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Eco-Friendly Multifinishing of cotton through Inclusion of Motmorillonite/chitosan Hybrid Nanocomposite

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ABSTRACT

Natural resources were used in synthesis of innovative hybrid nanocomposites for cotton multifinishing. The innovation is based on interaction of natural nanoclay and a biopolymer under the name montmorillonite (MMT) and chitosan (CTS) respectively. Thus aqueous slurry was prepared containing (MMT) and (CTS) along with citric acid and sodium hypophosphite. The slurry was sonicated to yield MMT/CTS hybrid nanocomposite. Different nanocomposites could be achieved through variation of concentration of both MMT and CTS as well duration of sonication. The as prepared MMT/CTS hybrid nanocomposites were completely homogeneous and remained stable for more than a month provided that the sonication is performed for at least 90 min. The hybrid nanocomposites were characterized using SEM, FTIR, TGA, X-ray diffraction and TEM analysis. To this end, the hybrid was applied to cotton fabric as per the pad-dry-cure method. Interaction of the newly synthesized MMT/CTS hybrid nanocomposites with cotton cellulose (Fabric) brought about, therein, inclusions of the nanohybrid. The impact of this was to impart to cotton fabric antimicrobial activity, easy care characteristics, thermal stability and reduced inflammability. Meanwhile, such inclusions increase substantially the tensile strength and elongation at break of the fabric. Dependence of the add-on and nitrogen content as a measure of the magnitude of the nanohybrid inclusions in the fabric is also reported.

INTRODUCTION

Chitosan (CTS) is the N-deacetylated derivative of chitin, Nevertheless this N-deacetylation is never complete. chitosan possess plenty of accessible amino groups rendering it polycationic polysaccharide. Indeed the extent of deacetylation, determines the grade of chitosan .[1] Previous reports [2] disclosed that chitosan is a disclosed biocompatible, biodegradable, nontoxic, linear copolymer polysaccharide. It consists of bothβ (1-4)-linked 2-amino-2-deoxy-D-glucose (D-glucosamine) and 2-acetamido-2-deoxy-D-glucose (N-acetyl-D-glucosamine) units. Chitosan acquires structural similarity to cellulose which is (made up of β (1-4)-linked D-glucose units. BY virtue of its gel-Forming property, CTS is used in designing of drug delivery system.

On the other hand, Montmorillonite (MMT) is one of thesmectite groups, composed of silica tetrahedral sheets layered between alumina octahedral sheets. The imperfection of the crystal lattice and the isomorphous substitution induce a net negative charge that leads to the adsorption of alkaline earth metal ions in the interlayer space. Such imperfection is responsible for the activity and exchange reactions with organic compounds. MMT also contains dangling hydroxyl end groups on the surfaces. MMT has large specific surface area and exhibits good adsorption ability, cation exchange capacity, standout adhesive ability, and drug-carrying capability. Thus, MMT is a common ingredient as both the excipient and active substance in pharmaceutical products [3]. The intercalation of organic species into layered inorganic solids provides a useful and convenient route to prepare organic-inorganic hybrids that bear the properties of both the inorganic host and organic guest in a single material [4]

Current work is under taken with the following objective:
-To establish conditions for synthesis of Montmorillonite /chitosan hybrid nanocomposite
-To characterize the as prepared hybrid nanocomposite;
-To set up formaulatios/conditions for application of the hybrid to cotton fabric;.
-To examine the properties conferred on cotton fabric via inclusion of the hybrid nanocomposite under investigation in the macromolecular structure of cotton and;
-To use the state-of-the –art facilities to understand the ultrafine structure of the hybrid and its impact on multifinishing of cotton.

MATERIALS AND METHODS

2.1. Materials.

Desized, scoured, and bleached plain weave cotton fabric (230 g/m^2) was kindly supplied by Misr/ Co. for Spinning and Weaving, MehallaElKubra (Egypt). Chitosan, medium molecular weight, Brookfield viscosity 80,000 cps, was purchased fro Aldrich Chemical (Germany). Citric acid and sodium hypophosphite were also purchased from Aldrich Chemical (Germany). Montmorillonite K10 (MMT) was the natural montmorillonite clay purchased from the local market; it was mainly Bentonite, acid-leached powder; having molecular weight 274-324-8, molecular formula $H_2Al_2\ (SiO_3)_4\text{-}mH_2O$. All chemicals used were of laboratory grade.

2.2. Methods.

2.2.1 Synthesis of CTS/ MMT hybrid nanocomposite

CTS, MMT, citric acid and sodium hypophosphite (SHP) were thoroughly mixed in water to form a slurry. Chitosan and montmorillonite concentrations (w/v) ranged from 0.25-1% and 0.025- 0.1% respectively whereas citric acid was used at a concentration of 5% and SHP at 4%. The slurry was subjected to sonication under conditions given in the text. Sonication resulted in MMT/CTS hybrid nanocomposite possibly through intercalation/ exfoliation of CTS into the layered MMT. The ultimate nano-product was in the form of stable nanoemulsion.

2.2.2 Application to cotton fabric

The synthesized hybrid nanocomposite (stable nanoemulsion) was applied to cotton fabric as per the pad-dry-cure method. Thus the fabric was padded in the emulsion containing CTS,MMT,Citric acid and SHP in two dips and two nips to a wet pickup or 100% followed by drying at 80^{o}C for 5 min then cured at 150^{o}C for 3 min. To this end, the fabric was submitted to 10 home laundering and drying cycles.

2.2.3 In Situ formation of MMT/CTS hybrid nanocomposite

Synthesis of MMT/CTS hybrid nanocomposite in concommitant with inclusion of the hybrid nanoparticles in the molecular structure of cotton could also be achieved. The fabric sample was introduced in the MMT/CTS slurry containing citric acid and SHP before sonication. Once this was the case, the slurry ingredients were sorbed within the cotton structure. Sonication would induce formation of the hybrid composite nanoparticles within the structure of the cotton fabric. However, for convenience and better fabric performance the synthesis and application were carried out in two separate steps as described above.

