

Preparation and Thermal Analysis of Cotton–Clay Nanocomposites

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Received 28 December 2002; accepted 18 November 2003

ABSTRACT: Nanocomposites were produced from cotton with montmorillonite clay used as the nanofiller material. Three exfoliation and intercalation methods with different solvents and clay pretreatment techniques were tested for the production of these organic–inorganic hybrids. The method that resulted in superior clay–cotton nanocomposites used a clay pretreatment with 4-methylmorpholine-*N*-oxide as the cotton solvent. The nanocomposites showed significant improvements in the thermal properties in comparison with unbleached cotton and cotton processed under

the conditions for nanocomposite preparation. The degradation temperature of the nanocomposites increased by 45°C, and the char yields for some compositions were twice those of unbleached cotton. The crystalline melt of the materials decreased by 15°C. Future research will include the development of textiles based on these cotton–clay materials and testing for flame-retardant properties and product strength. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 2125–2131, 2004

Key words: nanocomposites; flame retardance

INTRODUCTION

Over the last decade, polymer–clay nanocomposites have been the subject of much research interest. Nanostructured organic–inorganic composites are mixed on a nearly molecular level and behave much differently than conventional composites. They show large increases in their performance properties with the addition of small amounts of an inorganic filler material. The literature reports the use of montmorillonite clays as fillers for nanocomposites in which the matrix polymers are synthetic polymers, such as polyimides,¹ polyamides,² methacrylates,^{3,4} and polystyrene.⁵ Montmorillonite clays have a large surface area. This provides a large interfacial region in the nanocomposites, and the enhancement of tensile and thermal properties occurs at a very low percentage of incorporation of the clay filler material.

A recent article describes the development of flame-retardant textiles from the well-established polyamide 6 (nylon 6)/clay hybrid nanocomposite system.⁶ The polyamide 6/clay nanocomposite was melt-spun into a multifilament yarn used to construct a knit fabric. This textile showed a 40% decrease in the heat release rate in comparison with pure polyamide 6.

Cotton is the most important textile fiber for apparel use and is preferred over synthetic fibers for reasons such as comfort and feel.⁷ 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 wear. Most of these finishes have been developed for products that are not laundered, such as drapery and furnishing fabrics.^{8–14} In this article, the development of cellulose–clay nanocomposites for use as flame-retardant materials based on cotton is reported. These materials are designed to take advantage of the thermal stability and flame resistance imparted by silicate filler materials and should require no fire-retardant finish.

EXPERIMENTAL

Materials

Cotton linters and card waste, short-fiber cotton by-products of the milling process, were obtained from a laboratory scale mill operated by the Cotton Textile Engineering Research Unit at the Southern Regional Research Center (New Orleans, LA). All other materials were purchased from Aldrich Chemical Co. (Milwaukee, WI) and were used without further purification.

Instrumentation

Thermogravimetric analysis (TGA) was performed with a TA Instruments Hi-Res TGA 2950 (New Castle,

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DE). The samples were heated to 120°C and held isothermally for 1 h to normalize the moisture content. After air cooling, scans were run from 40 to 600°C at a heating rate of 10°C/min. Differential scanning calorimetry (DSC) was performed on a Mettler–Toledo DSC 821 (Columbus, OH). Temperature scans were run from 30 to 300°C at a heating rate of 5°C/min. X-ray diffraction experiments were performed at the University of New Orleans. Transmission electron microscopy (TEM) was performed at the University of Southern Mississippi.

Nanocomposite preparation

Cotton nanocomposites containing 0–15 wt % montmorillonite clay as a filler material were prepared in batches of 1–2 g according to the following procedures.

