Elucidation of the Nanoparticle Effect on the Grafting of Vinyl Monomers onto Cotton Fabric

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ABSTRACT: The grafting emulsion polymerization of vinyl monomers onto cotton was carried out in the presence of double-modified montmorillonite clay. The obtained results show that grafting with glycidyl methacrylate/montmorillonite gave a higher rate of grafting than grafting with methyl methacrylate/montmorillonite in all clay percentages, and also, the grafting yield of glycidyl methacrylate monomer onto cotton in the presence of montmorillonite clay had a higher value than that in the absence of the clay for all factors studied. Cotton grafted with glycidyl methacrylate/montmorillonite with a graft yield of about 50% was prepared according to the emulsion polymerization technique and was treated with different concentrations of dibutylamine solutions ranging from 1 to 4%. The obtained samples were characterized according to nitrogen content, thermal stability, scanning electron microscopy, mechanical properties, water absorption, and color strength according to acid, basic, and reactive dyes. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 492–501, 2009

Key words: emulsion polymerization; graft copolymers; nanocomposites

INTRODUCTION

Montmorillonite (MMT) is a raw material that is used in the preparation of polymer/clay nanocomposites[1] and is a very soft phyllosilicate mineral that typically forms in microscopic crystals. MMT, a member of the smectite family, is a 2 : 1 clay, which means that it has two tetrahedral sheets sandwiching a central octahedral sheet. The particles are plate-shaped, with an average diameter of approximately 1 μm. The MMT water content is variable, and it increases considerably in volume when it absorbs water. Chemically, it is hydrated sodium calcium aluminum magnesium silicate hydroxide $(Na, Ca)_{0.33}(Al, Mg)_2(Si_4O_{10})(OH)_2 \cdot nH_2O$. Potassium, iron, and other cations are common substitutes; the exact ratio of cations varies with the source. Nanocomposites are materials that are created by the introduction of modified clay nanoparticles into a macroscopic sample material (often referred to as the *polymer matrix*). This is part of the growing field of nanotechnology. After the addition of nanoparticles to the matrix materials, the resulting nanocomposites have received special attention because of their improved properties at very low loading levels compared with conventional filler composites.[2,3] In general, the nanoparticles are dispersed into the matrix during processing. The percentage by weight (called *mass fraction*) of the nanoparticles introduced can be very low because of the high surface-area-to-volume ratio of the nanoparticles. Nanocomposite materials are widely used in various fields depending on their composite nature and structure;[4] among these fields are applications in textiles, where there are two principle methods for the use of nanocomposites in textile applications. The melt spinning of the nanocomposite polymer,[5] which can be subsequently woven or knitted, has been demonstrated as a promising approach for textile fire-retardant applications.[6,7] Also, the coating of textile surfaces by nanocomposite formulation is another interesting way to use nanocomposites in textile application. In addition, the latter approach confers to textile surfaces other properties, such as impermeability to water or gases. Moreover, the incorporation of nanostructure in polymers for fire-retardant applications makes it possible to limit the toxicity of the degradation products compared with more traditional additives, such as halogenated products.[8–10] In addition, the use of nanocomposites allows a reduction in the weight content of additives.[7] Cotton is a widely used, natural, healthy, hygroscopic, and cheap textile material. Nearly 94% of its chemical structure consists of cellulose molecules, and cotton is used to produce regenerated cellulose fibers, which have numerous textile applications as well. A major drawback of cotton is its inherent ability to burn. Many

finishes have been developed to impart flame resistance to cotton. These finishes have limited use in textiles for apparel because of problems with the finish remaining on the fabric after laundering or problems with the fabric holding up to water.[5] Most of these finishes have been developed for products that are not laundered, such as drapery and furnishing fabrics.[11–13] The textile industry has a high demand for cotton with improved physical and chemical properties.[14] Vinyl grafting polymerization onto cellulose has been successfully developed.[12–21] In this study, we aimed to elucidate the effect of nanoparticles in the grafting emulsion polymerization of vinyl monomers onto cotton fabric with a redox initiation system by comparing the grafting percentage of cotton samples when the grafting took place in the presence and absence of modified MMT clay by studying the factors affecting the grafting percentage, including nanoparticle concentration, temperature, time, initiator concentration, and monomer concentration. Also, we studied the effect of the treatment of the grafted cotton samples with different concentrations of dibutyl amine.

EXPERIMENTAL

Materials

The cotton fabric we used consisted of normal bleached fibers (obtained from the Institute for Textile Chemistry and Chemical Fibers, Denkendorf, Germany). MMT clay with a cation-exchange capacity of 100 mequiv/100 g was supplied from Süd-Chemie (Moosburg, Germany). Most of the chemicals, including leucine, sodium persulfate, sodium bisulfite, benzene, methyl ethyl ketone, butanol, and methyl triethoxy silane, were acquired from Aldrich Chemical (Steinheim, Germany). Sodium dodecyl sulfate, hydrochloric acid, and dibutyl amine were obtained from Merck (Darmstadt, Germany). The monomers glycidyl methacrylate (GMA) and methyl methacrylate (MMA) were provided by Acros (KMF Laborchemie Handels GmbH, Sankt Augustin, Germany). The monomers were redistilled and stored at −20°C. Ferrous ammonium sulfate and sodium sulfate anhydride were supplied from BDH (Köln, Germany). We used acid dye, namely, Acid Red 8 (Aldrich); basic dye, namely, malachite green; and reactive dye, namely, Rosolin Red GR, which were supplied by Bayer AG (Leverkusen, Germany).