2.3. Testing and analysis

2.3.1.Fourier Transform Infrared spectroscopy (FTIR)

FTIR Spectroscopy was measured using FT-IR-FT-Raman, model: Nexus 670 (Nicollet-Madison-WI-USA). Cotton fabric was cut into very small pieces; these pieces were mixed with KBr. The spectral range was 400 to 4000 cm^{-1}

2.3.2. X-ray diffraction

X-ray diffraction patterns of samples were recorded on a STOE STADI P transmission X-ray powder diffractometer system by monitoring the diffraction angle from 5 to 65 (2h) using monochromatized Cu Ka (k = 1.54051 A°) radiation.

2.3.3. Scanning electron microscopy (SEM) measurements

Microscopic investigations of fabric samples were carried out using a Philips XL30 scanning electron microscope (SEM) equipped with a LaB6 electron gun and a Philips-EDAX/DX4 energy-dispersive spectroscope (EDS). Images were taken at different magnifications (from 1509 to 3, 0009), using secondary electrons (SE) in accordance with the clarity of the images. Fabric samples were fixed with carbon glue and metalized by gold vapor deposition to record images.

2.3.4. Transmission Electron Microscopy (TEM)

Shape and size were practically determined using TEM;JEOL-JEM-1200. Specimens for TEM measurements were prepared by placing a drop of colloidal solution on 400 mesh copper grid coated by an amorphous carbon film and evaporating the solvent in air at room temperature.

2.3.5.Antibacterial tests

All antibacterial activity tests were done in triplicate to ensure reproducibility. The antibacterial activity of fabric samples was evaluated against *Escherichia Coli* and *staphylococcus aureus,*(ATCC 1533) bacteria using disk diffusion method. A mixture of nutrient broth and nutrient agar in 1 L distilled water at pH 7.2 as well as the empty Petri plates were autoclaved. The agar medium was then cast into the Petri plates and cooled in laminar airflow. Approximately 105 colony-forming units of E. coli bacteria were inoculated on plates, and then 292 cm^2 of each fabric samples was planted onto the agar plates. All the plates were incubated at 37^oC for 24 h and examined if a zone of inhibition was produced around samples.

2.3.6. Fabric performance evaluation

The treated samples were evaluated for breaking strength and elongation at break in accordance with ASTM D5035. The conditioned wrinkle recovery angles (WRA) were evaluated according to AATCC Test Method 66.

2.3.7. LOI

Limiting oxygen index (LOI) values of some samples were measured according to ASTM D2863-08 standard method. In this order, 5 specimens of each sample were prepared in 5 cm×15cm and a mixture of oxygen and nitrogen is passed up through a cylinder containing the fabric specimen supported vertically. The minimum fraction of oxygen in a mixture of oxygen and nitrogen in which one specimen will just sustain burning is determined and reported as the LOI value [5]

2.3.8 Thermal analysis

Thermo gravimetric analysis (TGA) and differential thermal analysis (DTA) were carried out using a Perkin Elmer TG-DTA analyzer, model Pyris1, operating under nitrogen atmosphere with initial sample weights of 8mg. Once the sample has been prepared, it was placed into the TGA sample pan and distributed evenly across the pan bottom. The standard platinum sample pan (0319- 0264) was used for this application. The runs were performed over a temperature range of 50–600 ◦C at a heating rate of 10◦C/min under a continuous N_2 flow of 100 ml/min

RESULTS AND DISCUSSION

3.1.Characterization of the Chitosan/montmorillonite hybrid nanocomposite

Previous reports [6] stated that organic- inorganic hybrids that contain the properties of both the inorganic host and the organic guest in a single material can be prepared through interaction of organic species into layered inorganic solids. With this in mind, research is designed to synthesize a multifinish for cotton fabric based on intercalation/ exfoliation of CTS nanodispersion into layered nano-sized MMT in presence of citric acid as crosslinker and SHP as a catalyst for crossliking. Conversion of MMT and CTS to nano-sized materials is induced by sonication of their aqueous slurry containing citric acid and SHP. The ouput of this is MMT/CTS hybrid nanocomposite emulsion containing the crosslinker and its catalyst. Systematic investigations into factors affecting major characteristics of the hybrid nanocomposite such as concentrations of MMT and CTS as well as duration of sonication are studied. Accordingly, best formulation/ condition for synthesis of the hybrid nanocomposite (multifinish) could be achieved. Application of the as synthesized multifinish to cotton fabric imparted to cotton a happy combination of properties, namely, antibacterial activity, thermal stability, resistance to inflammability, case of case characteristics, in addition to increase in fabric weight and improved strength properties. Given below are the results obtained with the synthesis of the multifinish along with its characterization and application to cotton fabric.

3.1 Characterization of MMT/CTS hybrid nanocomposite

3.1.1 X-ray Diffraction

X-Ray diffraction (XRD)patterns of cotton containing MMT/CTS hybrid nanocomposite, pure CTS and pure MMT are shown in Figure 1. It is observed that mixing of the two natural polymeric components, i.e.CTS and MMT along with the crosslinker (i.e. citric acid) and its catalyst (i.e.SHP) causes no changes in the crystallinity of either polymeric components. On the other hand, in situ formation of the MMT/CTS hybrid nanocomposite in the molecular structure of cotton by sonification of MMT/CTS/cotton fabric in the presence of citric acid crosslinker and SHP catalyst results in a change in the XRD patterns. Similar situation was encountered where cotton fabric was treated with presynthesized MMT/CTS hybrid nanocomposite in presence of the crosslinker and its catalyst.

