Modification of Montmorillonite with a Cationic Softener for Finishing Cotton Fabric with Hand Builder Performance

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Abstract

Montmorillonite (Mont) was modified by cationic exchange with the cationic softener TEGO 28 (Di-Palm carboxyethyl hydroxyethyl methyl ammonium methosulfate). XRD analysis suggested that intercalation occurred in the modified Mont (mMont). Softening finishing solutions composed of pure TEGO 28 with and without mMont were treated on cotton fabrics by the pad-dry method and then evaluated for stiffness, whiteness, tear strength and thermal stability. TEGO 28 treatment alone increased the stiffness property of the finished fabrics, and this was increased further by the co-inclusion of mMont at 3 and 5% (w/v), but higher or lower mMont concentrations led to a marked and slight, respectively, reduction in stiffness, especially at 15% (w/v) mMont. The degree of whiteness of the finished fabrics decreased slightly with the addition of TEGO 28 alone and was further slightly decreased in a dose-dependent manner with the co-addition of increasing concentrations of mMont. In contrast, the tear strength and thermal stability of the finished fabrics both increased with increasing concentrations of mMont in the softening finishing solution.

Key words: Hand builder, Montmorillonite, Textile finishing, Softener, Stiffness

Introduction

In recent years, polymer nanocomposites have received considerable interest because of their superior thermal and mechanical properties. Polymer-clay nanocomposites are a class of hybrid materials composed of organic polymer matrices and nanoscale organophilic clay fillers. Of the nanoscale clays, montmorillonite (Mont) ⁽¹⁻ ³⁾ is of particular interest and has been widely used as a reinforcing material for polymers. The morphology of Mont is platelet, with a thickness of less than 1 mm and a width of between 100 nm and 1 µm. This morphological structure provides Mont with a very high surface area, and a high aspect ratio. These, and other properties, give Mont an advantage as a suitable compound for use as a reinforcing material. To this end the inorganic surface of Mont can be modified, for example with organic quaternary ammonium, to improve the organophilicity and provide more interactions with polymers ⁽⁴⁾. Quaternary amine is one type of cationic softeners that contains a nitrogen ion and possesses the ability to modify Mont so as to become organoclay Softeners are

Textile finishing, as the last step of textile processing, involves the addition of chemicals to textiles to achieve a product with the desired characteristics, such as tear resistance, softness, flame retardancy and color, depending on the application and requirement of the customer. Hand building finishes ⁽⁵⁻⁸⁾ is one of the most important types of final stage textile finishing. The main effects of altered fullness and stiffness that can be attained enable a very large diversity in hand design. Quaternary ammonium sulfate is a cationic softener normally used in textile finishing for providing the softness on the finished cotton fabric. In this study, di-(palm carboxyethyl) hydroxyethyl methyl ammonium methosulfate (TEGO 28) was used as a cationic softener to modify the inorganic surface of Mont. The modified Mont was then used as a component of a softening finishing agent for cotton fabrics. A new approach by adding modified Mont in softening finishing agent may provide several characteristics on finished cotton fabrics. Therefore, the objective of this study was to investigate the possibility of modifying Mont with TEGO 28 in order to use this modified Mont in

the finished product properties, and in particular for providing the desired increase in stiffness or firmness on cotton fabrics.

Materials and Experimental Procedures

Materials

The desized, scoured, and bleached plain weave cotton woven fabric used in this study was purchased from BekerTex Co., Ltd. The fabric count (65 x 60, 2.5 cm²) and weight (4.04 oz/yd²) were determined in house. Natural sodium montmorillonite was obtained from the Thai Nippon chemical industry Co., Ltd. Di-(Palm carboxyethyl) Hydroxyethyl Methyl ammonium Methosulfate (TEGO 28) was supplied from the V.P.C. Group, Bangkok, Thailand.

Modification of MMT with TEGO 28

TEGO 28 solutions at 1, 2 and 3% (w/v) were prepared in distilled water by vigorously stirring at 80°C for 30 minutes. Mont was separately dispersed in distilled water at 1.0 g/ 10 ml, and stirred for 30 minutes to homogeneity prior to addition into each softening solution. The TEGO 28 – Mont mixture was stirred with a high speed mixer at 2000 rpm for 1 hour and then filtered, washed with hot water and oven dried at 105°C for 24 hours. The dried and cooled TEGO modified Monts were then ground with a grinder and sieved with a nominal particle size of 120 mesh.

Preparation of the Softening Finishing Solution and Treatment of Fabrics

Various amounts, ranging between 1 and 15% (w/v), of modified Mont were used as a constitution in the softening finishing solutions, and were prepared by mixing the desired amount of modified Mont with 8% (w/v) of TEGO 28 solution. The mixture was stirred vigorously for 20 minutes and was then ready to be used to finish cotton fabrics, and in this work was applied by the pad-dry method.

Cotton fabrics were separately impregnated in each test aqueous softening finishing solution for 10 minutes, padded to give a wet pickup of about 80-90%, and then dried at 100°C for 3 minutes.