Methods

Double modification of MMT with leucine and methyl triethoxy silane as a coupling agent

A mixture of MMT and methyl triethoxy silane (10 wt % of MMT) was added to a solution of deionized water and ethanol (10/90 v/v); a separated solution of leucine (2× concentration of the clay on the basis of the cation-exchange capacity) and 2 mL of hydrochloric acid in 50 mL of deionized water was added to the solution. The mixture was then stirred for 3 h at 70°C. The white precipitate was obtained by filtration and dried *in vacuo* at 80°C for 24 h.

Grafting polymerization procedure

Pieces of cotton samples about 3 g in weight were placed in a 250-mL stoppered glass vessel containing the grafting solution at a specific temperature (50, 60, 70, or 80°C) with thermostatic shaker water bath. The grafting solution consisted of water, double-modified MMT clay, monomer, butanol, and emulsifier. The contents of the reaction vessel were shaken vigorously for 30 min. Ferrous ammonium sulfate and initiator were added to the flask, and the graft polymerization was held under shaking for the desired time (15–120 min) at the desired temperature. After the desired polymerization time, the grafted cotton sample was quickly removed from the grafting solution, and the homopolymer was extracted from the grafted cotton by Soxhlet extraction with methyl ethyl ketone in the case of the GMA monomer and benzene solvent in the case of the MMA monomer.[20] The extraction of homopolymers was repeated until a constant weight for the cotton sample was reached. The grafting percentage was calculated according to the following equation:

$$\text{Grafting \%} = (W_2 - W_1/W_1) \times 100 \qquad (1)$$

where W_2 is the weight of grafted cotton and W_1 is the weight of ungrafted cotton.

Dyeing methods[22] and determination of the color strength (K/S, where K is the adsorption coefficient and S is the scattering coefficient)

Each ungrafted cotton sample, cotton sample grafted with GMA, cotton sample grafted with GMA in the presence of MMT clay, and cotton sample grafted with GMA in the presence of MMT clay and treated with dibutyl amine were independently dyed with three types of dyestuff, namely, acid, basic, and reactive dyes. For acid dye, the dye bath was prepared by the dissolution of the dye in hot water; the sample was introduced into the bath at 60°C and held for 10 min. The temperature of the bath was raised to 90°C over a period of 60 min. The sample was rinsed with cold water. It was then soaped with a solution containing 5 g/L Na_2CO_3 and 1 g/L detergent, washed with cold water, and then dried. For basic dye, we carried out the dyeing process by pasting the dye with 1% acetic acid (on the basis of

sample weight) and then dissolving it in boiling water. The dissolved dye was added to the bath at 60°C, and the temperature was then raised slowly to 90°C. The dyeing was continued for 60 min, during which gluber salt (20% on the basis of sample weight) was added; the samples were rinsed with cold water and then soaped and washed, as with the acid dye. For the reactive dye, the dye was first dissolved in boiling water. The sample was placed in a bath containing gluber salt (80 g/L) and Na_2CO_3 (5 g/L) at 25°C for 10 min. The dissolved dye was then added to the bath. After 15 min, the temperature was raised to 60°C over a period of 30 min; then, the alkali sodium hydroxide (1 mL/L for 32.5%) was added. Again, dyeing was continued for 30 min. The sample was rinsed with cold water and acidified with 1 mL/L acetic acid (60%) at 40°C. The sample was then soaped for 10–15 min. Finally, the sample was washed with cold water and air-dried. All dyeing processes were carried out with conventional exhaustion methods at a dye concentration of 0.2% and a liquor ratio of 1 : 50. After dyeing, K/S was followed by the measurement of the reflectance with a spectrophotometer. This was followed by the substitution of the measured value of the reflectance in the following Kubelka–Munk equation:[22]

$$K/S = [(1 - R)^2/2R] - [(1 - R_t)^2/2R_t] = A \times C \quad (2)$$

where R is the decimal fraction of the reflectance of the colored sample, R_t is the decimal fraction of the reflectance of the uncolored sample, C is the dye concentration, and A is the proportionality factor.

Water absorption

The water absorption test was based on the immersion of cotton fibers in water for different time intervals (30, 60, and 120 min) at room temperature. Water absorption percentage ($S\%$) values were determined from the following equation:[23]

$$S\% = (M - M_0/M_0) \times 100 \quad (3)$$

where M is the mass of the swollen cotton fibers in distilled water at room temperature and M_0 is the mass of the same cotton fibers dried at 50°C.

Characterization

The nitrogen content was determined according to the Kjeldal method[24] with a Büchi 322 as a distillation unit and Büchi 343 as a control unit. Thermogravimetric analysis (TGA) was determined on a TGA 7 thermogravimetric analyzer (PerkinElmer instrument, Walthans, Massachusetts) under a nitrogen flow at heating rate of 10°C/min. The morphology and fracture surface of the composites were exam-

ined by scanning electron microscopy (SEM) analysis with a Zeiss DSM 962 microscope. The mechanical properties[25] of the cotton samples were measured with a Zwich Zugprüfgerät machine (Ulm, Germany) with a force of 10 kN. K/S was measured with a Textfash datacolor GmbH, Zubehoer 3381.