Method 1

Montmorillonite clay was exfoliated by rapid stirring in a 50% solution of 4-methylmorpholine *N*-oxide (MMNO) in deionized (DI) water in a 500-mL, three-necked, round-bottom flask under the ambient conditions. After 1 h of stirring, the solution became clear, and cotton was added to the flask. The cotton–clay–MMNO solution was heated to reflux with continued rapid stirring. After 1–2 h, the cotton dissolved. The resulting solution was viscous and amber in color. The flask was removed from the heat immediately, and the material was reprecipitated into acetonitrile. The material was filtered and washed again in acetonitrile; this was followed by three washes in DI water. The samples were dried overnight at 120°C *in vacuo*.

Method 2

Montmorillonite clay was pretreated with the ammonium salt of dodecylamine according to a previously published procedure.¹ The pretreated clay was then used in the following procedure. The pretreated montmorillonite clay was stirred rapidly in MMNO. After 30 min of stirring, cotton was added to the flask. The cotton–clay–MMNO solution was heated to reflux with continued rapid stirring. Approximately 1 h after reflux was reached, the cotton was dissolved. The viscous, amber-colored solution was removed from the heat and reprecipitated into acetonitrile. The material was filtered and washed a second time in acetonitrile. After filtration, the material was washed twice in DI water. After the final wash and filtration, the samples were collected and dried *in vacuo* at 120°C.

Method 3

An additional nanocomposite preparation method was performed, with the procedure described in

method 2, through the replacement of MMNO with a lithium chloride (LiCl)/dimethylacetamide (DMAc) solution.¹⁵

For each successful method of preparation, an aliquot of the solution was removed from the flask of the hot solution and pressed between glass slides to form films. The slides were submerged in acetonitrile and soaked for 1 h. After removal from the solvent, the slides were submerged in DI water and soaked. The cover slides were then removed, and the films were dried on the remaining piece of glass. The films were removed from the glass with a new razor blade.

Powder forms of the nanocomposites suitable for X-ray diffraction studies were produced by the precipitation of the hot solution into acetonitrile. The precipitate was filtered and washed three times in DI water for the removal of residual acetonitrile. Blocks of the nanocomposites were formed by the hot solution being poured into a Petrie dish. The solution solidified into a cakelike form upon cooling. The nanocomposite blocks were dried under heat and vacuum and then soaked in acetonitrile in an attempt to remove MMNO from the composite; this was followed by redrying under heat and vacuum.

RESULTS AND DISCUSSION

There are several strategies available for nanocomposite preparation. The four main processes are exfoliation and adsorption (exfoliation of the clay in a solvent in which the polymer is soluble), *in situ* intercalative polymerization (swelling of the clay with a monomer and subsequent polymerization), melt intercalation (mixing in the high-energy molten state), and template synthesis (formation of the silicate *in situ*).¹⁶ Because cellulose in cotton is a highly crystalline high-molecular-weight biomaterial that does not melt before the onset of decomposition, it was necessary to use exfoliation and adsorption as our preparatory method.

Cotton fiber, after ginning and mechanical cleaning, is approximately 95% cellulose, the remaining 5% being mostly naturally occurring waxes, proteins, and sugars. Its high degree of crystallinity and high molecular weight make it soluble in few solvents, most of which are complex and unusual. These include metal complexes such as cupriethylenediamine hydroxide, aqueous salt complexes such as saturated zinc chloride and calcium thiocyanate, and nonaqueous salt complexes such as LiCl/DMAc.⁷

The formation of montmorillonite-clay-filled cotton nanocomposites by exfoliation and adsorption was attempted in three ways. The first method involved the exfoliation of the clay in MMNO with no pretreatment. Because of the structure of the solvent (Fig. 1) and its similarity to the intercalation agents often used for montmorillonite clays,¹⁶ it was theorized that the exfoliation of the layers of silicate sheets making up

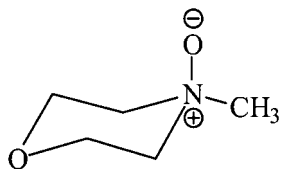


Figure 1 Structure of MMNO.

the clay and subsequent intercalation by the cellulose polymer could be carried out as a one-pot formulation. However, X-ray diffraction studies indicated that the clay was not exfoliated by this method. Although the resulting cotton-clay materials prepared by this method did show an increase in the thermal stability in comparison with untreated cotton, it was expected that the increase would be more pronounced in true nanocomposites because of the nanoscale interactions between the clay and cellulose. It is likely that this method failed to exfoliate the clay because the cyclical MMNO molecules have a molecular size too small to change the *d*-spacing between the silicate layers significantly.