Obviously, as the main peak of MMT appears at $2\theta=8.85^o$ (D=0.99 nm) space the cotton fabric containing MMT/CTS hybrid composite nanoparticles displays sharp peaks at $2\ \theta=12\ ^o$ (D= 1.5 nm) and $2\ \theta=21\ ^o$ (D=1.02 nm). This indicates that MMT/CTS ions are located in the interlayer of the super molecular structure of cotton [7]. This state of affairs implies that MMT clay nanoparticles are partially exfoliated by CTS leading to hybrid composite nanoparticles which are dispersed into the moleclular structure of cotton. By and large increasing the basal B and C usually confirms the location of CTS and cotton ions between the layers of MMT clay. It is understandable that by virtue of their greater number of hydroxyl sites (OH- groups) cotton cellulose can undergo interaction with the hydroxyl OH groups on the MMT surface. Such interaction is supported by stronger interactions of the CTS hydroxyls due to larger molecular volumes of CTS. This is due to the broaden and interaction of MMT at $2\ \theta=22\ ^o$ as shown in fig.1

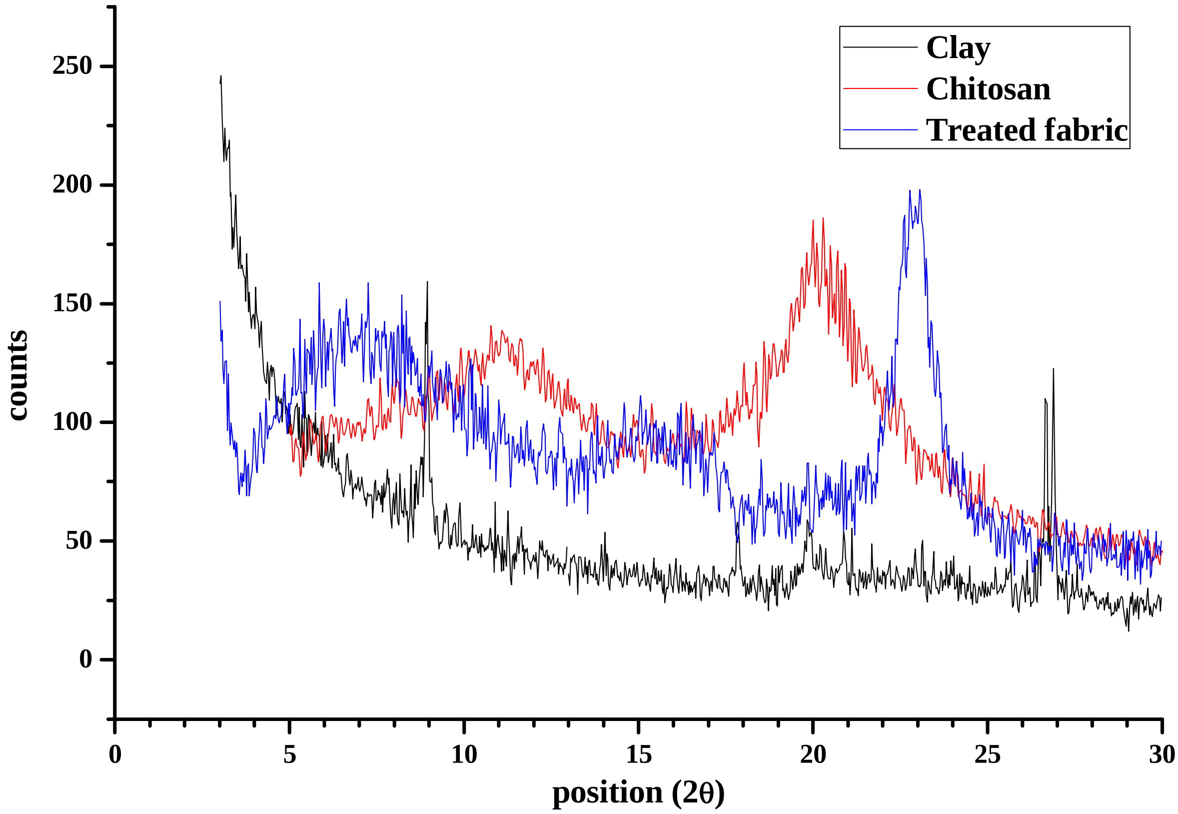


Figure 1 XRD of pure clay (i.e.MMT),pure chitosan (CTS), cotton containing MMT/CTS hybrid nanocomposite

3.1.2 FTIR spectroscopy of chitosan/montmorillonite hybrid nanocomposite and cotton treated thereof:

FTIR spectra of the cotton fiber and cotton treated with sonnicated chitosan as a control sample and also their nanoslurry with montmorillonite clay at different montmorillonite clay concentration 1,3,5% are shown in figure 2(a,b) from wave number 750-4000 cm-1. The characteristic features of the spectrum of the cotton are due to as the main constituent [8] . Abroad absorption band in the region of 3600–3200 cm-1 is characteristic of hydrogen bonded O-H stretching vibration [9] . and is common to all the spectra.The O-H stretching vibration sharpness (intensity) decreases due to thr treatment of cotton fibers by chitosan/montmorillonite hybrid nanocomposite. . The C-H stretching vibration of methyl and methylene groups associated with crosslinking of is observed near 2902 cm-1 . It decreases due to the surface modification of cellulose by the presence of montmorillonite in the nanocomposite (Fig 2) The band at 1641 cm-1 indicates the absorbed water in crystalline cellulose [10] and this band is disappears due to the chemical treatment of fiber using MMT/CTS hybrid nanocomposite . The absorption band at 1359 cm-1is assigned to C-H bending in crosslinked cellulose containing the hybrid nanocomposite [11]. After montmorillonite/chitosan hybrid nanocomposite treatment, the water is partially removed from cotton fiber. As a result, the bands were shifted to lower value which indicates that the hydrophilic nature of cotton fibers is considerably reduced [12]. Thus, the interfacial adhesion between the fiber and the nanocomposite is reflected in Figs 2 a, b However, the IR spectrum of montmorillonite in the nanocomposite , the intensity of peaks corresponding to O-H and C=O further decreases, while the peaks at 1620 cm-1 appears after involvement of nanomontmorillonite (MMT) in the hybrid nanocomposite.. These results confirm the interaction of the MMT nanoparticles with both chitosan and the cotton fibers[13]. Indeed , The above statements confirm the suggested chemical reaction mentioned above in Fig(2 a,b)