RESULTS AND DISCUSSION

Factors affecting the graft polymerization of the vinyl monomers onto the cotton fibers

Effect of the concentration of the double-modified MMT clay

Graft polymerization onto cotton fibers was carried out with two types of vinyl monomers, namely, GMA and MMA, in the presence of different weight percentages of double-modified MMT clay ranging between 2 and 20 wt % with the emulsion technique in the presence of a redox initiation system consisting of potassium persulfate as an oxidizing agent, sodium bisulfite as a reducing agent, and sodium dodecyl sulfate as an emulsifier. The reaction was carried out at 70°C for 60 min at a 3% monomer concentration. The results are illustrated in Figure 1 which shows that, for both monomers used, the grafting yields initially increased with increasing MMT clay concentration and then decreased. From the data illustrated in this figure, we concluded that GMA–MMT showed the highest rate of grafting in all of the clay weight percentages. The difference in the grafting yield between GMA–MMT and MMA–MMT was due to the difference in the behaviors of the monomers, which depended on such factors as the relative tendency to activation, polarization of vinyl double bonds, ability of the monomer molecules to convert to free radicals, ability of the monomer radicals to graft or be homopolymerized, miscibility, and diffusion of the monomer radicals from the aqueous phase to the fiber phase.[20]
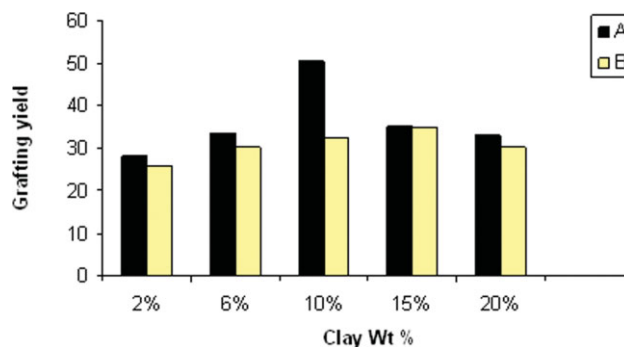

Figure 1 Effect of the weight percentage of MMT on the grafting yields of (A) GMA and (B) MMA monomers on cotton. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

As shown by the data illustrated in Figure 1, for GMA–MMT, the graft yield increased gradually with increasing MMT clay weight percentage to attain a maximum at 10 wt % MMT clay; then, it fell. This could be interpreted in terms of the coating of cotton fiber surfaces by MMT clay at high clay concentrations, and then, the surface of the cotton fibers became closed to GMA penetration.

Effect of the temperature

The effect of the temperature on the graft yield of GMA onto the cotton fibers at constant concentrations of initiator, emulsifier, and monomer was studied within the range 50–80°C, and the results are illustrated in Figure 2. Regardless of the presence of MMT clay (10 wt %), as the temperature increased, the grafting yield also increased, reached a maximum value, and then decreased. The initial increase in the graft yield may have been because increasing the temperature increased the efficiency of the redox initiation system and then enhanced the rate of the grafting reaction. The maximum grafting yield was observed at 70°C for GMA–MMT and also in the absence of MMT clay. The grafting yield of GMA onto cotton in the presence of MMT clay was higher than in the absence of clay at all temperatures. The decrease in the grafting yield at higher temperatures in the two cases was due to the favored chain termination reactions and the increase of the homopolymer formation at high temperatures.[14]

Effect of time

The effect of time on the graft yield was investigated with different reaction time intervals, which were 15, 30, 45, 60, 75, 90, 105, and 120 min, as shown in Figure 3; in both cases, the rate of the grafting started very fast and then tended to level off after 60 min for GMA and after 90 min for GMA–MMT. This deportment could be attributed to the depletion of both the mono-
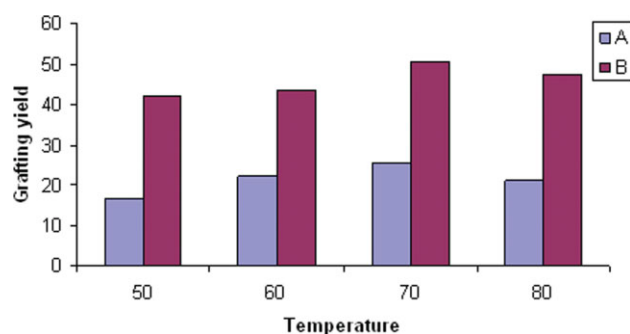

Figure 3 Effect of time on the grafting yields of (A) GMA and (B) GMA–MMT on cotton. [Color figure can be viewed in the online issue, which is available at www.interscience. wiley.com.]
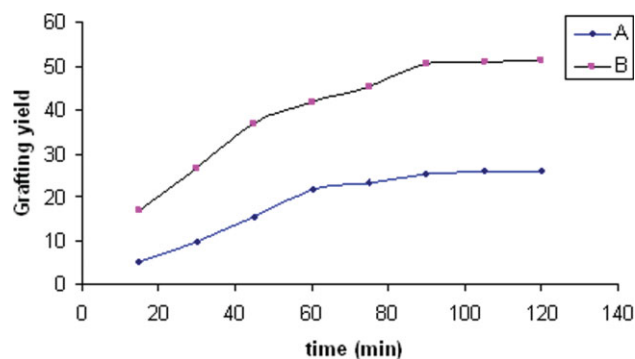
mer and initiator and changes in the components of the system as the reaction proceeded.[20] Also, the grafting yield of the GMA monomer onto cotton in the presence of MMT clay was higher than in the absence of clay at all time intervals.

