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Improved flame retardancy on polyester fabrics using chitosan-modified clay

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Abstract

The main objective of the present study was an improvement in flame retardancy (FR) of polyester fabric using modified clay as a green flame retardant. For this purpose, the polyester fabric was first treated with an alkaline agent, then nano-clay was modified with chitosan to form organo-clay and used as a flame-retardant finish for coating samples. To investigate the physical properties of samples, the water absorption and bending resistance of pristine polyester, alkaline, and modified clay-treated polyester were measured. Modified clay and surface-treated polyester fabrics were characterized using X-ray diffraction (XRD), Fourier Transform Infrared spectrometer (FTIR/ATR), and scanning electron microscopy (SEM). The study revealed that chitosan-modified clay treatment affects the flame retardancy of polyester samples through an increase in limiting oxygen index (LOI), char yield, and a decrease in melt dripping while burning.

Keywords: Chitosan, Nanoclay, Polyester, Alkaline Treatment, Flame Retardancy.

1. Introduction

Polyester fibers have been widely used in textile industries due to their low production costs, high strength -easy-care properties, dimensional stability, high thermal stability, and chemical resistance [1,2]. However, due to its poor wettability and lack of functional groups, the finishing of polyester fabrics has been a challenge in the textile industry [3,4]. On the other hand, their combustibility and serious dripping during combustion, highly limit their application. Therefore, surface treatment, flame retardancy and drop resistance of polyester (PET) have become interesting topics to be experimentally addressed [5]. Conventional flame retardants like halogen-based, pose threats due to their emission of toxic gases such as hydrogen bromide (HBr) and hydrochloric acid (HCl) during combustion, which are harmful to the human inspiratory system, their risks by emission of dioxins and furans (carcinogens) during incarnation, and also their corrosively. Recently, with increasing environmental awareness, technologists and scientists have made considerable efforts to replace non-biodegradable and toxic flame retardants with biodegradable and natural ones. "Green" alternatives such

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as "clay" have been reported to be effective in polymer flammability improvement. Clay, mostly montmorillonite, has a barrier and char-forming properties essential to be used as a flame retardant. [6-8]. Due to negative -surface charges of montmorillonite, a positively charged polymer can modify it. Many cationic polymers, such as Alkyl Ammoniums have been used to modify negatively charged clay. However, in this study, considering the biocompatibility of flame retardant, chitosan, a cationic biopolymer, was used as a macromolecular intercalant [8,9]. Chitosan is a linear, semi-crystalline polysaccharide derived by the deacetylation of chitin. Chitosan also has free amino groups making it a positively-charged polyelectrolyte in PH below 6, which contributes to its higher solubility compared to chitin [6,10-12]. Polyester needs to be alkaline treated to form crosslinking with the chitosan part of modified clay. Polyester goes through nucleophilic substitution and is hydrolyzed by aqueous sodium hydroxide. The hydroxyl ions attack the electron–deficient carbonyl carbons of the polyester to form an intermediate anion. Chain scission follows and produces hydroxyl and carboxylated end groups. On the other hand, the incorporation of nano-scale into textile surface leads to a high interfacial interaction which significantly improves the properties of the material [9,10,13-15].

The main objective of present study was to investigate the effect of nanoclay on flame retardant property of alkaline treated polyester fabrics.

2. **Experimental**

2.1. Materials and method

100% scoured and bleached plain-woven polyester fabric (160gr/m2) was used. Nanoclay used was natural montmorillonite; Cloisite Na+ was purchased from Rockwood. Medium molecular weight chitosan powder with a degree of deacetylation (DD) of 75-85% was obtained from Aldrich. Sodium hydroxide (NaOH), Citric acid (C6H8O7), and acetic acid (CH3COOH) were purchased from Merck. To investigate chemical bonding FTIR/ATR technique (Tensor 27, Bruker) was employed. The adsorption infrared spectroscopy was recorded at 1 cm intervals in the wave number range 500–4000 cm.

