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Synthesis and characterization of fire retardancy phosphorous-PMMA/modified MMT nanocomposites



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Abstract

polymethylmethacrylate (PMMA) was synthesized by free radical addition polymerization using high-power ultrasound technique in presence of peroxodisulphate as initiator, then reacted with different concenterations of phosphoric acid. Montmorillonite (MMT) clay was modified using Cetyl Trimethyl Ammonium Bromide (CTAB). This study aims to investigate the effect of different concentrations of phosphoric acid used in polymer/clay modification on the fire-retardant properties of treated cotton fabrics. Firstly, the prepared polymer/clay nanocomposite and the cotton fabrics (either treated or untreated) were characterized using different physico-chemical techniques viz., FTIR spectra, Scanning Electron Microscope (SEM), SEM-EDX and Transmission Electron Microscope (TEM). The thermal stability of the prepared phosphorous polymer/clay nanocomposite was investigated using TGA and DSC analysis. Flammability tests and the fire-retardant properties of treated and untreated cotton fabrics were determining the rate of burning and Limited Oxygen Index (LOI) % values. The tensile strength of treated and untreated cotton fabrics were determined The data revealed that, increasing concentration of phosphoric acid led to increase the flammability resistance more than the untreated cotton fiber and all treated samples showed lower burning rate than that of the untreated one.

Keywords: Cotton fabric, fire retardant, Montmorillonite (MMT) clay, limited oxygen index and flame retardant.

1. Introduction

Cancer continues to pose a significant global health challenge, with breast and liver cancers being among the most prevalent One of the most common natural fibers that used as clothing materials is cotton.Cotton posses excellent properties such as hygroscopic nature, softness, warmness, biodegradation, launderability as well as it is comfort [1]. Its further application has been affected due to high flammability and poor hydrophobicity of cotton fibers [2]. So, the treatment of cotton fibers with new multifunctional materials becomes very necessary that provides these fibers with both of flame retardancy and water repellency. These treated cotton fibers as flame retardant can be used in manufacture textile used in protection especially in military organizations and the airline industry [3].

Montmorillonite (MMT) is a type of silicate clay having an inner octahedral layer sandwiched between two silicates and is used for rubber fillers but its use in different applications has been limited due to the presence of many impurities in nature montmorillonite. To overcome this problem, modified layered montmorillonite (polymer-layered MMT nanocomposites) has been synthesized to control the chemical composition by fine tuning the preparation conditions which contains fewer drawbacks. Modified layered montmorillonite can be obtained by introducing into the crystal lattice of montmorillonite some of transition metal ions such as iron that showed interesting properties. Generally, complete exfoliation of the clay is the ideal goal in the formation of nanocomposites [4]. The bad dispersion of the silicate into discrete monolayers is another problem that hindered further application of the clay in industrial production. Therefore, the modifications of layered silicates with organic compounds are necessary before the preparation of clay-based nanocomposites. Polymethylmetha acrylates (PMMA) nanocomposites can be synthesized in situ polymerization which the addition of MMT increased the ratios of termination by disproportion in relation to recombination [5].

The mechanism of working flame retardant based on phosphorus as follows: during the heating of treated fibers, phosphoric acid derivatives was liberated which a glassy layer was formed by this acid. This layer retarded the propagation of flame as well as the carbon char formation also acts as a two-way barrier, i.e. it obstructs the passage of flammable gas from the polymer to the flame that protects the polymer layer from the flame [6,7]. In the present work, the effect of different concentrations of phosphoric acid used in polymer preparation of the fire-retardant phosphorus/polymer/MMT nanocomposite was evaluated. Flammability test and Limiting Oxygen Index (LOI) were evaluated to investigate the performance of treated cotton fabrics [8-15]. These tests were also carried on cotton blends; but these tests give only incompletely information for the flammability of polymeric material [16,17]. The treated and

untreated cotton fabrics were investigated to determine the rate of burning and Limited Oxygen Index (LOI) values before and after washing cycles. Furthermore, the morphology of burnt cotton fabrics either treated or untreated was studied.