Effect of the initiator concentration

The effect of the initiator concentration on the grafting of GMA and GMA–MMT onto the cotton fibers is shown in Figure 4. Grafting was carried out at initiator concentrations ranging from 0.25 to 2.0 mmol/L. The data illustrated in Figure 4 shows that, in case of GMA–MMT, the grafting percentage rapidly increased as the initiator concentration increased until the initiator concentration was 1.5 mmol/L. Above this concentration, the grafting continued to increase but less rapidly. For the GMA monomer, the graft yield increased significantly as the initiator concentration increased to an initiator concentration of 1.0 mmol/L. After this concentration, further increases in the initiator concentration decreased the grafting yield. This may have been because, at high initiator concentration, the free radicals reacted with
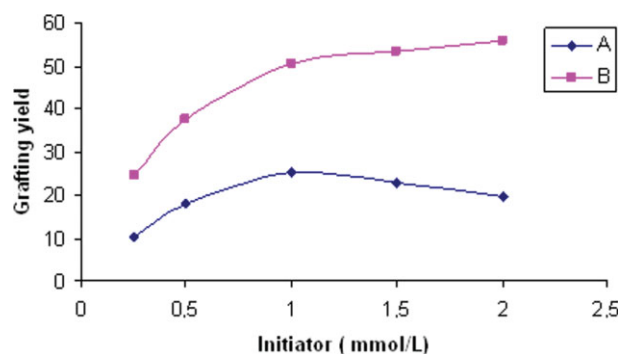

Figure 2 Effect of temperature on the grafting yields of (A) GMA and (B) GMA–MMT on cotton. [Color figure can be viewed in the online issue, which is available at www. interscience.wiley.com.]

Figure 4 Effect of the initiator concentration on the grafting yields of (A) GMA and (B) GMA–MMT on cotton. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figure 5 Effect of the monomer concentration on the grafting yields of (A) GMA and (B) GMA–MMT on cotton. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
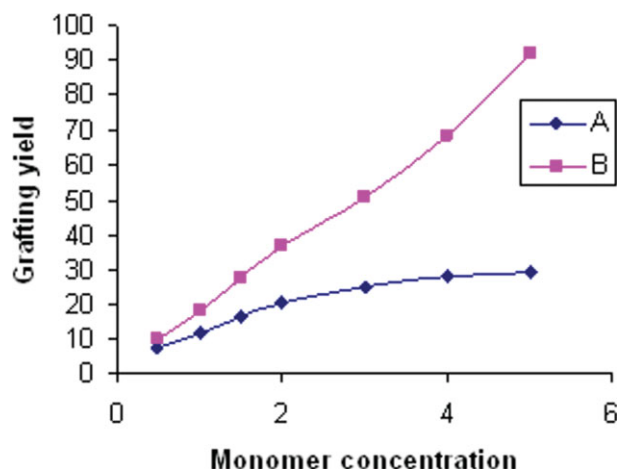
the cellulose macroradical and growing polymer chains, which resulted in termination or combination reactions; consequently, the grafting yield decreased.

Effect of the monomer concentration

Figure 5 shows the effect of the GMA monomer concentration in the range 0.5–5.0% on the grafting yield at constant initiator and emulsifier concentrations. It was obvious that, regardless of the presence of double-modified MMT clay, the grafting yield increased with increasing monomer concentration within the range studied. This may have been because, at high monomer concentrations, a higher number of growing polymer chains was available, which were mainly used for the grafting polymerization. Another probable explanation could be associated with the greater availability of monomer molecules at higher monomer concentrations in the proximity of the cotton fibers. As shown in Figure 5, the rate of grafting tended to level off at a monomer concentration of 3% for the GMA monomer, but no noticeable leveling for the grafting rate was noted for GMA–MMT.

From the previous results for all factors studied, it was obvious that there was a great effect of the addition of the double-modified MMT clay on the grafting yield of the GMA monomer onto cotton fibers by the emulsion polymerization technique in the presence of a redox initiation system.

Characterization of the cotton fibers grafted with GMA monomer in the presence of the double-modified MMT clay and treated with dibutyl amine

The chemical modification of cotton fibers is mainly carried out to improve their properties for end-user application. Desirable properties for cotton fibers are

thermal stability, mechanical properties, and dye uptake. In this study, GMA monomer (3%) was grafted onto cotton fibers in the presence of double-modified MMT clay (10 Wt %) with the emulsion polymerization technique in the presence of a redox initiation system (1.5 mmol/L) at 70°C for 90 min to obtain grafted cotton with a graft yield of about 50%. The grafted cotton fibers were treated with four different concentrations of dibutylamines (DBAs) ranging from 1 to 4% and with a liquor ratio of 1 : 20 for 3 h at 80°C. The treated cotton samples were thoroughly washed with deionized water and dried at 50°C. Unmodified cotton (B), grafted cotton with GMA (G), grafted cotton with GMA–MMT (GM), and the four mentioned grafted cottons with DBA (GMAm$_1$, GMAm$_2$, GMAm$_3$, and GMAm$_4$) were subjected to different tools of characterization and evaluation. It is well known that imparting a *tert*-amino group to polymeric material such as starch, cellulose, and polyester would certainly affect their hydrophobic character to some extent.[26] The magnitude of the hydrophilic–hydrophobic properties of the modified polymer is greatly dependent on the number and type of alkyl groups attached to the nitrogen atom of the *tert*-amino group.