Surface modification of non-treated, hydrolyzed and modified clay-treated fabrics was observed by a bal-tech scd 005 scanning electron microscope, at an acceleration voltage of 26kV and magnification of 2500X. XRD analyses were performed at room temperature using a Philips X-ray diffractometer from 2θ (2° -10°), using CuKα with a wavelength of 1.54Å.The wettability of fabrics was determined based on the international standard method AATCC-39-1980.The time of disappearing spherical shape of water drop while pouring from burette on fabric was measured. A bending test showing the stiffness of fabric was carried out based on the ASTM-D 1388 standard test method in which a fabric with specified width and length is slid at a given rate in a direction parallel to its long dimension until its leading-edge projects from the edge of a horizontal surface. The length of the overhang is measured when the tip of the specimen is depressed under its own mass from this measured length; the bending length and flexural rigidity are calculated. To synthesize modified clay, 2.5 g of clay was poured into 125 ml of distilled water and stirred for 1 hour on a steamer heater. Then, a 1% acetic acid solution was prepared and finally isolated from chitosan in 1% acetic acid solution and stirred until the whole amount of chitosan was dissolved. The clay was put on heater at 300 rpm, and at a temperature of 60 ° C. Then, the chitosan solution was slowly added to it. The solution was stirred for 4 hours and then centrifuged. The powdered clay-chitosan composite was dried after drying and passed through the 200 mesh. To improve the adhesion of modified clay to the surface of polyester fabric, an alkaline pretreatment was applied. Polyester samples were treated in 10% o.w.f concentration of NaOH for 60 min at boil with liquor ratio1:20. After washing the samples, they were naturalized in acetic acid 1% at a ratio of 1:20 for 15 min at room temperature.Figure1 shows the steps of preparing modified clay via chemical hydrolysis following surface treatment of polyester fabric.

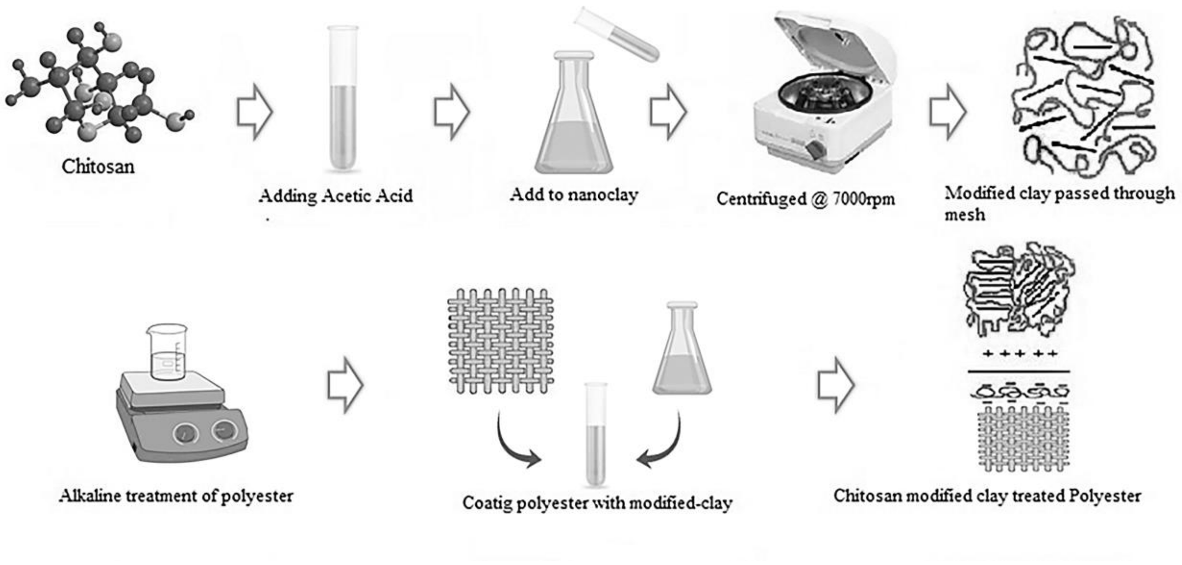

Figure 1. Diagram of modified clay preparing and surface treatment of polyester

Three different percentages of modified clay (1%, 3% and 5% o.w.f) were used to treat fabrics. Neat polyester and alkaline treated one were immersed in 8 % (o.w.f) concentration of citric acid (as cross-linking agent) and modified clay for 30 min at 50°C.

