber's salt as the exhausting agent and 15 g/L trisodium phosphate as an alkali for reacting the dye onto the cellulose. Dye bath exhaustion values were calculated as above.

RESULTS AND DISCUSSION

Figure 1 shows the results on graft add-on and graft yield by varying the HEMA concentration under optimum conditions of reaction. It may be observed that the graft yield is maximum at 4% (w/v) HEMA concentration, whereas the graft add-on increased with increase in the HEMA concentration and ultimately leveled off. Thus, 4% (w/v) HEMA gave the maximum graft yield of 8.85% and the maximum graft add-on of 35.42% [Fig. 1(a) and (b)].

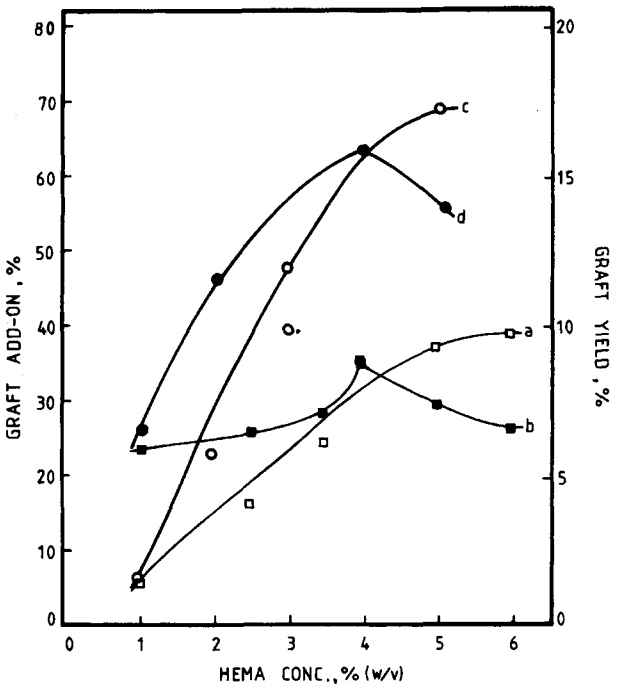

Figure 1 Effect of HEMA concentration on graft add-on and graft yield: (□) graft add-on and (■) graft yield in absence of TEGDMA; (○) graft add-on and (●) graft yield in presence of TEGDMA.

Table I Effect of Preswelling on Grafting of HEMA onto Cotton Cellulose

HEMA Concentration, % (w/v)	Cotton Sample	Graft Add-on (%)	
		Without TEGDMA	With 0.15% (w/v) TEGDMA
1.0	Unswollen	5.94	6.42
	NaOH-swollen	9.08	9.56
2.0	Unswollen	9.33	23.23
	NaOH-swollen	13.23	27.72
3.0	Unswollen	16.78	39.42
	NaOH-swollen	23.02	46.52
4.0	Unswollen	35.42	63.72
	NaOH-swollen	40.83	68.02

The use of sodium hydroxide-preswollen cotton gave enhanced graft add-on values at each concentration of HEMA used (Table I). Addition of a small quantity [0.15% (w/v)] of the bifunctional monomer TEGDMA to the HEMA grafting bath showed further increase in the graft yield to 15.93% and in the graft add-on to 63.73% [Fig. 1(c) and (d)]. Such an increase also was observed for preswollen substate (Table I). The explanations for the enhanced graft level by using preswollen substrate and/or by adding TEGDMA to the HEMA grafting bath have been given in detail earlier.[18] It has been proposed that the presence of a small quantity of TEGDMA in the grafting bath increases the graft add-on mainly through its action as a bridging molecule between already existing HEMA graft chains onto the cellulose backbone and the HEMA homopolymer chains present in the bath.

Effect of Grafting on Moisture Regain

Figure 2 indicates that the moisture regain of the grafted sample initially decreased markedly followed by a slow steady rise with increase in the graft add-on. Earlier, we observed a similar trend for grafting of HEMA alone onto cotton.[4] Interestingly, in that case, the high HEMA graft add-on of 67.95% was obtained using 5% (w/v) HEMA (uranyl nitrate initiator), in the absence of TEGDMA, on swollen cotton, giving a moisture regain value of 9.02%. In the present case also, a graft add-on of 73.23% using 4% HEMA in the presence of TEGDMA on swollen cotton gave a moisture regain of 9.10%, a value slightly and appropriately higher with the graft add-on value. This observation further supports that the very small quantity of bifunctional monomer, TEGDMA, does not produce any significant cross-linking between the HEMA graft chains to hinder the moisture sorption but acts mainly as a link between the graft chains and homopolymer chains of HEMA to further enhance the graft add-on level.