Nitrogen content

Figure 6 shows the relation between the nitrogen contents in the grafted cotton samples and the DBA concentrations used in the treatment of these samples. It was obvious that the nitrogen content increased with increasing DBA concentration from 1% (GMAm$_1$) to 3% (GMAm$_3$), after which, the nitrogen content decreased at 4% (GMAm$_4$). The increment of amine concentration led to more interaction via the opening of the epoxy functional group of GMA, according to Scheme 1.

After a DBA concentration of 3%, the nitrogen content decreased, which may have been due to the fact that the high amine concentration conferred a
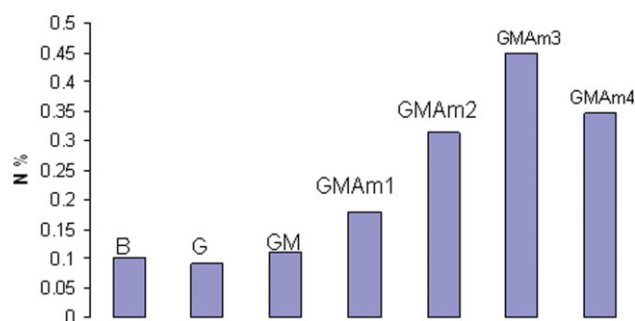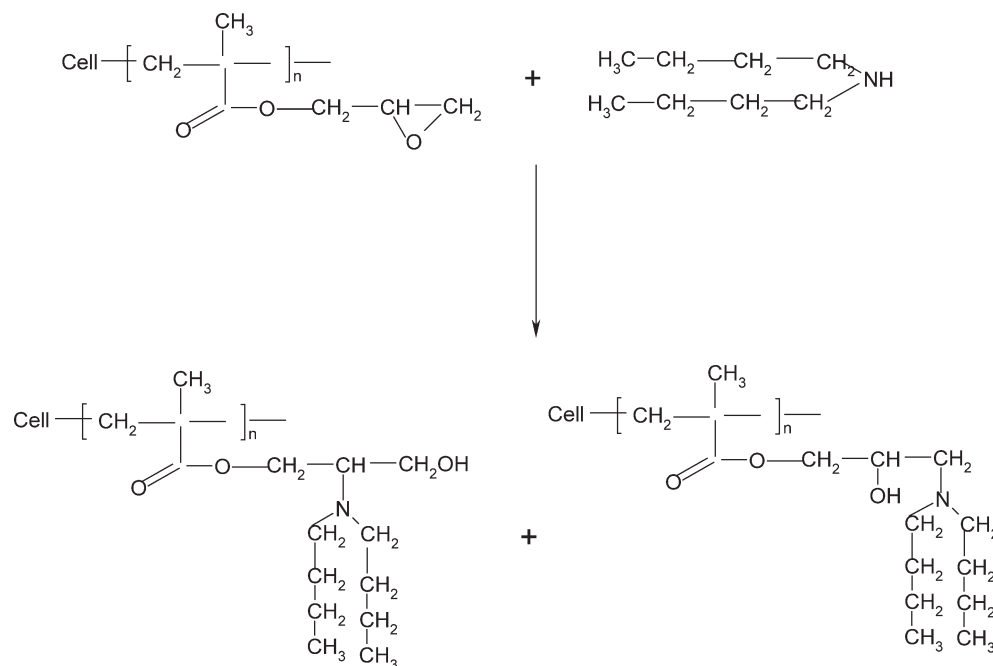

Figure 6 Nitrogen percentages of an unmodified cotton sample and treated samples. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Scheme 1

suitable basic medium, which affected the solubility of amino acids existing between the MMT clay interlayers.

Thermal stability

TGA is a simple and accurate method for studying the decomposition pattern and the thermal stability of a polymer. Figure 7 compares the TGA curves of samples B, G, GM, and GMAm$_3$ within the temperature range 50–500°C. The TGA results of the samples are listed in Table I, which shows that the degradation temperatures of sample GM were higher than that of
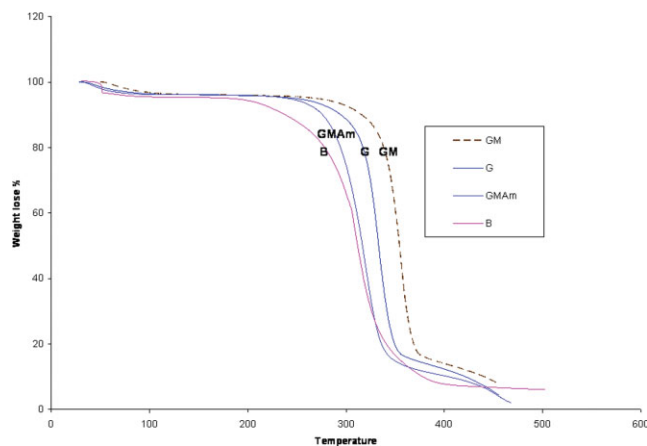
sample G because of the effective role of MMT clay in the increase of the thermal stability of the fibers. As clearly shown in the table, the degradation temperatures of sample G were higher than that of sample B, which could have mainly been related to the deposition of poly(glycidyl methacrylate) on the cotton fibers. On the other hand, it is obvious that sample GMAm$_3$ had a lower degradation temperature than samples G and GM, which could have been because of the degradation effect caused by the action of the medium pH, for the grafting bath for either the acidic GMA or alkaline DBA solution.