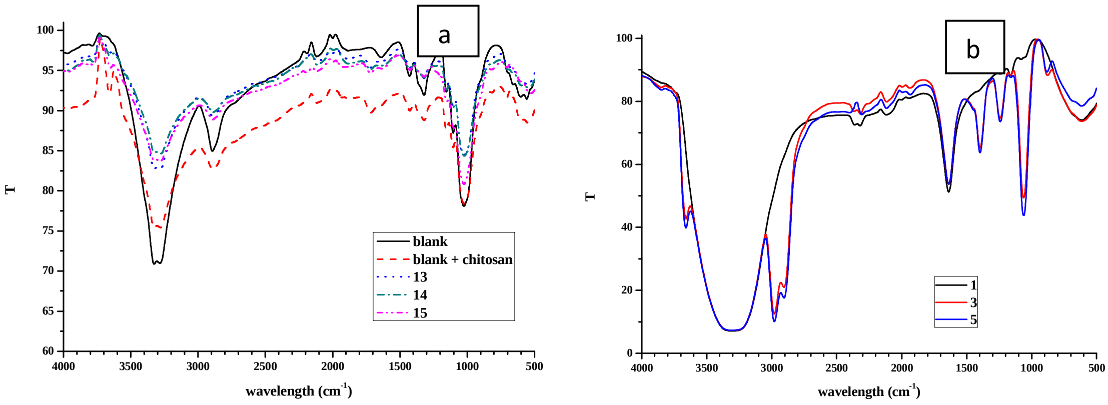


Figure 2 (a,b): FTIR spectra of the cotton fiber and cotton treated with chitosan/montmorillonite hybrid nanocomposite (a); FTIR spetra of chitosan/ montmorillonite nanocomposite prepared using different montmorillonite concentration 1,3,5% (b)

3.1.3 SEM of cotton treated with chitosan/montmorillonite hybrid nanocomposite

Figures 3(a-c) disclose the scanning electron micrographs of cotton before and after being treated with MMT/CTS hybrid nanocomposite. Fig 3a exhibits the SEM of cotton before the treatment (blank). The blank cotton is characterized by clear and smooth surface. Fig. 3b shows the formation of a continuous nanocomposite film with an even matrix, without any cracks or pores on its surface. SEM shows that the surface of the fiber became rough due to the inclusion of MMT/CTS hybrid composite nanoparticles in the molecular structure of cotton. The higher the time of sonnication the higher is the roughness. Figure 3c reveals that MMT/CTS hybrid nanoparticles are well dispersed in their chain film matrix, where there is certainly no or a little agglomeration of nanoparticles [14].

The presence of MMT/CTS hybrid nanocomposite in the cotton structure is proved by EDX shown in Fig 4. EDX reveals the presence and the percent of SiO2 on cotton sample treated with the nanocomposite. The percent of SiO2 amounts to 1.4% when MMT was used at a concentration of 0.5% during preparation of the nanocomposite.

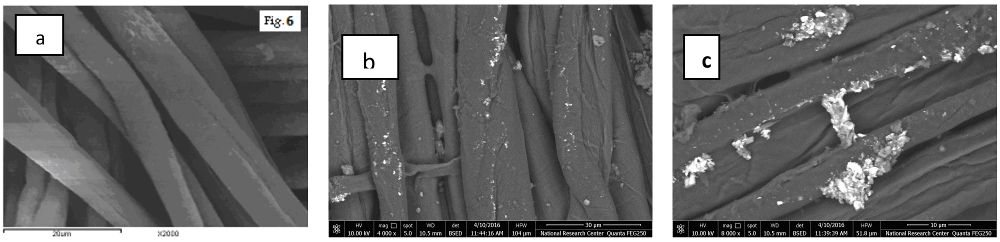
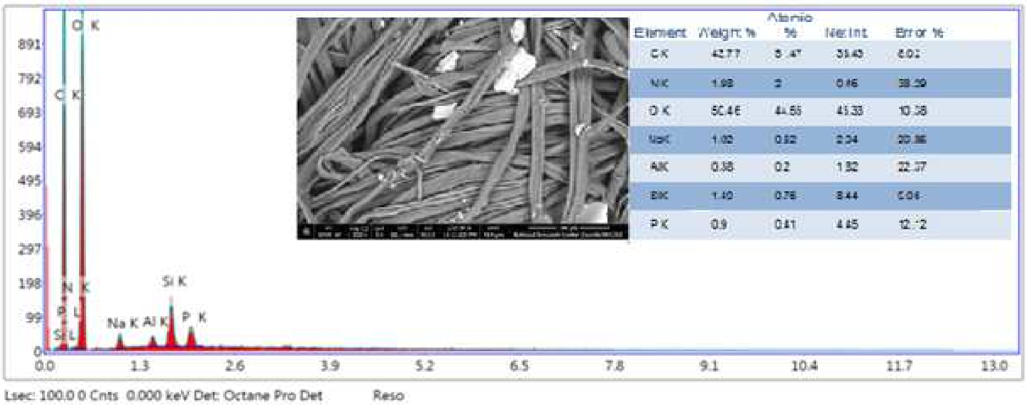


Fig 3 (a-c) SEM of cotton treated with Chitosan/montmorillonite hybrid nanocomposite

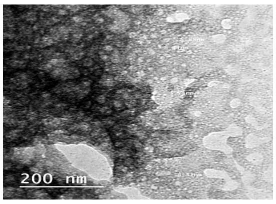


Element	Weight %	Atomic %	Net Int.	Error %
C K	42.77	51.47	31.43	6.02
N K	1.98	2	0.46	38.39
O K	50.46	44.55	45.33	10.38
NaK	1.02	0.52	2.34	20.36
AlK	0.38	0.2	1.32	22.37
SiK	1.40	0.78	8.44	6.04
P K	0.9	0.41	4.45	12.12

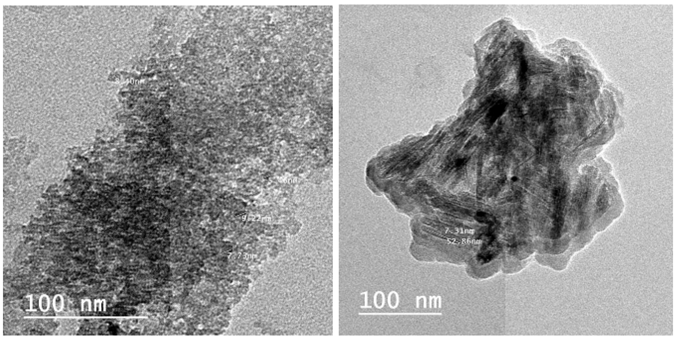
Fig 4 EDX of cotton treated with Chitosan/montmorillonite hybrid nanocomposite