The second method of composite preparation involved a traditional pretreatment of the clay with the ammonium salt of dodecylamine to separate the silicate sheets of the montmorillonite before stirring in MMNO. X-ray diffraction studies showed that the diffraction peaks for the montmorillonite clay were not present in the nanocomposites (Fig. 2). This dem-

onstrated a loss of the long-range pattern in the inter-layer spacing of the silicate sheets that made up the clay; in other words, exfoliation of the clay took place when this method was used, and this indicated that the desired nanoscale organic-inorganic hybrid had been formed. TEM was used to confirm this result. The TEM micrographs obtained indicated that the montmorillonite clay was fully exfoliated within the cotton cellulose matrix.

The third method involved the use of the LiCl/DMAc solvent system. LiCl/DMAc has been established as a solvent for cellulose,¹⁵ and DMAc is a traditional solvent used in the dissociation of montmorillonite clay after pretreatment with the ammonium salt of dodecylamine.¹ The cotton used in these experiments did not dissolve in LiCl/DMAc. A recently published article indicates that with the high-molecular-weight cellulose found in cotton, more rigorous conditions are required with this solvent system before dissolution can occur.¹⁷

With the model of composite types arising from the interactions of layered silicates and polymers put forth by Alexandre and Dubois¹⁶ (Fig. 3), the materials produced with methods 1 and 2 can be classified. The increase in the thermal stability, coupled with the lack of evidence for the exfoliation of the layered silicates seen in the composites produced in method 1 (no pretreatment of the clay), strongly suggests that a microcomposite was formed. The improved properties and clay exfoliation seen in the composites result-