Mechanical properties

Table II shows the mechanical properties, expressed as the tensile strength, elongation (%) at F_{max} (the elongation at maximum force), and elongation (%) at

Figure 7 TGA thermograms of an unmodified cotton sample and treated samples. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE I
Degradation Temperatures of an Unmodified Cotton Sample and Treated Samples

Degradation temperature	B	GMAm$_3$	G	GM
$T_{10\%}$	237	275	294	315
$T_{30\%}$	295	304	325	346
$T_{50\%}$	311	316	333	354
$T_{70\%}$	325	327	341	361
$T_{90\%}$	377	404	421	440

$T_{10\%}$ = temperature of 10% degradation; $T_{30\%}$ = temperature of 30% degradation; $T_{50\%}$ = temperature of 50% degradation; $T_{70\%}$ = temperature of 70% degradation; $T_{90\%}$ = temperature of 90% degradation.

TABLE II
Variation of the Mechanical Properties, K/S Values, and Water Absorption of an Unmodified Cotton Sample and Treated Samples

Sample code	DBA concentration	Mechanical properties			K/S			Water absorption (%)		
		Tensile strength	Elongation at break	Elongation at maximum force	Acid dye	Basic dye	Reactive dye	30 min	60 min	120 min
B	—	230	24.7	25.7	1.18	0.63	1.71	92.43	109.98	126.50
G	—	252.9	26.4	26.3	2.65	1.45	1.47	81.84	88.15	98.70
GM	—	258.4	26.9	27.2	3.01	2.30	1.27	52.81	58.44	76.60
$GMAm_1$	1%	246.4	25.6	25.9	3.66	1.39	5.05	57.24	70.65	79.30
$GMAm_2$	2%	263.5	28.2	28.4	3.80	1.70	5.27	60.17	76.83	82.04
$GMAm_3$	3%	267.1	29.9	30.1	3.24	1.09	6.37	52.80	73.18	79.70
$GMAm_4$	4%	273.2	31.2	33.5	3.21	0.86	7.13	48.90	68.80	70.80

break, of the modified and unmodified cotton samples. As shown in the table, the tensile strength and elongation were increased after grafting with GMA, which may have been due to the plasticizing effect of GMA grafted in the matrix of the cotton, which increased again in the presence of MMT clay. Meanwhile, the tensile strength and the elongation of the grafted cotton sample treated by the DBA solution decreased at the 1% DBA concentration, which could have been because of the opening up of the cotton structure after interaction between the epoxy group of the GMA monomer and the amino group of DBA. Increasing the DBA concentration over 1% induced an observed increment in the tensile strength and elongation because of a substantial improvement in the uniformity of the interfiber structure via more deposition of the reacted amine compound inside the fiber matrix.

Water absorption

The $S\%$ values calculated from eq. (3) are listed in Table II; it is evident that $S\%$ decreased after grafting with GMA–MMT. The treatment of grafted cotton samples with different DBA concentrations was accompanied by an increase in the water absorption properties until a certain DBA concentration was reached, after which $S\%$ decreased again. The increase in the water absorption with increasing DBA concentration was ascribed to the pronounced effect of the created tertiary amino group with its superior hydrophilic character in the molecular structure of the cotton fibers. As the nitrogen content increased, the magnitude of the butyl alkyl group also increased, which caused the creation of hydrophobic centers at the cotton surfaces and prevented more water absorption.

