



PREPARATION AND CHARACTERIZATION OF CELLULOSE/CLAY NANOCOMPOSITES

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INTRODUCTION

Over the last decade, polymer-clay nanocomposites have attracted much research interest. Nanostructured organic-inorganic composites are combined on a near molecular level. The resultant composite materials behave much differently than conventional composites. The materials show large increases in performance properties with the addition of small amounts of inorganic material. The literature reports the use of montmorillonite clays as fillers for nanocomposites in which the matrix was synthetic polymers such as polyamides¹, methacrylates², and polystyrene³.

Recent research has described the development of flame retardant textiles from the well-established polyamide-6 (Nylon 6)/clay hybrid nanocomposite system.⁴ The presented research reports the development of cotton/clay nanocomposites. Such nanocomposites have the potential to be used in flame retardant textiles. Montmorillonite clays have a large surface area, which provides a substantial interfacial region in the nanocomposite that is expected to lead to an enhancement in tensile and thermal properties of cotton fiber at very low percent addition of the filler material.

Experimental

Materials. Cotton linters and card waste were obtained from the Cotton Textile Engineering Research Unit at the United States Department of Agriculture's Southern Regional Research Center. All other materials were purchased from Aldrich Chemical Co. and used without further purification.

Instrumentation. Thermogravimetric analyses (TGA) were performed on a TA Instruments Hi-Res TGA 2950. Samples were heated to 120 °C and held isothermally for 1 h to remove moisture. After air cooling, scans were run from 40 °C to 600 °C at a heating rate of 10 °C/min. Differential scanning calorimetry (DSC) was performed on a Mettler Toledo DSC 821. Temperature scans were run from 30 °C to 300 °C at a heating rate of 5 °C/min. X-ray diffraction was performed at the University of New Orleans.

Nanocomposite preparation. Cotton nanocomposites utilizing 0-15 weight percent montmorillonite clay as filler

material were prepared in batches of 1-2 grams of material 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 neck round bottom flask at 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 hours, the cotton dissolved. The resulting solution was viscous and amber in color. The flask was removed from heat immediately, and the material was reprecipitated into acetonitrile. The material was filtered and washed for a second time in acetonitrile, followed by three washes in DI water. The samples were dried overnight at 120 °C under vacuum.

Method 2: Montmorillonite clay was pre-treated with the ammonium salt of dodecylamine according to a previously published procedure.¹ The pre-treated clay was then used in the following procedure. Pre-treated 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 reaching reflux, the cotton was dissolved. The viscous amber colored solution was removed from 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 under vacuum at 120°C.

Method 3: An additional nanocomposite preparation method was performed, using the procedure described in method 2, but replacing the MMNO with a lithium chloride/dimethylacetamide solution.⁵

For each successful method of preparation, an aliquot of solution was removed from the flask while the solution was still hot 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. One slide was then removed and the film was dried on the remaining piece of

glass. The films were removed from the glass using a new razor blade.

Thermal analyses by TGA and DSC were performed on all materials produced.

Results and Discussion

Formation of montmorillonite clay-filled cotton nanocomposites was attempted by three methods. The first method involved exfoliation of the clay in MMNO with no pretreatment. Due to the structure of the solvent (Figure 1), it was theorized that exfoliation of the layers of silicate sheets making up the clay and subsequent intercalation by the cellulose polymer could be carried out as a "one pot formulation". X-ray diffraction studies indicated that the clay was not exfoliated by this method. Although the resulting cotton/clay materials did show an increase in thermal stability when compared to untreated cotton, it was expected that the increase would be more substantial in true nanocomposites due to the nanoscale interactions of the clay and cellulose polymer.

The second method of composite preparation involved pre-treatment of the clay with the ammonium salt of dodecylamine to separate the silicate sheets of the montmorillonite prior to stirring in MMNO. X-ray diffraction studies showed that exfoliation of the clay had taken place with this method, indicating that the desired nanoscale interactions had occurred.

The third method attempted involved the use of the LiCl/DMAc solvent system. LiCl/DMAc has been established to as a solvent for cellulose⁵, and DMAc is a traditional solvent used in dissociation of montmorillonite clay after pretreatment with the ammonium salt of dodecylamine.¹ We were unable to dissolve the cotton cellulose in LiCl/DMAc. A recently published paper indicates that with the high molecular weight cellulose found in cotton, this solvent system requires more rigorous treatment to allow dissolution.⁶

TGA was performed on these materials (Figure 2). The various compositions showed no significant change in decomposition temperature compared to cotton treated under the same conditions with 0% filler added. However, the final char yields of the materials of varying compositions are significantly different. Materials containing 7%, 10%, and 15% filler showed char yields of around 40% of the material starting weight. In the DSC analyses, no glass transition temperature (T_g) was found below the onset of decomposition for any materials tested, including the control sample with 0% filler. Furthermore, the addition of the clay did not seem to affect the crystalline melt that occurs in cellulose only at the onset of decomposition. The nanocomposites were superior to earlier composites in strength and reduced water uptake.

After drying, the films produced from these nanocomposites were opaque and brittle. Upon exposure to atmospheric conditions, the films quickly absorbed moisture from the air and became more pliable and transparent.

Conclusions

Nanocomposites have been produced from cotton with montmorillonite clay used as the nanofiller material. Various exfoliation and intercalation methods were attempted in production of these organic-inorganic hybrids. The resulting nanocomposites show improvements in thermal properties when compared with cotton itself. Future research will include the production and characterization of fibers from these cotton/clay materials and testing for flame retardant properties and product strength.

FIGURES AND TABLES

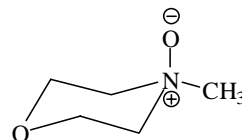


Figure 1. Structure of 4-methyl morpholine oxide

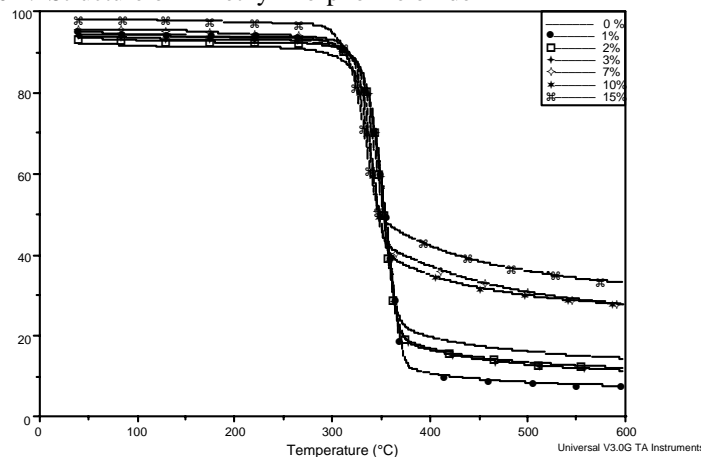


Figure 2. TGA thermograms of cotton/clay nanocomposites

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