The initial decrease in moisture regain is due to the hindrance of the graft chains of the bulky monomer to the availability of the cellulosic —OH groups. At higher graft add-on levels, however, the —OH groups of the graft chains are available for moisture sorption. Since the number of such groups

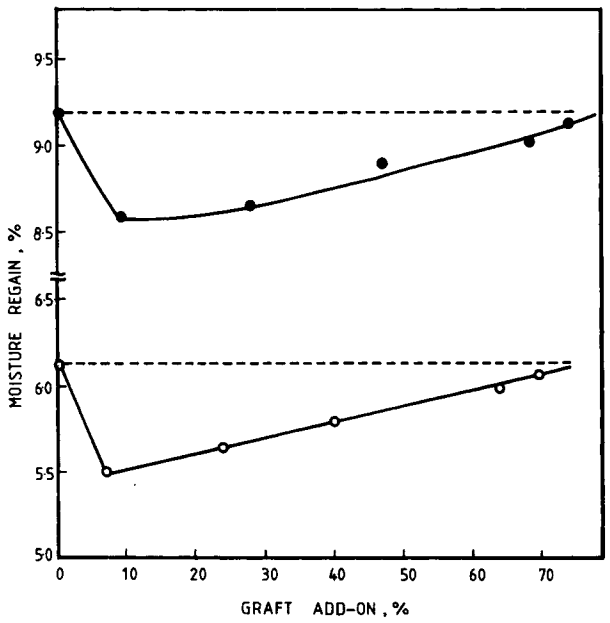

Figure 2 Effect of graft add-on on moisture regain of HEMA–TEGDMA grafted cotton: (○) unswollen cotton; (●) swollen cotton.

is limited depending upon the level of graft add-on, the rise in moisture regain is not rapid enough as compared to the initial sharp decrease.

Effect of Grafting on Dyeability

The unswollen and swollen cotton samples, grafted with HEMA in the presence of TEGDMA, showed a decrease in the dye uptake for both direct and reactive dyestuffs (Fig. 3). The direct dye dyeing depends on the accessibility of the substrate, whereas the reactive dye forms covalent bonds with available hydroxyl groups in the substrate. With the increase in graft add-on, the direct dye uptake decreases linearly due to the decreased accessibility of the grafted substrate to the bulky dye molecules. On the other hand, in the case of reactive dye dyeing, the decrease is not linear, being rapid initially with increasing graft add-on followed by very slow decrease at considerably high graft amounts. This is obvious, since, initially, the amount of primary hydroxyl groups of cellulose available to the reactive dye for the reaction goes on decreasing rapidly; at higher graft add-on levels, however, a certain amount of hydroxyl groups from the grafted chains is available and, hence, the rate of decrease of the reactive dye uptake slows down. The decrease in dye uptake, thus, is solely dependent on increase in the graft add-on irrespective of the presence of small amounts of TEGDMA.

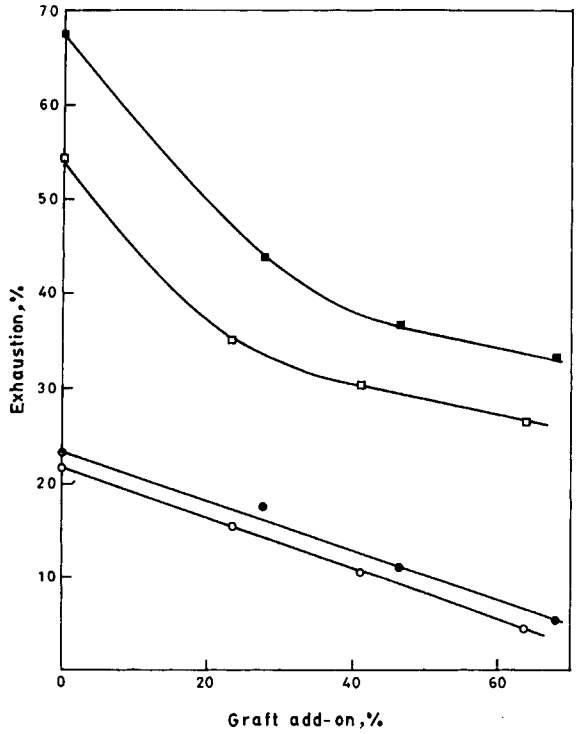

Figure 3 Effect of graft add-on on direct and reactive dye dyeing: (○) unswollen cotton-direct dye; (●) swollen cotton-direct dye; (□) unswollen cotton-reactive dye; (■) swollen cotton-reactive dye.