3.1.4. TEM of MMT/CTS hybrid nanocomposite

Fig.5a shows that TEM of Chitosan (CTS) nanoparticles obtained through sonication of CTS material under condition similar to those used in synthesis of MMT/CTS hybrid nanocomposite. Evidently, the nanoparticles of Chitosan are spherical in shape and polydispressed. The average particle size of these Chitosan particles is 17 nm. On the other hand, fig. 5b and 5c depict the TEM images of Chitosan after its involvement via exfoliation with MMT to yield MMT/CTS hybrid nanocomposite. As is clear, in contrast with the spherical shape of Chitosan and its poly disperselity , the hybrid composite nano particle appear look-like highly stable coating; the high stabilization is unequivocally due to interaction of MMT with the free amino group of Chitosan molecules [15]. The TEM image of MMT/CTS hybrid nanoparticles exhibit an average particle size of 8 nm.



5a TEM of Chitosan



5b,c TEM of MMT/CTS hybrid nanocomposite

3.2 Evaluation of performance of cotton fabric treated with different MMT/CTS hybrid nanocomposite

Different MMT/CTS hybrid nanocomposites were brought about by changing the concentration of chitosan, concentration of montmorillonite and the sonication time during synthesis of the hybrid nanocomposites. The different hybrid nanocomposites obtained were applied to cotton fabric according to the pad- dry –cure method. The impact of such application on the fabric performance properties are examamined and represented as given under.

3.2.1 Chitosan Concentration

Table 1 shows variations of the percent inclusion (add-on) of the hybrid nanocomposite onto the cotton fabric with chitosan concentration used in the synthesis of MMT/CTS hybrid nanocomposite when the latter was applied to cotton fabric. Effect of these variations on nitrogen content and creases recovery angle is also shown in table 1. The results indicate that the add-on, nitrogen content, creases recovery angle of the treated cotton fabric increases by increasing concentration of Chitosan. This means that the higher chitosan concentrations act in favor of better interaction of the MMT/CTS hybrid nanocomposite with cotton fabric. The poly disperisity of chitosan and its exfoliation within the layers of MMT along with its reaction with the latter via amino groups and chemical attachement to the cotton fabric through citric acid bridges would accelerate for the favorable and impact of chitosan on the said properties. It is understood that citric acid catalyzed by sodium hypophosphite (SHP) induces ease of care characteristics through formation of crosslinks between adjacent cellulose chains thereby enhancing the crease recovery [16].

Figure 5A shows the chitosan concentration used in synthesis of MMT/CTS hybrid nanocomposite versus both tensile strength and elongation at break of cotton fabric treated with these nanocomposites. It is seen that the tensile strength increases as the chitosan concentration increases upto 0.7% then sharply decreases. Opposite trend is observed with the elongation at break. The latter decreases by increasing the chitosan concentration upto 0.7% then increases thereafter.

It is worthy to report that the tensile strength increases from 29 to 44 Kgf, a point which can be interpreted in terms of the larger surfaces area of MMT/CTS hybrid nanocomposite inclusions in the cotton structure which act as a connection link between the nanocomposite inclusions and the reinforced cotton fibers. This high improvement in tensile strength could be achieved upon using 0.7% chitosan. Higher concentration of chitosan viz 1% causes the tensile strength to fall down to 38 KGF. Greater exfoliation of MMT at higher concentration of CTS would create a highly viscous environement which impede mobility of MMT in MMT/CTS hybrid nanocomposite. Concomitantly, a relatively firm structure may be formed after the nanocomposite inclusion in the cotton structure leading to a decrement in the mobility of the CTS chains during stretching owing to the good dispersion and exfoliation of CTS chains into MMT platelets. The ultimate effect of this are restricted segmental movement and rigidity in cotton structure leading to decreased tensile strength. In confirmation with this is the opposite trends brought about by the results of the elongation at break as shown in figure 5A.

Figure 5B represents a histogram showing the effect of chitosan concentration used in the synthesis of MMT/CTS hybrid nanocomposite on the limited oxygen index (LOI) for cotton fabric treated with these nanocomposite. This histogram makes it evident that the MMT/CTS hybrid nanocomposites exerts a positive effect on LOI regardless of concentration of CTS. That is, the hybrid nanocomposite under investigation has the tendency to resist inflammability.

Effect of chitosan concentration used in synthesis of MMT/CTS hybrid nanocomposite on the add-on, nitrogen content, and resilience of cotton fabric treated thereof

Chitosan Concentration (%)	**Addon (%)**	**N Content (%)**	**CRA**	
			Warp	Weft
Blank	0	0.01	90	95
0.00	2	0.05	98	102
0.25	10	0.11	126	122
0.5	19	0.12	128	130
0.75	27	0.13	130	135
1.00	34	0.15	132	133

Condition of the MMT/CTS nanocomposite synthesis MMT, 0.5% ;Citric acid, 5%; SHP, 4%; Temp. 50^{o}C; Sonication time 1 hr.

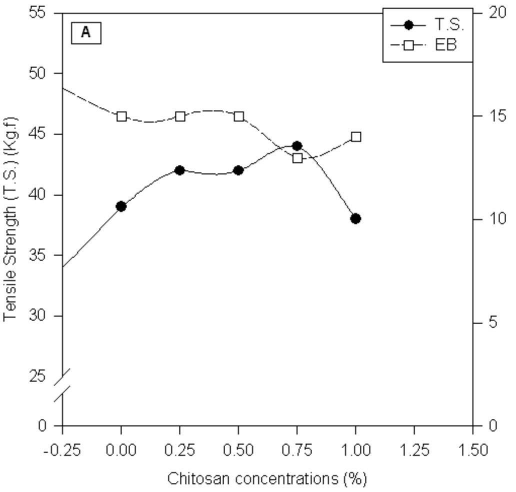


Figure 5A Effect of chitosan concentration used in synthesis of MMT /CTS on the tensile strength and elongation at break of fabric treated with the nanocomposite