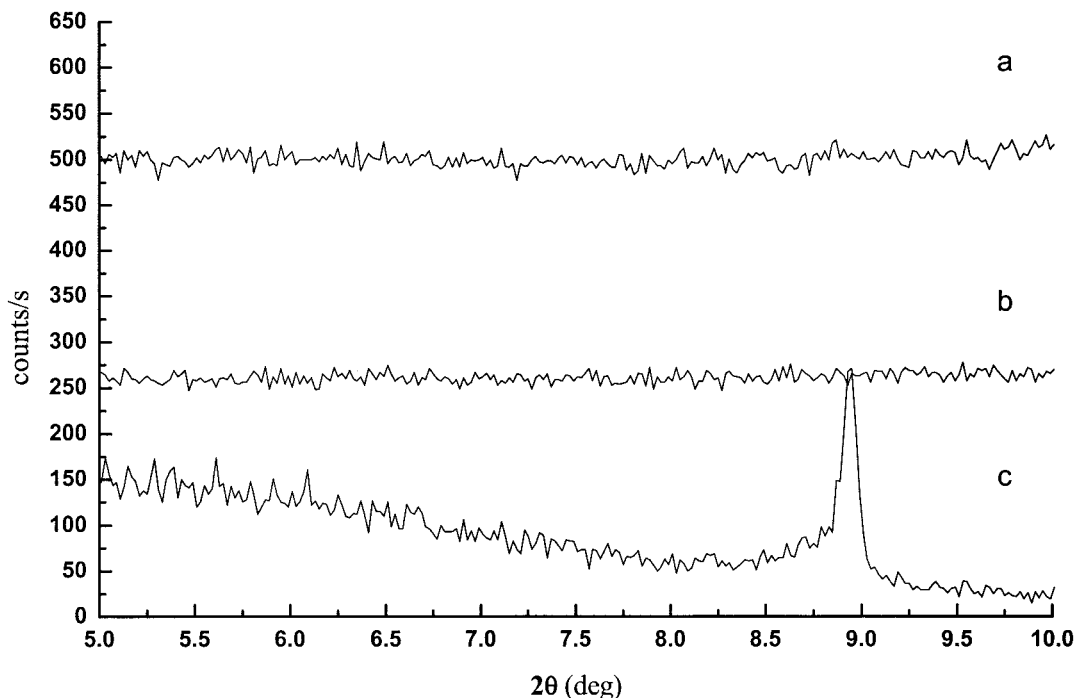


Figure 2 XRD patterns of (a) the control cotton sample, (b) the nanocomposite with 15% montmorillonite filler, and (c) the montmorillonite clay.

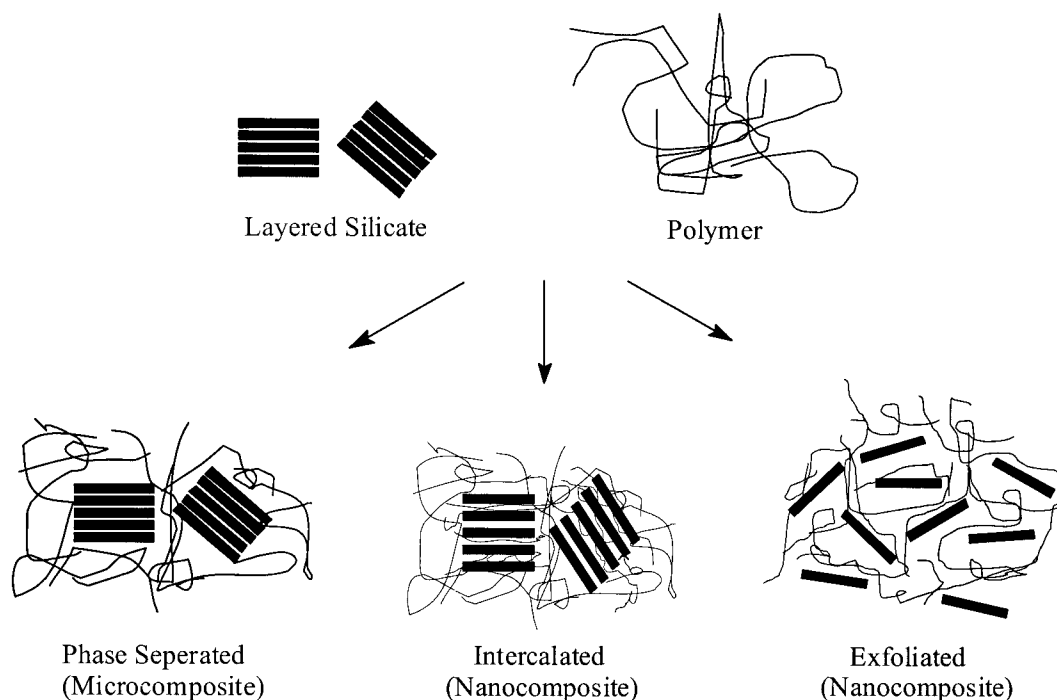


Figure 3 Schematic of the different types of composites arising from the intercalation of layered silicates and polymers: phase-separated composites (microcomposites), intercalated nanocomposites, and exfoliated nanocomposites.

ing from method 2 (the pretreatment of the clay with dodecylamine) indicates that these materials are true exfoliated nanocomposites. Qualitatively, the nanocomposites prepared by method 2 were superior to the composites prepared by the other methods in both strength and reduced water uptake. The nanocomposite materials produced by method 2 are the focus of the rest of this article.