X-ray Diffraction (XRD) and Fabric Evaluation

The X-ray patterns of pure Mont and TEGO 28 modified Monts were obtained with the use of a Rigaku Rint 2000 DMX diffractometer with monochromatic Cu- K_{α} radiation.

Stiffness, tear strength and whiteness properties of untreated and finished cotton fabrics were evaluated by standard methods; specifically ASTM D 1388-96, AATCC 110-2000 and ASTM D 2261-96 for stiffness, whiteness and tear strength, respectively. Note that the tear strength and stiffness tests were carried out in the warp direction.

Thermal Stability Analysis

Thermogravimetric analyses (TGA) were performed with METLER TOLEDO TGA/SDTA 851^e. Cotton fabrics for testing were placed in the balance system and heated from 50 to 1000°C at a heating rate of 20°C/min in a nitrogen atmosphere.

Results and Discussion

Structural Properties of Modified Mont

The basal peak position, d-spacing and XRD patterns of pure Mont and of Mont modified by three different concentrations of TEGO 28 are summarized in Table 1 and Figure 1. Pure Mont shows a strong diffraction peak typically at 7.08 A°, corresponding to a basal spacing layer of 12.49 A°. However, after modification with TEGO 28 at the three different concentrations, the diffraction peak of the modified Monts at 2θ = 7.08 A° disappeared and was instead substituted by a different basal peak position, located within 1.39 to 1.47 A°, the 2 theta value decreasing slightly with increasing modifying TEGO 28 concentration. The correspondingly, and significantly, larger interlayer values for these three different modified Monts in comparison with pure Mont indicate the likely formation of an intercalated nanostructure. The modified Mont derived from 3% (w/v) TEGO 28 treatment had the lowest diffraction peak (highest interlayer spacing), indicating that the softener chains were intercalated into the silicate layers and the coherent order of Mont-Na⁺ was destroyed the most. Therefore, 3% (w/v) TEGO 28 modified

Mont was selected to be used in the softening finishing solution used to finish cotton fabrics by the pad-dry method in all further studies reported here, and is simply referred to as mMont hereafter.



Figure 1. X-ray patterns of pure Mont and TEGO 28 modified Mont.

Table 1. Basal peak position and d-spacing ofpure Mont and TEGO 28 modifiedMont.

Amount of TEGO 28	Basal peak position (2θ)	d-spacing (A°)
0	7.08	12.49
1	1.47	60.05
2	1.43	61.73
3	1.39	63.50

Physical Properties of the Finished Cotton Fabric

The stiffness or firmness of the untreated and finished cotton fabrics were evaluated and are summarized, in terms of flexural rigidity, in Table 2. The cotton fabrics treated with softening solution containing only TEGO 28 cationic softener had a higher stiffness than that of untreated cotton fabric. However, the inclusion of mMont resulted in a further increased fabric stiffness that varied with the concentration of mMont incorporated into the finishing solution. The maximal stiffness was observed at 5% (w/v) mMont and declined slightly and significantly at lower or higher concentrations, respectively. In summary, a minimal stiffness was observed at 15% (w/v) mMont whilst a 3-5% (w/v) mMont

concentration was optimal for enhanced stiffness. Although mMont clearly has the capability to improve the stiffness (mechanical properties) of the textile, this skewed dose-dependent response of the resultant fabric stiffness may be explained by the unique morphology of mMont which has a very large surface area and a good sorption capability, allowing the potential efficient adsorption of atmospheric moisture and a resultant softening of the fabric. As the mMont concentration increased in this proposed scenario, the enhanced stiffness attained, perhaps leveling of at around 5% (w/v) mMont, would increasingly be countered and exceeded by the increasing softness derived from enhanced water adsorption and retention. As such, this may affect the use of such textiles in extreme environments, such as deserts and the tropics with very low and high humidity, respectively, and requires further clarification. Nevertheless, 3-5% (w/v) mMont clearly enhances the fabric flexural rigidity.

Besides flexural rigidity, other fabric characteristics are important including the tear strength and color (whiteness). These parameters were therefore also investigated and are summarized for untreated and finished cotton fabrics in Table 3. Cotton fabrics finished with TEGO 28 alone revealed enhanced tear resistance in the warp direction. Although this tended to further increase slightly with increasing mMont concentrations, this required at least 10% (w/v) mMont to attain any significant further increased tear resistance over that seen with TEGO 28 alone.

In terms of color, the whiteness of the cotton fabric was slightly decreased when finished with TEGO 28 softening finishing solution alone, and was further significantly decreased in a dose-dependent manner by the addition of mMont at concentrations of 3% (w/v) and above.