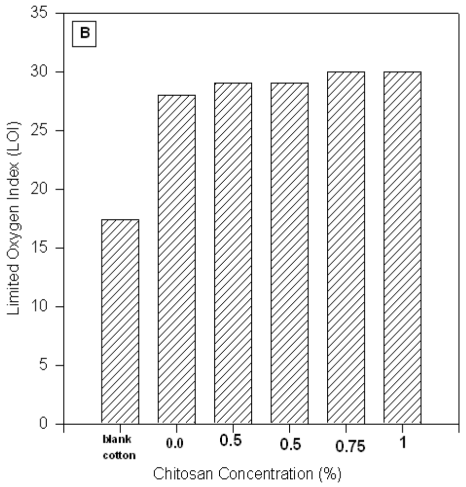


Figure 5B Effect of chitosan concentration used in synthesis of MMT /CTS on the tensile Limited Oxygen Limited of fabric treated with the nanocomposite

3.2.2 Montmorillonite concentration

Results of table 2 are concerned with the impact of increasing MMT concentration during the synthesis of MMT/CTS hybrid nanocomposite on the add-on, nitrogen content and crease recovery of cotton fabric treated thereof. These results display trends very close to those of table 1 and, therefore, could be described and explained on similar basis. Higher concentrations of MMT most probably favor better exfoliation of CTS in MMT layers. Once this is the case, the MMT/CTS hybrid nanocomposite formed would expedite its interaction with the cotton fabric.

Figure 6A shows the relationship between MMT concentration used in synthesis of CTS /MMT hybrid nanocomposite and both the tensile strength and elongation at break of cotton fabric. Obviously, the tensile strength increases significantly and so does the elongation at break by increasing the MMT concentration within the range studied. the tensile strength attains a value of about 48KgF upon using MMT at concentration of 1% while elongation at break exhibits a value of about 17% under the same condition. This suggests that the following recipe for finishing of cotton fabric (concentration w/v) : CTS,0.75% ; MMT, 0.25%; citric acid, 5%; SHP, 4%; temp.,50^{o}C ; sonication time, 1 hr.

Under such condition inclusion and interaction of the MMT/CTS hybrid nanocomposite within the molecular structure of cotton seem to occur smoothly without disruption and/or degradation of the cotton structure. Instead, they provide extra strength through formation of flexible matrix which is intimately associated via strong physical and chemical bonding with the cotton fabric. The intensity of crosslinks seems also to be moderate as evidenced by the relatively low values of crease recovery. these features taken together are behind the happy combination of properties conferred on cotton fabric.

Figure 6B shows, in a histogram form, the effect of MMT concentration used in the synthesis of MMT/CTS hybrid nanocomposite on the limited oxygen Index of cotton fabric treated with these nanocomposites. It is apparent that result of LOI indicates that resistance to flammability is higher at higher MMT concentrations. This means that presence of MMT at a concentration of 1% during the synthesis of MMT/CTS hybrid nanocomposite is a must be ensure resistance to inflammability of the cotton fabric treated with current nanocomposite under the condition specified in the aforementioned paragraph.

Table 2: Effect of MMT concentration used in synthesis MMT/CTS hybrid nanocomposite on the add-on, nitrogen content and crease recovery of cotton treated thereof.

montmorillonite clay Concentration (%)	Addon (%)	N Content (%)	CRA	
			Warp	Weft
Blank	**0**	**0.01**	**90**	**95**
0.00	**11.9**	**0.14**	**120**	**125**
0.25	**6.7**	**0.16**	**131**	**140**
0.5	**10.4**	**0.18**	**130**	**135**
0.75	**10.1**	**0.21**	**125**	**130**
1.00	**12.4**	**0.26**	**122**	**120**

Condition: CTS Concetration,0.75%; Citric acid, 5%; SHP, 4%; Temp, 50^{o}C; Sonication time, 1hr

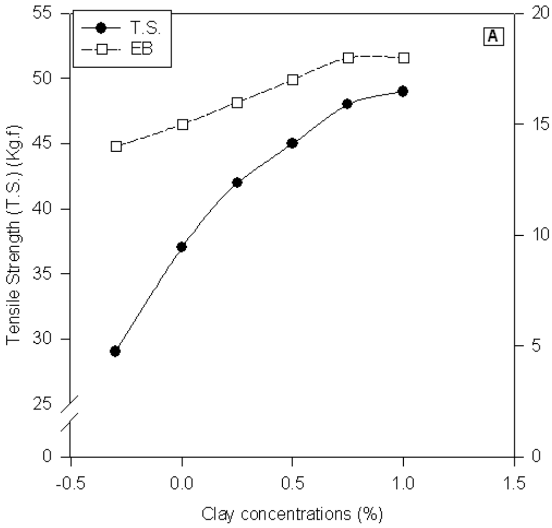


Figure 6A Effect of MMT concentration used in synthesis of CTS/MMT hybrid nanocomposite on the tensile strength and elongation at break of cotton fabric treated therof

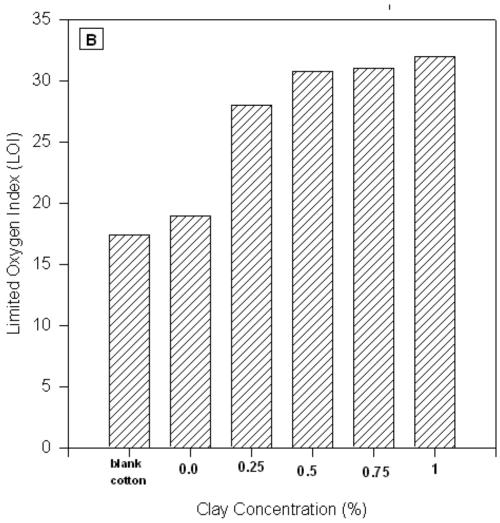


Figure 6B Effect of MMT concentration used in synthesis of CTS/MMT hybrid nanocomposite on the limited oxygen index of cotton fabric treated thereof

3.2.3 Sonication time:

Table 3 contains the results of add-on, nitrogen content and crease recovery of cotton fabrics treated with the current hybrid nanocomposites which were prepared under the effect of different sonication times. As is evident, increasing the sonication time from 1 to 3 hr has particularly no effect on the said properties of the treated fabrics. Longer than 1 hour sonication seams meaningless; but from the practical point of view, it was observed that longer duration of at least (1.5hr) is a prerequisite to ensure high stability of the nanocomposite emulsions for more than a month duration [17].