2. Experimental

2.1. Materials

Pure materials are used in this work without further purification,distilled water was used whenever water was necessary. Cetyl Trimethyl Ammonium Bromide (CTAB, 99%) ($C_{19}H_{42}BrN$) (m.p 237 to 243°C) was obtained from Sigma Aldrich Co., USA. Montmorillonite (MMT) with a cation exchange capacity about 120 mmol/100 g was obtained from the international company for mining and investment. Peroxodisulphate was purchased from (Merck, India). Sulfuric acid (H_2SO_4) (m.p 10.31°C) (b.p 337°C), Toluene ($C_6H_5CH_3$) (m.p $-95.0^{\circ}C$) (b.p 110.60°C), ammonium chloride (m.p 338°C) (b.p 520°C) and phosphoric acid (H_3PO_4) (m.p 42.35°C) (b.p 212°C), were obtained with percent (85 %) from (Merck, India).

2. 2. Cotton Fiber

Unbleached 100 % cotton fabric (area density 550 g/m²) was supplied from Misr for Control and Instrumentation (MCI) Egypt Company and was cut into pieces with dimension 5 cm ×15 cm before use. The fabrics were hyper acoustically rinsed with bi-distilled water, scoured in 2% non-ionic detergent at pH 7, dried in an oven at 90 °C for 20 min, and then kept for storage in drier. Before the experiments at least 24 h, the soaked samples were prepared under standard atmospheric pressure at humidity $65\pm2\%$ and temperature $20\pm1°C$ [18,19].

2.3. Methods

2. 3.1. Synthesis of polymethylmethacrylate (PMMA)

Polymethylmethacrylate (PMMA) was obtained by polymerization of methyl methacrylate (MMA) in aqueous solution of peroxodisulphate as initiator using a high-power ultrasound technique. The polymerization process was performed by mixing 400 ml of 0.1 M solution of MMA with 100 ml of 0.02 M aqueous solution of peroxodisulphate in a flat-bottom glass beaker. Using a Transonic Digital Ultrasonic water bath (Model Elma T490DH, Germany) with waves of fixed frequency 40 kHz at a constant power 100 W/cm² the reaction system was immersed for 300 min with kept stirring at temperature of 30° C. Then 100 ml of 2.0 N of sulfuric acid was slowly added along inner walls of polymerization reaction and kept the reaction for precipitation at 24 hr which PMMA was found at the bottom of the polymerization vessel as a thick mass. The product of PMMA was obtained by filtration, air dried under atmospheric conditions and finally in an oven at 50° C for 60 min [20].

2. 3. 2. Preparation of clay Nano hybrids MMT

Organo MMT was obtained according to procedure in ref [21]. 25 g of Montmorillonite (MMT) was heated at 80 °C for 2 hrs under stirring with 800 ml of bi-distilled water and followed by the slowly addition of Cetyl Trimethyl Ammonium Bromide (CTAB) (12.5 g in 100 ml distilled water) solution with continuous stirring for 10 hrs to complete the cationic exchange reaction. The product of modified MMT was obtained by filtration, followed by washing several times with bi-distilled water, and dried at room temperature .

2. 3. 3. Preparation of phosphorous-PMMA/modified MMT nanocomposite

A mixture of 1.0 gm of modified MMT and phosphoric acid with different concentrations of 3% (P1), 5% (P2), 7% (P3), 9% (P4) and 11% (P5) were added to a solution of 1.0 gm PMMA in toluene in a separate reactions. 2% ammonium chloride was added to each reaction as a catalyst and the reaction was kept for stirred for6 hrs. The phosphorous-PMMA/MMT hybrids was precipitated after the end of reaction by adding distilled water. The products were dried in air at room temperature and kept for further investigation [22].