The liquor ratio was 1:50. Then, samples were dried at 100°C for 5 min and subjected to a thermo fixation at 120 °C for 2 min. In the end, all samples were washed in detergent for 5 min at 50°C so unbounded clay could be removed. The weight differences of samples after alkaline treatment and modified clay coating were measured according to equation (1):

$$W\ \%=\left|\frac{W_1-W_2}{W_1}\right|*100 \qquad (1)$$

$W\%$ equals the percentage difference in weight of the fabric, and are the weight of the fabric before and after treatment, respectively? The bending test was carried out according to the standard ASTM-D-1388 test method. The bending test was carried out according to the standard ASTM-D-1388 test method. A sample of specified width and length was placed on the top of the device and covered with a ruler. The fabric and the ruler were moved together until the sagging edge of the fabric touched the inclined plane. The length indicated on the ruler was recorded as the bending length. The water droplet adsorption time test was done according to the AATCC-39 1980 standard test method. A drop of water was poured from the burette to the surface of the fabric. The time of disappearing water drop was measured. LOI was measured using a Toyoseiki instrument on samples (100×6×3mm3) according to standard ASTM D2863. A mixture of nitrogen and oxygen passed through, and samples were fixed vertically. The minimum oxygen content in a mixture of nitrogen and oxygen at which a sample just burns is determined and given as the LOI value. The drip resistance was observed and reported. The weight of sample before and after complete burning was measured to obtain char residue.

3. RESULTS AND DISCUSSION

3.1. Physical Properties

Table 1 shows the weight difference, bending length, and water absorption time of alkaline-treated and untreated polyester fabrics. The time for water droplet adsorption on PET fabric is 4.12 Sec (Table 1). After the alkaline treatment of polyester fabric, water droplet adsorption reached 2.18 Sec. It can be attributed to the physical or chemical changes in an alkaline-treated polyester fiber, which may affect water adsorption. Alkaline treatment changes the structure of fiber using pores and cracks to enhance the hydrophilicity of PET. It promotes surface wetting further, and water drop could penetrate the pores and cracks. In addition to physical changes, due to the chemical changes, the alkaline hydrolysis causes chain cleavages as OH- attacks ester-bonded carbonyl carbon resulting in hydroxyl (–OH) and –COO groups on the fiber surface (Figure 2) [7].

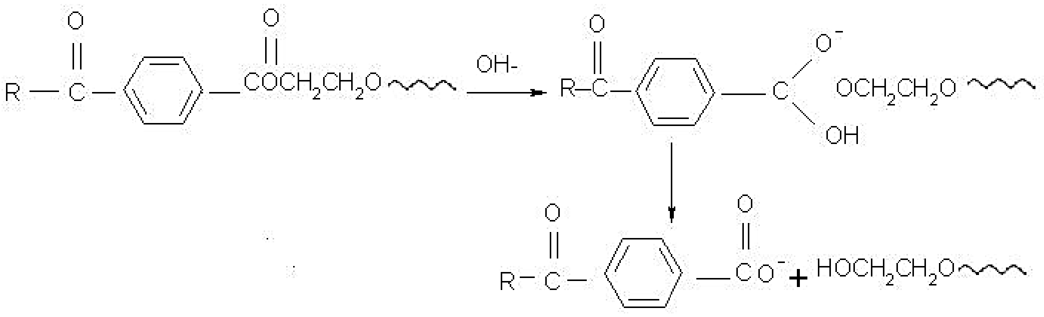

Figure2. Alkaline treatment of polyester Fiber.