Figure (7A) exhibits variations in tensile strength and elongation at break of the nanocomposites-treated cotton fabrics with duration of sonication. It is clear that both strength properties increase by prolonging the sonication time to 1.5 hour, decreases marginally after 2 hour sonication then levels off thereafter. A salient feature is the improvement of the strength properties examined irrespective of the sonication time and despite that the treatment took place concurrently with crosslinking. This is rather in agreement with the results of Figure 7A which is pertaining to MMT concentration study.

Figure (7B) depicts histogramically the impact of the time of sonication given for the synthesis of MMT/CTS hybrid nanocomposites on limited oxygen index (LOI) of cotton fabrics treated with these composites. Results reveal that the LOI increases by increasing the sonication time to 0.75 hour. Longer sonication time has little or no effect on LOI. It is certain, however, that the values of LOI obtained can be taken to indicate that the treated cotton under investigation acquires resistance towards inflammability.

Table 3: Add on, nitrogen content and crease recovery obtained with cotton fabric treated with MMT/CTS hybrid nanocomposites which were prepared at different sonication time

Sonication time(hr)	Addon (%)	N Content (%)	CRA	
			Warp	Weft
Blank	**0**	**0.01**	**90**	**95**
0.00	**4.26**	**0.12**	**111**	**115**
1	**10.1**	**0.21**	**125**	**130**
1.5	**10.3**	**0.22**	**126**	**132**
2	**10.2**	**0.22**	**126**	**133**
3	**10.2**	**0.22**	**127**	**133**

Condition: Chitosan Concetration:0.75%, Montmorillonite clay concentration: 0.25%, citric acid: 5%, SHP, 4%, temp. 50^{o}C

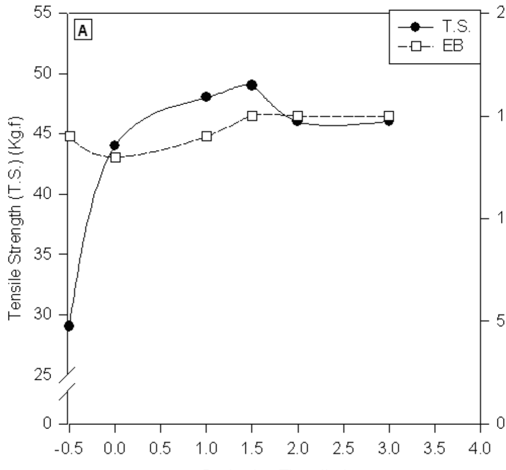


Figure 7 A Effect of sonication time given for synthesis of MMT/CTS hybrid nanocomposite on the tensile strength and elongation at break of cotton fabric treated with nanocomposite

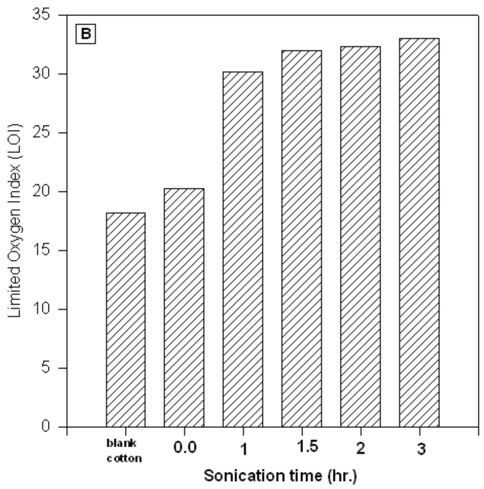


Figure 7B Effect of sonication time given for synthesis of MMT/CTS hybrid nanocomposite on the Limited Oxygen Index of cotton fabric treated with nanocomposite

3.2.4 Thermogravimetric analysis (TGA)

Cotton fabric treated with CTS /MMT hybrid nanocomposite in concommitant with citric acid crosslinking catalyzed by SHP along with untreated cotton were submitted to TGA. Figure 8 shows representative TGA curves. The weights remaining of the tested samples at a decomposition temperature of 400^{o}C are also shown in the same figure.

Results of figure 8 imply that when the temperature was raised from above 390^{o}C upto 540^{o}C, the untreatead cotton fabric displayed faster rate of degradation than the treated cotton fabric. As the combustion temperature of untreated cotton is around 350^{o}C, it would degrade rapidly at temperature above this temperature.The treated cotton fabric exhibited higher percent of the weight remaining at 400^{o}C than the untreated cotton fabric. Conclusion arrived at from temperatures above 600^{o}C assumed that cotton fabric treated with MMT/CTS hybrid nanocomposite contained around 22% (wt/v). The nanocomposite decreased the rate of degradation as evidenced by the results of the weights remaining which were higher than those of untreated cotton as well as those of cotton fabric treated with low concentration of the nanocomposite (e.g 0.5%). Inclusion of MMT/CTS hybrid nanocomposite in the molecular structure of cotton increased the thermal stability (decreased thermal degradation). The ability of higher amounts of the hybrid nanocomposite containing silicate layers of MMTcaused further inhibition of the permeation of oxygen and restricting the thermal motion, thereby increasing the thermal stability.

The maximum rate of decomposition patterns of the cotton fabric treated with the said hybrid nanocomposite are observed at two stages (Fig.8). The first stage is observed within a temperature range of 275.5–313.3 °C and is attributed to the degradation of tiny nanocellulosic impurities.. The second stage is brought into focus within the temperature range of 367.5–380.1 °C indicating the degradation of cellulose and other cellulosic matters from the fiber which lead to the char formation [18] , [19]. Inclusion of MMT/CTS hybrid nanocomposite in the molecular structure of cotton exerts a positive effect on thermal degradation of the cotton fabric. This is indicated by higher thermal stability of cotton fabrics treated with these nanocomposites.