2. 3. 4. Fabrication process of phosphorous-PMMA/modified MMT nanocomposite flame-retardant binding of the cotton fabric (CF)

The standard method for the treating of fibers is Pad-dry-cure method .In brief, CF of the required dimension was first immersed in a petri dish containing a solution of phosphorous-PMMA/modified MMT nanocomposite with DMSO with (different concentrations of phosphoric acid) for 3-4 min. After the fabric was completely saturated time with the solution, it was dried in an oven at 90 °C for another 3 min and followed by curing at 160-180 °C for 2.5 min [23]. Then, we washed treated cotton fabrics more than one time, which is a laboratory procedure used to wash fabrics at home.

The weight gain (WG) of amount FR loaded on CFs can be determined as the total amount of dry FR material added. In order to accurate determination, untreated and treated CF samples were dried until weight becomes constant. The value of WG % was calculated as follows:

$$WG(\%) = \frac{W_2 - W_1}{W_1} \times 100\%$$

where W1 and W2 represent the weight of the untreated and treated CF samples, respectively.

2. 3. 5. Flammability tests

In this test, samples of dimensions 130 x 40 x 3 mm maintained at room temperature and 50% humidity for 48 hours prior to analysis, were used. According to ASTM D635, ISO 3795 fora horizontal burning test was applied for

showing the flammability of CF samples. In this test, the sample is held horizontally and fired by natural gas at its end. The flame arrival time was measured from a first reference mark (25 mm from the end) to a second reference mark (100 mm from the end). For 10 seconds, the ignition of the test fabrics with a gas burner was continous and then removed while recording the after flame and afterglow times.

2. 4. Characterization Techniques

2. 4. 1. FT-IR measurements

By Thermofisher Nicolete IS10, USA in the range of 400–4000 cm⁻¹ Spectrophotometer (Chemistry Department, Faculty of Science, Benha University), the spectra of the fabrics samples were reported.

2. 4. 2. Morphology and particle size

The surface morphology and particle size of phosphorous-PMMA/modified MMT nanocomposite can be investigated using JEM-1230 electron microscopy scanning electron microscope (SEM, FEI Inspect S, Oxford USA) of acceleration beam of (25–30) k.v under vacuum pressure 60 Pa. This microscope provide a spot size of (5–6) using back scattering detector for Z-imaging and an X-ray diffractometer.

2. 4. 3. Thermogravimetric analysis

SDT Q600 V20.9 Build 20, USA, thermogravimetric analyzer was used to investigate the Thermal behaviors of phosphorous-PMMA/modified MMT nanocomposite samples at heating rate of 10 °C/min. The analysis was performed under atomspheric of N₂ gas from room temperature to 800°C.

2. 4. 4. Limiting oxygen index (LOI)

ASTM D2863-97 standard method was performed for measuring LOI values of some selected CF samples [24].

4. 5. Tensile strength test

According to BS EN ISO [25], the tensile strength of the untreated and treated fabric samples was assessed using six specimens (three for the warp and three for the weft) and a gauge length of 200 mm with a stain rate of 30 mm/min. The specimens were 50 mm wide.

3. Results and Discussion

3.1. Synthesis of polymethylmethacrylate (PMMA) and phosphorous-PMMA in presence of modified MMT nanocomposite

Polymethylmethacrylate (PMMA) and phosphorous-PMMA/modified MMT nanocomposite were prepared, the preparation of nano hydrid MMT with CTAB is shown in **Scheme 1**. As mentioned above, preparation of PMMA by free radical addition polymerization in the presence of high-power ultrasound as shown in **Scheme 2**, the mechanism of the preparation of flame retardant of Phosphorous PMMA/MMT nanocomposite [26] as shown in **Scheme 3** and the reaction between Phosphorous PMMA/MMT nanocomposite and cotton fabrics as shown in **Scheme 4**.