In comparison between alkaline and nano clay-modified treated polyester, the decrease in wetting time of clay-treated polyester was observed due to improving the hydrophilicity of fabric in the presence of chitosan-clay nanocomposite.

The bending strength shows either stiffness or softness of fabric, which directly affects the handle of the fabric. As Table 1 shows, the bending length reached from 2.8 cm to 1.9 cm by alkaline treatment of polyester fabric, which makes the fabric more flexible comparing with untreated polyester. This result is in agreement with previous works, which indicate it as an outcome of surface etching, resulting in weight loss of hydrolyzed polyester. Bending length decreases slightly in chitosan/clay nanocomposite-treated fabrics compared to alkaline-treated ones. This slight decrease in bending length could be because of penetrating nano clay in the pores of polyester fiber, which could not affect the flexibility of fabric significantly [10,13- 16].

Table1. Weight difference, Bending Length and Water Absorption Lesults

Sample	Weight difference (%)		Bending length(cm)	Water adsorption time(S)
Polyester	--------		2.8	4.12
Alkaline treated polyester	31.5	-	1.9	2.18
1% Modified- clay treated polyester	0.14	+	1.7	1.48
3% Modified- clay treated polyester	0.35	+	1.65	1.35
5% Modified- clay treated polyester	0.44	+	1.5	1.1

3.2 X-ray diffraction (XRD)

The XRD patterns of unmodified clay and modified clay are shown in Figure 3. It shows that the peak characteristic of the nano clay has shifted from 2 θ = 7.8 ° to 2θ = 3.7 ° after the modification, which indicates an increase in the interlayer spacing due to the penetration of the chitosan molecular chains into the nano clay layers.According to Bragg`s equation, the d-spacing has increased from 1.128 nm in unmodified clay to 2.365 nm in modified clay.