Thermal Stability of the Finished Cotton Fabric

The thermal stability of the untreated and finished cotton fabrics were examined by TGA. Representative TGA curves are shown in Figure 2, whilst the weights remaining of the tested samples at a decomposition temperature of 400°C are summarized in Table 4. Figure 2 shows that treatment of the cotton fabrics with only TEGO 28 softening finishing solution or with TEGO 28 softening finishing solution containing mMont at different contents did not significantly alter the temperature of onset of thermal degradation. The onset of thermal degradation of those finished cotton fabrics was similar to that of untreated cotton fabric. The rate of degradation of the untreated cotton fabric was slower than that of those finished cotton fabrics treated either with only TEGO 28 softening finishing solution or with softening finishing solution containing both TEGO 28 and mMont at various concentrations in the temperature range of 250-380°C. This may be because this temperature range was the decomposition temperature of TEGO 28 softening agent. With temperatures increasing above 390°C to 540°C, the rate of degradation of untreated cotton fabric started to degrade faster than that of those finished cotton fabrics. The combustion temperature of cotton was around 350°C, so that the pure cotton or untreated cotton would degrade rapidly at the temperature above combustion temperature of cotton. The finished cotton fabrics showed a higher percent of weight remaining at 400°C than untreated cotton fabric as shown in Table 4. At temperatures above 600°C it could be concluded that the finished cotton fabric treated with TEGO 28 containing either 10% (w/v) or15% (w/v) mMont decreased the rate of degradation as is shown in the results of weights remaining which were higher than those of untreated cotton and those of finished cotton with 0-5% (w/v) fabric treated mMont concentrations. The inclusion of mMont at 10 and 15% (w/v) revealed a dose-dependent further, and slight, increase in thermal stability (decreased thermal degradation). The ability of high amounts

of mMont at 10% and 15% (w/v) to enhance this

would likely result from the intercalation of TEGO 28 into the mMont silicate layers further inhibiting the permeation of oxygen and restricting the thermal motion, and thus increasing the thermal stability. Accordingly, TEGO 28 based softening agent containing mMont at 10 and 15% (w/v) may show the potential to be used as a flame-retardant finish. This may be because the mMont used in the softening agent for finishing treatment was clay mineral particles in the nanometer size having ability to lower flammability of the finished cotton fabric. It has been believed that the nano-dispersed silicate layers of organoclay drastically influence reaction kinetics, product transfer, and volatilization, with enhancement of the char formation in the polymer matrix while flaming⁹. The application in this area of modified Mont incorporated with cationic softener will be studied further for more details with respect to flame retardancy and burning behaviors.



Figure 2. TGA curves of untreated cotton fabric and finished cotton fabrics treated with softening solution with different mMont (3% (w/v) TEGO 28 modified Mont) contents.

Tested sample	es	Amount of mMont ^a in softening solution (%)	Fabric weight in mg cm ⁻²	Average sagged length (cm)	Flexural rigidity (mg.cm)
Untreated fab	ric	0.0	13.6	2.05	117.2
Finished f	fabrics	0.0	14.3	2.14	140.1
treated	with	1.0	14.7	1.99	115.8
softening solu	ition	3.0	14.6	2.27	170.8
		5.0	15.0	2.27	175.5
		10.0	15.3	2.02	126.1
		15.0	15.4	1.61	64.3

 Table 2. The flexural rigidity (stiffness) of untreated and finished cotton fabrics.

^amMont: 3 % (w/v) TEGO 28 modified Mont

Tested samples	Amount of mMont ^a in softening solution (%)	Tear strength (N) in warp direction	Whiteness index
Untreated fabric	0.0	26.0	77.7
Finished fabrics treated with softening solution	0.0	29.4	74.7
	1.0	30.2	74.2
	3.0	32.0	71.7
	5.0	28.4	69.0
	10.0	33.8	63.6
	15.0	33.3	60.9

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^amMont: 3 % (w/v) TEGO 28 modified Mont

Table 4. Residual weight during the thermal degradation at 400°C of the untreated and finished cotton fabrics.

Tested samples	Amount of mMont ^a in	Weight remaining
	softening solution (%)	(%) at 400 °C
Untreated fabric	0	15.2
Finished fabrics treated with	0	25.6
softening solution	1.0	27.6
	5.0	29.3
	10.0	30.1
	15.0	31.8

Conclusions

Modification of montmorillonite organoclay by cationic exchange with a 3% (w/v) solution of the cationic softener of TEGO 28 (Dicarboxyethyl hydroxyethyl Palm methvl ammonium methosulfate) appears to induce intercalation at the nanoscale. This modified Mont (mMont), with pure TEGO 28 cationic softener (8% (w/v)) appears to have potential use in cotton fabric treatment by the pad-dry method since it can increase the stiffness (or potentially increase softness at higher mMont levels) without detriment to the enhanced tear strength induced by TEGO 28 treatment alone. Although mMont further reduced the whiteness of the treated fabrics, this was only slight at levels below 5% (w/v). Interestingly, the mMont at 10 and 15% (w/v) reported here additionally reduced thermal degradation. However, its potential application as a flame retardant or for improving thermal

stability of cotton fabrics requires more evaluations.

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