After drying, the films produced from these nanocomposites were opaque, brittle, and difficult to remove from the glass intact. When exposed to atmospheric conditions, the films quickly absorbed moisture from the air and became transparent and more pliable. The powdered form of the nanocomposites was uniform and white, even after exposure to atmospheric conditions. Powdered and film forms of the nanocomposites did not show any deviation from the water uptake behavior expected from untreated cotton. The larger blocks (Fig. 4), however, took up excessive amounts of water from the atmosphere. The large water uptake in the nanocomposite blocks was due to residual MMNO in the material after processing. This problem could be alleviated by more meticulous workup of the material to ensure that the hydroscopic solvent is removed completely.

TGA was performed on these materials as a basic measure of their thermal stabilities. The temperature of degradation (T_{dec}), defined as the 10% weight loss, for processed cotton containing no filler was 282°C. The addition of the montmorillonite clay as a filler in

amounts as small as 1% increased T_{dec} to 325–327°C (Fig. 5). This significant increase in the thermal stability at low filler contents is a common property of synthetic polymer–clay nanocomposites. It appears that the mechanism of thermal degradation in this naturally occurring polymer is similarly inhibited by the presence of the exfoliated silicate sheets.^{16,18}



Figure 4 Photograph of a cotton–clay nanocomposite. The nanocomposite sample depicted had a diameter of 4 in.

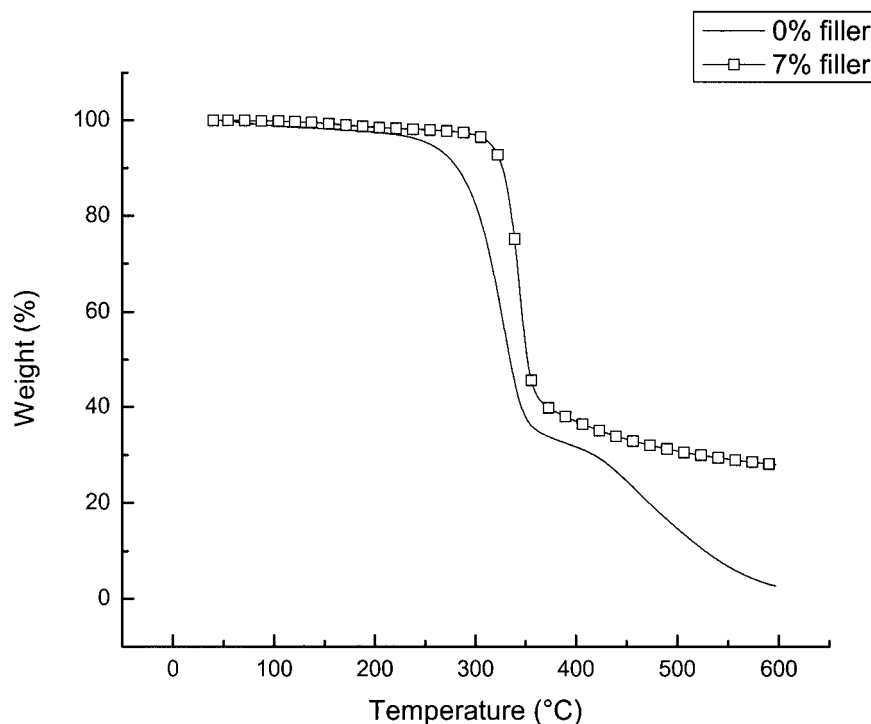


Figure 5 TGA thermograms comparing the control sample with 0% filler to the nanocomposite containing 7% filler.