Scheme 2. Synthesis of Polymethylmethacrylate (PMMA)



Scheme 4: Reaction between Phosphorous PMMA and cotton fabrics in presence of clay hybrid.

3.2. FT- IR spectra of synthesized phosphorous-PMMA/modified MMT nanocomposite

The FT-IR spectra of PMMA, Nano hybrid MMT and phosphorous-PMMA/modified MMT nanocomposite are shown in **Fig.(1a-c)**). The most important band frequencies (cm⁻¹) were collected in **Table (1)**. Inspection of **Fig.(1-a)** showed that the spectrum of PMMA exhibited two strong peaks at 2951 and 1724 cm⁻¹ of C-H and C=O stretching, respectively [27,28]. FT-IR spectrum of the nano hybrid MMT (**Fig. 1-b**) exhibited one strong and one weak band at 1001 and 910 cm⁻¹due to Si-O and Al-O stretching, respectively. In addition, several new bands appeared which were assigned to the OH stretching at 3619 cm⁻¹, while C-H symmetric and asymmetric appeared at 2916 and 2849 cm⁻¹, respectively. In addition to NH₂ appeared at 1634 cm⁻¹, -CH₃ and -CH₂ asymmetrical stretching was observed at 1485 cm⁻¹ and -CH₃ and -CH₂ symmetrical stretching were appeared at 1342 cm⁻¹, which these peaks is due to the modification of MMT by the addition of CTAB [29]. The spectrum of phosphorous-PMMA/modified MMT nanocomposite (**Fig. 1-c**) showed a medium band at 2322 cm⁻¹ due to the stretching vibration of (P-OH) [22,30], while two new peaks related to O-P-O and P-O-C stretching were appeared at 1040 and 500 cm⁻¹, respectively. As shown, the intensity of these bands enhanched with the increasing in clay loading [30].

Fig. 2(a-b) showed the ATR-FTIR spectra of untreated and treated CF samples. The most important band frequencies are collected and assigned in **Table** (1). Most of the band intensities are increased and show sharpness after treatment, indicating more amorphousity of the fabric [31, 32].

Sample	Frequency; cm ⁻¹ (Assignment)		
РММА	2951 (V _{CH}), 1724 (V _{C=0})		
MMT	1001 (V _{Si-0}), 910 (V _{Al-0})		
Modified MMT-CTAB	3619 (V _{OH}) , 2916 (sym.V _{CH}), 2849 (asym. V _{CH})1634 (V _{NH2}), 1485 (sym.V _{CH3-CH2}), 1342 (asym.V _{CH3-CH2})		
Phosphorous PMMA/modified MMT nanocomposite	2322 (V _{P-OH}), 1040 (V _{O-P-O}), 500 (V _{P-O-C})		
Cotton samples	3296 for untreated shifted to 3335 after treating ($V_{\text{O-H}}$ and/or $V_{\text{N-H}}$), 1726 ($V_{\text{C=O}}$), 1067($V_{\text{O-P-O}}$), 1036 ($V_{\text{Si}-\text{O}}$), 917($V_{\text{Al}-\text{O}}$) and 547 ($V_{\text{P-O-C}}$)		

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Fig.1. FT-IR spectra for (a) PMMA, (b) Nano hybrid MMT and (C) phosphorous-PMMA/modified MMT nanocomposite.



Fig.2. Spectra of ATR-FTIR for (a) Untreated and (b) Treated CF using phosphorous-PMMA/modified MMT composites

3. 3. Morphology of synthesized phosphorous-PMMA/modified MMT nanocomposite

The morphology of synthesized phosphorous-PMMA/modified MMT nanocomposite was studied by SEM and TEM techniques. The morphology of PMMA and modified MMT was confirmed by TEM technique as shown in (**Fig.3a,b**) respectively which shows nanospheres structure in PMMA and produced exfoliated or lamellar structure in modified nano MMT. The image of SEM in **Fig.3-c** showed the surface structure of the phosphorous-PMMA/modified MMT nanocomposite which illustrated that homogenous nucleation promotes the formation of nanostructures as spheres. The morphology of the phosphorous-PMMA/modified MMT nanocomposite was confirmed by TEM technique as shown in (**Fig.3-d**) which shows nanospheres structure with average diameter of 20-40 nm. Considering the effect of phosphoric acid content, it is observed that the sample having phosphate content showed high stability in the nanostructures as indicated from SEM and TEM images which were shaped in nanospheres [33].