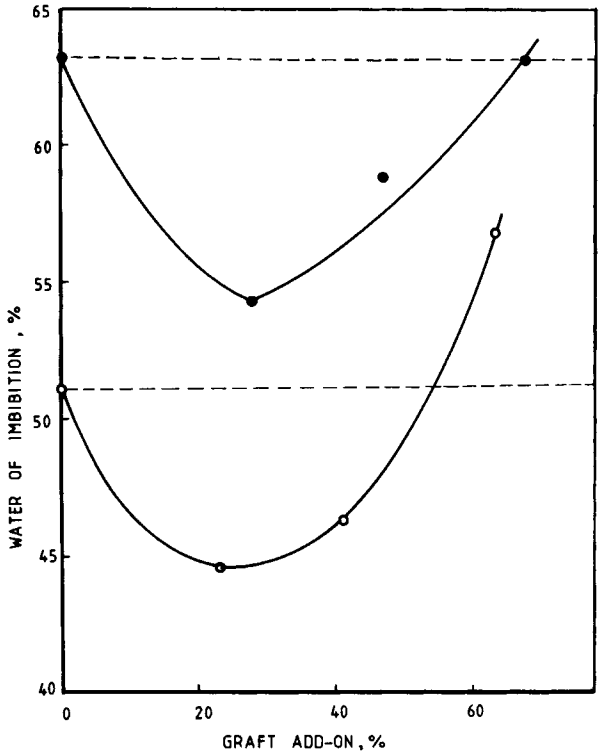

Figure 4 Effect of graft add-on on water of imbibition: (○) unswollen cotton; (●) swollen cotton.

Effect of Grafting on Water of Imbibition

The water of imbibition showed an initial rapid decrease followed by an equally rapid increase with the increasing graft level of HEMA in the presence of TEGDMA onto both unswollen and swollen cotton (Fig. 4). The water molecules become absorbed on the cellulosic chains and form hydrates, followed by formation of further monolayers covering the chains in the accessible regions of the substrate.[19]

The graft chains in the fiber structure restrict the penetration of water. Initially, at the lower graft add-on values, a smaller number of graft chains in the fiber hinders the absorption of water molecules onto cellulosic chains. However, with further increase in graft add-on, obtained by incorporation of TEGDMA, longer and longer graft chains are formed that increase the diameter of the fiber by about 20%, as has been observed under a projection microscope. Apparently, the accessibility of fiber as far as tiny water molecules are concerned increases, making more and more room for them to get in.

Comparison Between Moisture Regain and Dyeability

Moisture regain and dyeability, although both depend primarily on the accessibility of the fiber structure, have shown different trends with increase in the graft add-on (Figs. 2 and 3). The hydroxyl groups of cotton cellulose and/or those from graft chains should be available for any interaction with moisture or dyestuffs. The molecules of moisture, being extremely small as compared to those of the dyestuffs, have better penetrating ability and access to the hydroxyl groups, even though the graft chains cause some hindrance initially at low graft add-on. However, on grafting the fiber to any level, although little diameteral swelling was observed in the substrate, the graft chains cause hindrance mainly to the bulky dye molecules and, hence, the dye uptake of both the direct and reactive dyestuffs shows a continuous decrease, although of a different nature.

Comparison Between Moisture Regain and Water of Imbibition

The hydroxyl groups provide the sites for moisture sorption, whereas, in the case of the water of imbibition, the water molecules in the liquid state simply penetrate the fiber structure in its accessible region and form monolayers on the chain molecules irrespective of the availability of the hydroxyl groups.

In both cases (Figs. 2 and 4), initially at low graft add-on levels, there is a sharp decrease with increase in the graft add-on. However, with further increase in the graft add-on, the increase in moisture regain is very slow as compared to that in the water of imbibition values. The slow increase in the moisture regain may be attributed to the slowly increasing amount of hydroxyl groups made available by the grafted chains with increasing graft add-on. At higher graft add-on, the fiber diameter and, hence, the accessibility of the fiber, has been observed to increase, making more and more room for penetration of the liquid water molecules and, hence, the amount of water of imbibition increases sharply. It may be noted that although this increase in accessibility is enough to increase the water of imbibition, it is not sufficient for diffusion of bulky dye molecules.

Thus, to attain the levels of moisture regain and the water of imbibition as those of the original ungrafted cotton, it requires 72% graft add-on for the former as against only 55% graft add-on for the water of imbibition.

It may be concluded that the addition of a very small amount of a bifunctional monomer TEGDMA in the HEMA grafting bath improves the graft add-on significantly, making major changes in the fiber structure that are reflected in the different properties such as moisture sorption, dyeability, as well as the imbibed water. Thus, it is possible to obtain higher graft levels even with the use of low-energy UV radiations by adopting different techniques.

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