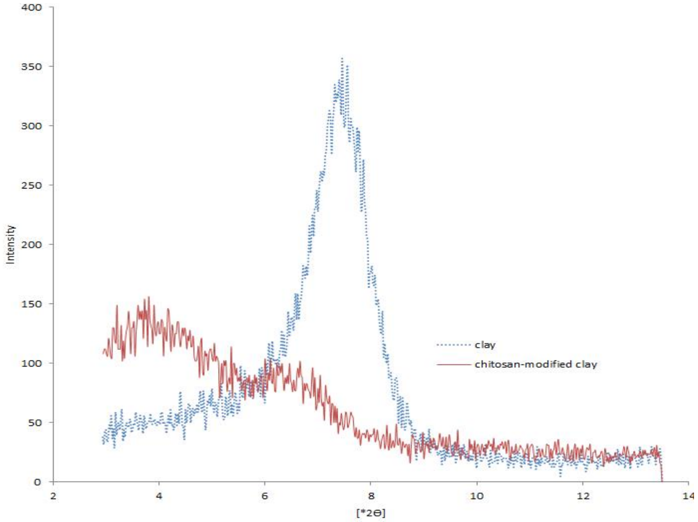

Figure (3). XRD diagram of unmodified and chitosan-modified clay

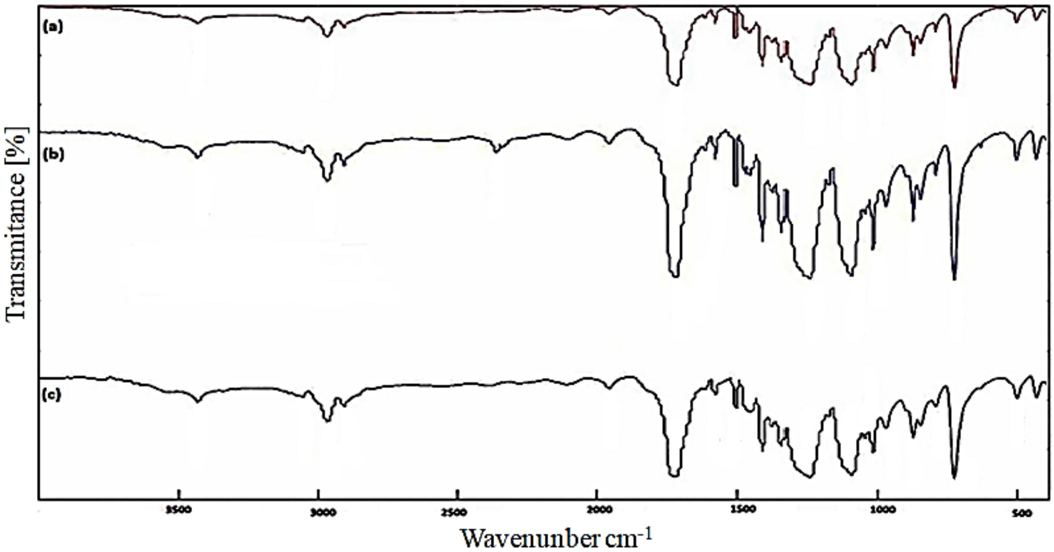

Figure 4. FTIR/ATR spectra of (a) Polyester, (b) Alkaline treated polyester, (c) modified-clay treated polyester

3.3 Fourier Transform-Infrared Spectroscopy (FTIR/ATR)

Figure 4 shows the spectra of a) untreated, b) alkaline treated, and c) modified clay-treated polyester. The presence of high peaks between 700 cm^{-1} to 1700 cm^{-1} agrees with previous research, in which, as in Figure 4(a) stretching vibration band of C=O at 1017.32 cm^{-1} and C-O-C at 1341.68 cm^{-1} are attributed to the ester groups of polyester. In Figure 4(b), the peak at 2361.33 cm^{-1} confirmed the presence of carboxylic groups (-COOH) in alkaline-treated polyester. In Figure 4(c), disappearing peak related to carboxylic groups shows that modified clay reacted strongly via hydrogen bonding with polyester. [14,16]

3.4 Scanning Electron Microscopy (SEM)

Figure 5 shows SEM micrographs of a) untreated polyester, b) alkaline treated polyester, c) 1%, d) 3% and e) 5% modified clay treated polyester. Polyester fiber had a smooth surface, while alkaline treatment made some pores and scars on the surface of polyester (4a and 4b). The pores made by alkaline hydrolysis could be sites for penetrating modified clay. This phenomenon can be seen clearly in Figure 5 (c-e). When the content of modified clay increased to 5%, the pores were almost filled by modified clay nanoparticles (Figure. 5e) [7].