SEM

Figure 8(a–d) shows SEM images of the untreated cotton sample (B), the sample grafted with GMA (G), the sample grafted with GMA–MMT (GM), and the grafted sample treated with DBA (GMAm) at
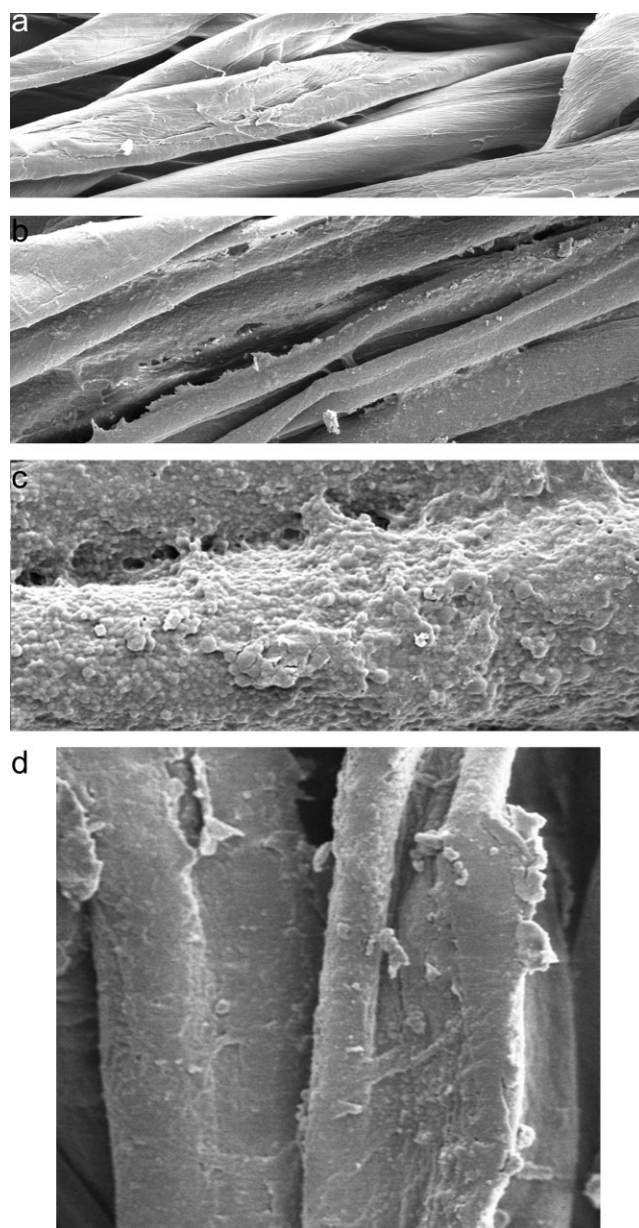

Figure 8 SEM images of (a) an unmodified cotton sample, (b) a cotton sample grafted with GMA, (c) a cotton sample grafted with GMA–MMT, and (d) a cotton sample grafted with GMA–MMT and treated with DBA.

1000× magnification. From the micrographs, it is clear that the untreated fibers were completely separated from each other, whereas in the grafted sample, full fibers were noticed, which may have been because of the formation of the fiber bundles between cotton and polymer during the polymerization process. Also, some aggregates of MMT clay were noticed on cotton fibers in the GM sample, which was good evidence for the success of the grafting process. For the micrograph related to the grafted cotton treated with DBA, we observed that the cotton surface showed smooth fibers and soft grain, and the fibers interfered with each other.

Color measurement

Seven sets of ungrafted cotton sample (B), cotton sample grafted with GMA (G), cotton sample grafted with GMA in the presence of MMT clay (GM), and cotton sample grafted with GMA in the presence of MMT clay and treated with different concentrations of dibutyl amine (GMAm$_1$–GMAm$_4$) were independently dyed with three types of dyestuff, namely, acid, basic, and reactive dyes. The dying properties, expressed as K/S, are illustrated in Figures 9–11 and are listed in Table II. For acid dye, the GM sample acquired an improvement in the K/S value compared with the G sample, and both improvements were greater than that of the unmodified sample. Moreover, the imparting of the tertiary amino group to the molecular structure of the cotton fibers via the reaction of the GM sample with DBA (up to a 2% DBA concentration) caused a considerable increase in the K/S value. The K/S values for the acid dyed cotton samples followed the descending order

$$\text{GMAm}_2 > \text{GMAm}_1 > \text{GMAm}_3 > \text{GMAm}_4$$
$$> \text{GM} > \text{G} > \text{B}$$

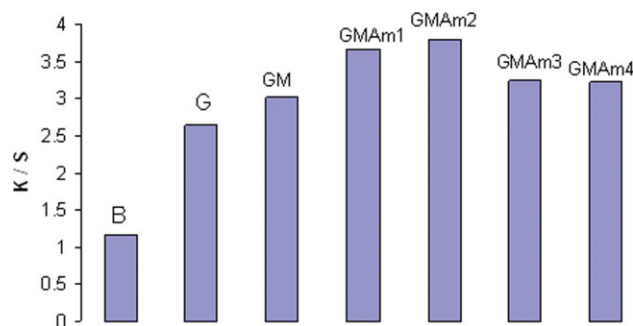The noticeable increment of the K/S values for the G, GM, and GMAm samples compared with that for

Figure 10 Effect of a basic dye on the K/S values of an unmodified cotton sample and treated samples. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
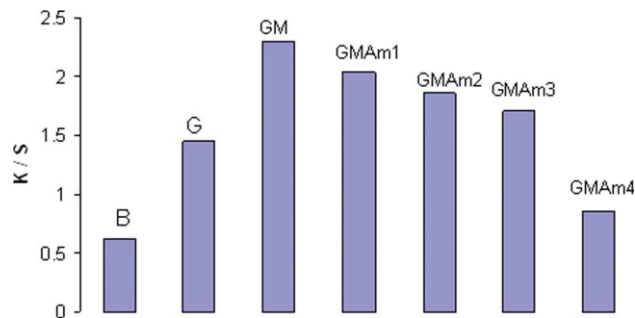
the unmodified sample could be due to the following aspects: (1) the opening of the structure of the cellulose cotton fibers through grafting and/or DBA treatment, (2) the direct interaction between the acid dye and GMA-containing cotton via the ring opening of epoxy groups, and (3) the increase in the magnitude of the acid dye accumulation and penetration through the GMAm samples due to the hydrogen bonding between the acid dye and additional basic tertiary amino functional group.[27] The gradual increase of the dying behavior from GMAm$_1$ to GMAm$_2$ could have been due to the relatively higher nitrogen content for GMAm$_2$ (Table II), which, in turn, brought a significant increase in the dye hydrogen bond interaction. On the other hand, the observed decrease in the K/S values for GMAm$_3$ and GMAm$_4$ could have been due to the blocking of the fiber porosity by dibutyl amine, which caused a limitation of dye penetration.