The final char yields of the materials with various filler compositions are also significantly different (Fig. 6). Materials with 1, 2, and 3% filler showed slight

increases in the char residue in comparison with cotton processed under similar conditions. The char yields shown for these compositions are, however,

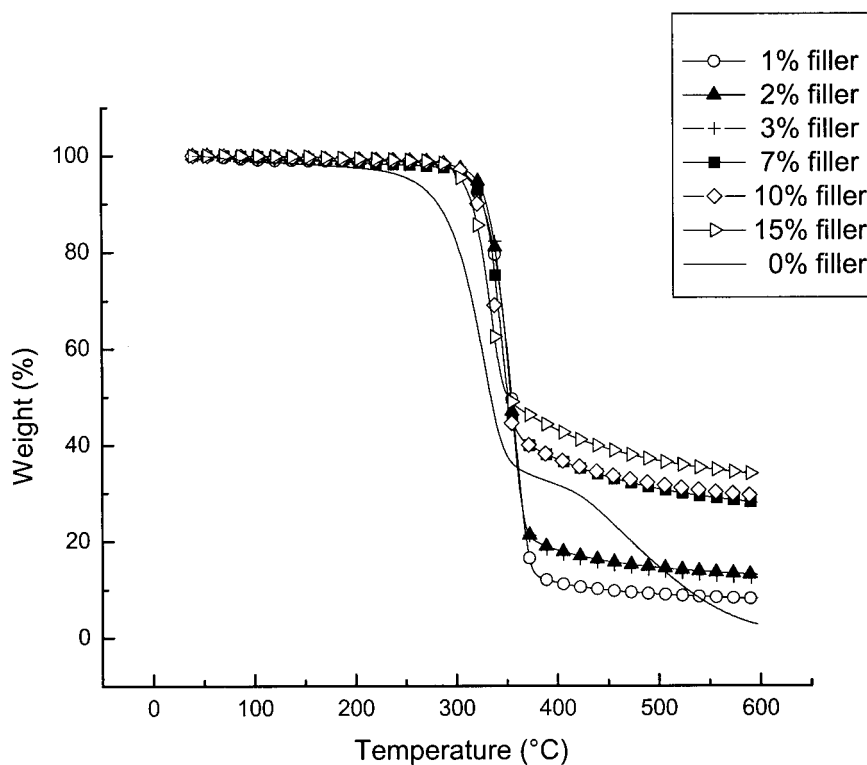


Figure 6 TGA thermograms comparing nanocomposites with various filler contents.

TABLE I
Char Yields of Nanocomposites with Various Filler Contents

Sample (wt % clay)	T_{dec} (°C)	Char yield (%)
0	326	3
1	327	8
2	331	12
3	327	13
7	327	28
10	321	30
15	316	34

very similar to those found in unbleached cotton. The nanocomposites that contained 7, 10, and 15% filler showed char yields of around 35% of the material starting weight. All char yields are listed in Table I.

The formation of char in TGA experiments is one measure of flame retardancy. Previous publications have reported that the flame-retardant effect found in synthetic polymer–clay nanocomposites arises from the formation of char layers, which comes from the collapse of exfoliated and/or intercalated structures within the nanocomposites. The silicate structure is believed to act as an insulator and a mass transport barrier, slowing the escape of volatile decomposition products. This appears to hold true for these naturally occurring polymer–clay nanocomposites as well.

In the DSC analyses, no glass-transition temperature (T_g) was found below the onset of decomposition for any of the materials tested, including the control

sample with 0% filler. This is a typical result for cotton. Cotton cellulose has a high degree of crystallinity and limited untethered amorphous content and, therefore, rarely shows a T_g in DSC thermograms. The nanocomposite material had a crystalline melting temperature (T_m) about 15°C lower than that of the control sample (186 vs 172°C; Fig. 7). The control cotton sample, which underwent dissolution in MMNO, was probably a mixture of cellulose II and cellulose III.⁷ These thermal data indicate the possibility that the addition of the clay filler changed the crystal structure of the cellulose. More intensive crystallography work will be necessary to confirm this change and to determine unit cell dimensions.