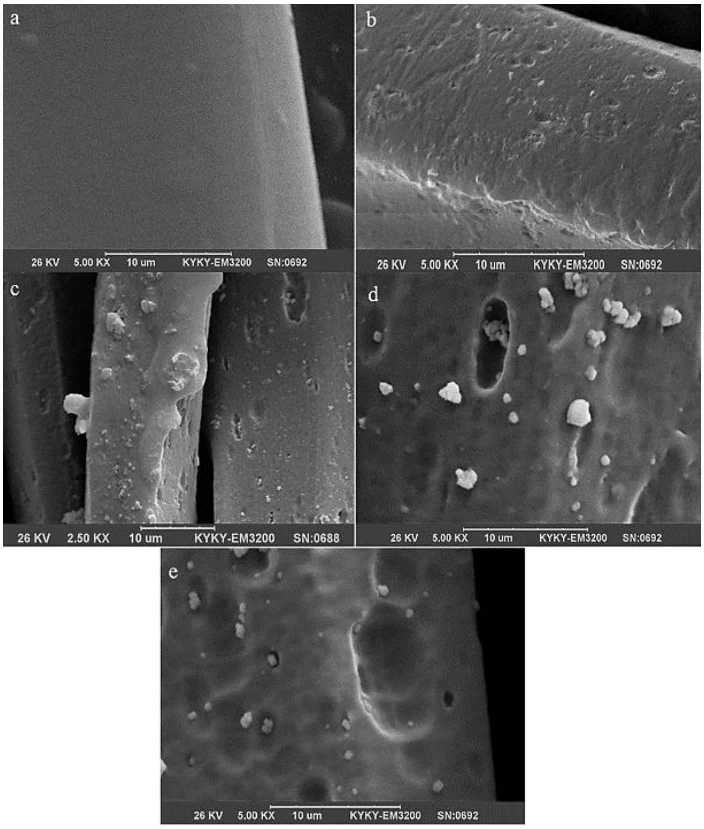

Figure 5. SEM micrographs of a) polyester, b) alkaline polyester, c) 1% modified clay, d) 3% modified clay and e) 5% modified clay treated polyester

3.5 Limiting oxygen index (LOI)

The results of the LOI test are given in Table 2. As it can be noted LOI values of modified clay treated polyester increase compare to pristine polyester. During combustion, clay forms carbonaceous char in a condensed phase, resulting in a reduction in the flammability of clay-treated polyester (Figure 6). The ceramic-like carbonaceous silicate char acts as a barrier and isolates the underlying polymer matrix. However, it is found that as the content of chitosan–treated clay increases from 3 to 5 %, the LOI value decreases from 22.8 to 20.8. It can be due to the formation of a barrier layer during the combustion of the sample, which limits the propagation inside the sample but increases flame- spread over its surface. The LOI results also show that polyester burns with heavy dripping, while polyester treated with modified clay shows drip resistance due to the formation of a network-structured protective layer during burning. The char residue of the treated samples at the end of the LOI test is more than pristine polyester, confirming the ceramic-like char formation of the flame retardant mechanism of modified clay treated samples [6,7].

Table2. LOI values of untreated and modified-clay treated samples

Sample	LOI	Drip	Char residue ($^{w}/_{w_0}$)
Polyester	19.7	Heavy	0.78
1% Modified- clay treated polyester	22.1	Scarce	0.12
3% Modified- clay treated polyester	22.8	No	0.37
5% Modified- clay treated polyester	20.8	No	0.48

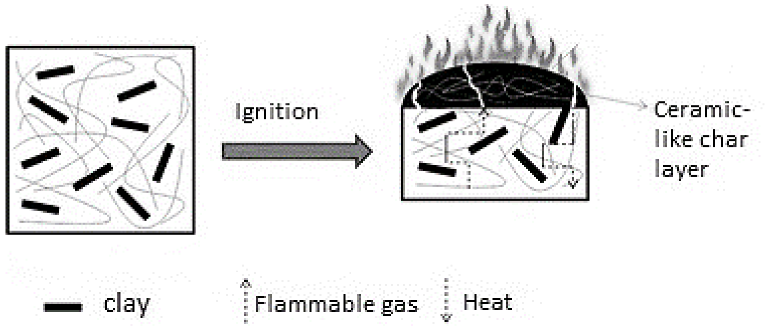

Figure6. Schematic of ceramic like char formation mechanism during ignition of modified clay-treated polyester

4. **Conclusions**

In this study, the effect of flame-retardant property of modified clay-coated polyester samples was investigated. In order for nanoclay to be able to react with polyester, polyester fabrics were first treated with an alkaline agent and then coated with nanoclay that had already been modified with chitosan; a biocompatible and cationic polymer. The results indicate that nanoclay could be an effective flame retardant for polyester due to its barrier effect through the formation of ceramic-like char on the polyester surface during combustion. The mentioned barrier can inhibit heat, energy and oxygen transfer between flame and polyester fabric. The char value and drip resistance of treated samples are further evidence of the flame retardant effect of nanoclay on polyester.

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