In case of basic dye, it is known that cellulose fibers have no affinity for basic dye, and even those that are adsorbed have low wet fastness. For adsorption, the fiber must possess acidic groups.[22] From the K/S values, it was obvious that the unmodified sample had quite a poor K/S value; the higher K/S value was observed after GMA, which had an acidic

Figure 9 Effect of an acid dye on the K/S values of an unmodified cotton sample and treated samples. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
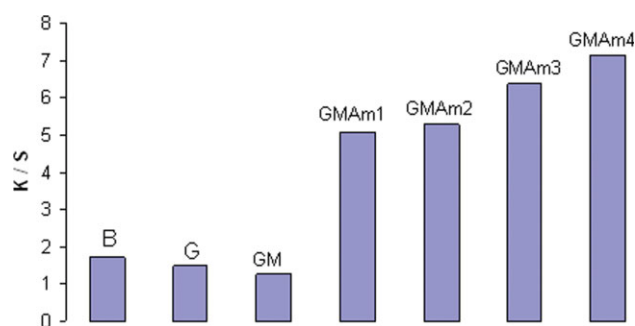

Figure 11 Effect of a reactive dye on the K/S values of an unmodified cotton sample and treated samples. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

group, was used. The samples that were treated by DBA had low K/S values; this was due to the repulsion forces between the alkali character of DBA and basic dye. The K/S values for the acid-dyed cotton samples followed the following descending order:

$$GM > G > GMAm_1 > GMAm_2 > GMAm_3$$
$$> GMAm_4 > B$$

For reactive dye, it is known that reactive dye has a good affinity toward cotton fabrics, in which dying proceeds through chemical bonding between the hydroxyl groups of the cellulose and the dye.[22] The K/S values for the reactive-dyed cotton samples followed the following descending order:

$$GMAm_4 > GMAm_3 > GMAm_2 > GMAm_1$$
$$> B > G > GM$$

From the values of K/S, it was clear that the GMAm samples had higher K/S values than the untreated one followed by the grafted samples, which had the lowest K/S values; this could be attributed to the repulsion force between the anionic epoxy content of the cotton and the anionic nature of the reactive dye. The enhancement in the K/S values with increasing nitrogen content could be simply have been due to the higher basicity of the cotton fabrics, which led to an increase in the extent of the nucleophilic substitution reaction between the dye molecules and cotton fabrics.[28]

CONCLUSIONS

Factors affecting the grafting polymerization of vinyl monomers onto cotton fibers

1. The grafting yield of GMA–MMT onto cotton increased gradually with increasing MMT clay weight percentage to attain a maximum at 10 wt % MMT clay and then decreased.
2. GMA–MMT showed a higher rate of grafting than MMA–MMT in all clay weight percentages.
3. The grafting yield of the GMA monomer onto cotton in the presence of MMT clay was higher than in the absence of clay with all of the factors studied, as follows:
   a. Temperature: The maximum grafting yield was observed at 70°C.
   b. Time: The rate of grafting started very fast and then tended to level off after 90 min.
   c. Initiator concentration: The grafting percentage increased rapidly as the initiator concentration increased to an initiator concentration of 1.5 mmol/L. Above this concentration, the grafting continued to increase but less rapidly

d. Monomer concentration: The grafting yield increased with increasing monomer concentration within the range studied with no noticeable leveling for the grafting.

Characterization of cotton fibers grafted with GMA monomer in the presence of double-modified MMT clay and treated with dibutyl amine

1. Nitrogen content: The nitrogen content increased with increasing DBA concentration from 1% (GMAm_1) up to 3% (GMAm_3), after which the nitrogen content began to decrease at 4% (GMAm_4).
2. Thermal stability: The degradation temperatures of the GM sample were higher than that of the G sample, whereas the degradation temperatures of the G sample were higher than that of the B sample. On the other hand, it was obvious that the GMAm_3 sample had a lower degradation temperature than the G and GM samples.
3. Mechanical properties: The tensile strength and elongation increased after grafting with GMA and increased again in the presence of MMT clay, whereas increasing the DBA concentration over 1% induced an observed increment in the tensile strength and elongation.
4. Water absorption: S% decreased after grafting with GMA–MMT. The treatment of grafted cotton samples with different DBA concentrations was accompanied by increasing water absorption properties up to a 2% DBA concentration, after which S% decreased again.
5. SEM: The untreated fibers were completely separated from each other, whereas full fibers were noticed in the grafted sample. Also, some aggregates of MMT clay were noticed on the cotton fibers in the GM sample, and the cotton surface showed smooth fibers in the grafted cotton treated with DBA solution.
6. Color measurement: Three types of dyestuff were used:
   a. Acid dye: $GMAm_2 > GMAm_1 > GMAm_3 > GMAm_4 > GM > G > B$.
   b. Basic dye: $GM > G > GMAm_1 > GMAm_2 > GMAm_3 > GMAm_4 > B$.
   c. Reactive dye: $GMAm_4 > GMAm_3 > GMAm_2 > GMAm_1 > B > G > GM$.

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