It must be noted that T_m for the control sample was low; a crystalline melt is not typically seen in cotton until 250–270°C, near T_{dec} .¹⁹ Because of the relatively low T_m value of the control cotton sample, gel permeation chromatography was attempted on untreated cotton and control samples of cotton that had undergone preparation and processing identical to that of the nanocomposites (0% filler). This was done to determine if the heat treatment or solvent effects were causing significant chain scission resulting in lower molecular weight cellulose. No molecular weights were obtained, but the solution viscosities indicated that the processed sample was lower in molecular weight than the unprocessed sample. The dissolution of cellulose often causes some degree of chain scission. Because of the high molecular weight of cotton cellulose (the weight-average molecular weight is often

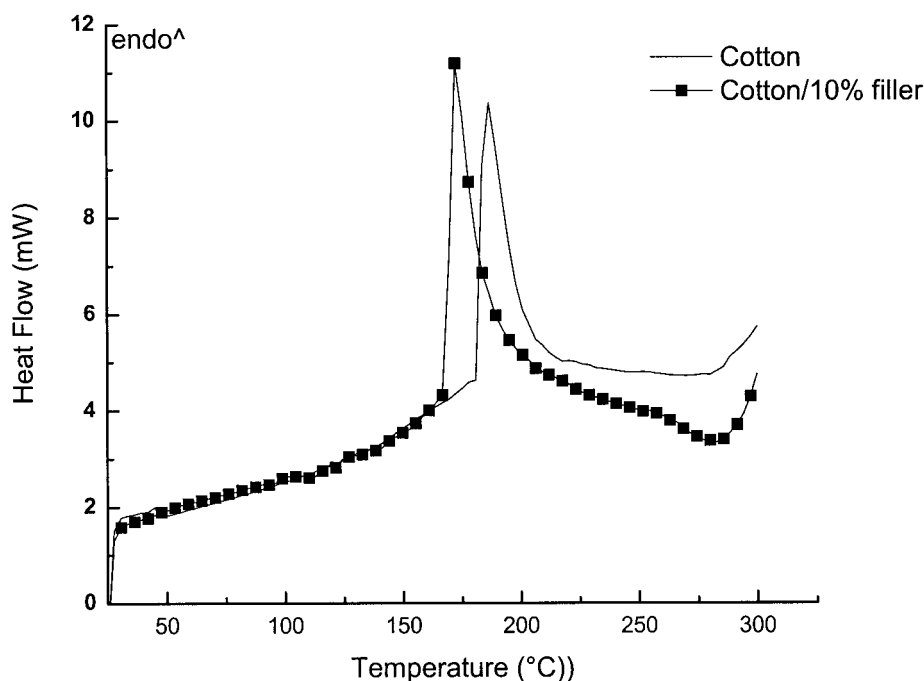


Figure 7 DSC thermograms of cotton nanocomposites with 0 and 10% filler.

reported in the range of $1.5\text{--}3 \times 10^6$), a reduction in the molecular weight due to chain scission is not likely to cause a significant reduction in the final properties.^{7,17}

CONCLUSIONS

Nanocomposites have been produced from cotton, with montmorillonite clay used as the nanofiller material. Three intercalation and exfoliation methods were tested for the production of these organic-inorganic hybrids. The LiCl/DMAc method was unsuccessful. The use of clay without pretreatment produced microcomposite materials. The most successful method of nanocomposite preparation used the pretreatment of the montmorillonite clay with an alkyl amine salt and dissolution with MMNO, which produced a true nanocomposite material. These materials showed a 45°C increase in T_{dec} with all tested filler contents. Nanocomposites at all filler contents also showed a major increase in the char formation, more than doubling the residue yields seen in unprocessed cotton samples.

Future research will include the development of a small-scale wet spinning apparatus to produce fibers from these nanocomposites materials with 5–7% filler for optimum improvements in the thermal properties. Ultimately, these fibers will be used to construct fabrics that will be evaluated for strength properties and flame resistance.

The author gratefully acknowledges John Wiley from the University of New Orleans for performing X-ray diffraction on these materials and Kenneth Mauritz for performing transmission electron microscopy.

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