Analysis of the activation energy is helpful for measuring the thermal stability of the treated cotton fabric. The results obtained above is due to the inclusion of MMT/CTS hybrid nanocomposite in the cotton structure whereby the interfacial adhesion between treated fabric increases [20,21]

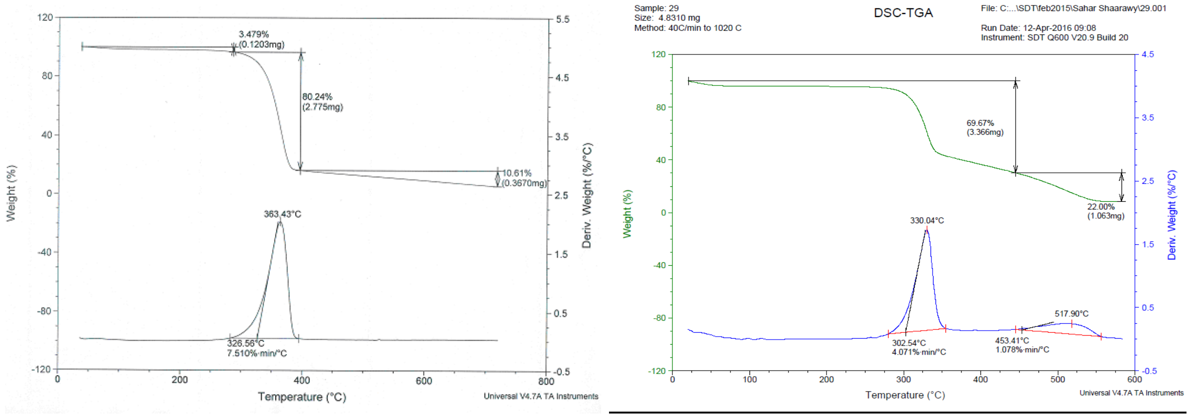


Figure 8 TGA of untreated cotton fabric and cotton fabric treated with MMT/CTS hybrid nanocomposite concomitantly with citric acid crosslinking catalyzed by SHP

3.2.5 Antibacterial Activity

The designed experiments in figure 9 show the reduction percentages of E.coli and S.aureus bacteria of cotton fabric treated with MMT/CTS hybrid nanocomposites. As appeared increasing chitosan concentration in the composite decreases the bacteria growth considerably on both types of the bacteria. S.aureus exhibits a little more resistance than E.coli. The main difference among these two bacteria relates to their cellular wall and peptide glycan thickness as it is more for Gram-positive bacteria which shows a relatively higher resistance against antibacterial agents. Current MMT/CTS hybrid nanocomposites have a complementary effect and signify a noticeable reduction in E.coli Gram-negative.

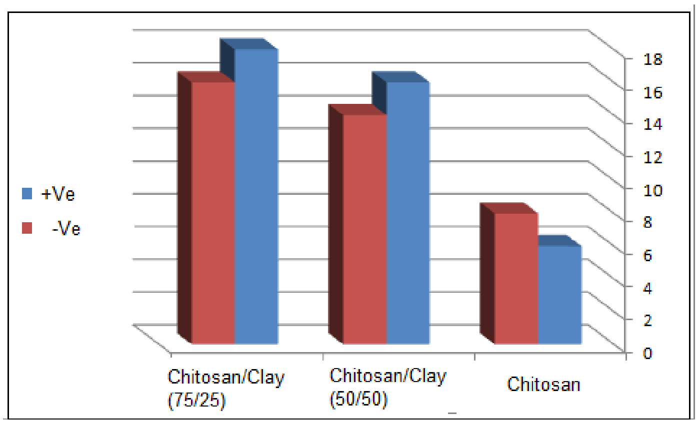


Fig 9 Reduction percentages of E.coli and S.aureus bacteria of cotton fabric treated with only chitosan vis-à-vis fabric treated with MMT/CTS hybrid nanocomposites using different ratios of MMT:CTS.

CONCLUSION

Unique ecofriendly and highly effective multifinishing agents are brought into focus through a through investigation into factors affecting the preparation of these finishes as well as, their characterization and application to cotton fabrics. Preparation of these finishes is based on innovative formulation which comprises montmorillonite (MMT) and chitosan (CTS) along with citric acid and sodium hypophosphite (SHP). While MMT is a naturally occurring nanoclay, CTS stands for a natural biopolymer. Citric acid is biologically manufactured and used in current formulation as crosslinker catalyzed by SHP.

The aforementioned four materials were mixed in an aqueous slurry. The slurry was then subjected to sonication whereby a homogenous highly poly dispersed aqueous emulsion was formed. This homogeneous polydispersion represents the MMT/CTS hybrid nanocomposite occurring as a result of interaction via intercalation/exfoliation of CTS within the MMT platelets (layers). Citric acid catalyzed SHP comes to play essentially during application of the hybrid nanocomposite to the cotton fabric where it has dual functions : a) crosslinking adjacent cellulose chains to improve ease of care characteristics of cotton fabric and b) support inclusion of the hybrid nanocomposite in the molecular structure of the cotton fabric.

Different hybrid nanocomposite were prepared through variation of the concentration of both MMT and CTS as well as time of sonication .The as fabricated MMT/CTS hybrid nanocomposite remained stable for more than a month provided that the sonication is performed for at least 90 min. World –class facilities viz SEM, FTIR, TGA.XRD and TEM analysis were employed for characterization of the hybrid nancomposite. In-situ formation of the hybrid nanocomposite on the fabric was performed but prefabrication of the nanocomposite followed by application to cotton fabric using the pad dry cure method was more plausible. The most appropriate formulation (condition) for synthesis of the hybrid nanocomposite were: concentrations (w/v) of: MMT 1%; CTS, 0.25; citric acid 5%, SHP 4%; Temp. 50°C; sonication time 90 min.

It is envisaged that interaction of the newly synthesized MMT/CTS hybrid nanocomposite with cotton cellulose (fabric) occurs through inclusions of this nanocomposite into the molecular structure of cotton fabric. Crosslinking of cotton with citric acid catalyzed by SHP would also support the intimate association of the nanocomposite inclusions within the cotton structure. Thus the ultimate output of this is a multifinshing of cotton including increase in fabric weight, ease of care characteristic, antibacterial activity, thermal stability and resistance to inflammability.

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