Fig.3. (3-a) TEM of PMMA, (3-b) TEM of modified MMT, (3-c) SEM and (3-d) TEM of the synthesized phosphorous-PMMA/modified MMT nanocomposite.

Fig.4 showed the SEM-EDX and mapping spectrum of the phosphorous-PMMA/modified MMT nanocomposite sample. EDX elemental mapping spectra showed the presence of phosphorous element in phosphorous-PMMA/modified MMT nanocomposite. All peaks of the elements which were characterized to PMMA and modified MMT appeared. Also, the phosphorous peak clearly appeared onto the surface of PMMA/modified MMT nanocomposite. The images showed that homogeneous distribution of phosphorous element with other elements of PMMA and modified MMT which proved the formation of phosphorous-PMMA/modified MMT nanocomposite [34].



(c)

Fig.4. SEM-EDX and mapping spectra of the synthesized phosphorous-PMMA/modified MMT nanocomposite.

3. 4. Thermogravimetric analysis

The thermogravimetric analysis (TGA) of the prepared materials was studied to support the chemical structure. The thermal degradation behavior is represented in (**Fig. 5-a**). The thermogram reflects the thermal stability of the sample up to 376.07°C, so represents the TGA curve of the prepared phosphorous-PMMA/modified MMT nanocomposite, which illustrated that it decomposes through three decomposition steps whose pattern are recorded as follows:

(i) The first step takes place within the temperature in range of $63.78-175.31^{\circ}$ C (account to around 10 % weight loss), this loss is due to low thermal stability of organic ammonium compounds in the MMT and loss of physically absorbed solvent and untreated monomers by the evaporation. (ii) In second step, the degradation occurs within the temperature range of 175.31-376.07 °C of weight loss 27 % which this loss is related the degradation occurs in polymeric network. (iii) At the temperature range of 376.07–600 °C, the third step occurs (account to around 12 % weight loss), assigned to the decomposition of the carbonaceous residue.

The differential scanning calorimetry DSC of the prepared nanocomposite represented in (**Fig. 5-b**). In the DSC curve of phosphorous-PMMA/modified MMT nanocomposite, there are exothermic peaks at temperatures of 94.95, 175.80 and 372.79 °C, which indicate the exothermic reaction of the synthesized phosphorous-PMMA/modified MMT nanocomposite.

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Fig.5. (a) TGA and (b) DSC of the synthesized phosphorous-PMMA/modified MMT nanocomposite.

3. 5. Flammability test

Flammability tests for untreated cotton sample and five treated samples using different concentrations of phosphorous-PMMA/modified MMT nanocomposite [3% (P1), 5% (P2), 7% (P3), 9% (P4)and 11% (P5)] were measured by a horizontal burning test according ASTM D635, ISO 3795. The results are represented graphically in **Fig.(6)** and reported numerically in **Table (2)**. Inspection of the obtained data showed that, in general, the treatment with different proportions of phosphoric acid plays an important role in flame retardant efficiency and the treated samples exhibit a lower burning rate than that of the untreated one. Also, among the treated samples, it is found that, sample P3 (treated by 7% phosphoric acid) has the lowest burning rate (0) followed by sample P5 (treated by 11% < acid) with a burning rate (30) compared to the burning rate of the untreated cotton sample (80). In general, the burning rate of the treated cotton samples lies in the order P3 < P5 < P4 < P2 > P1 **Fig. (7)**. Increasing of concentration of phosphoric acid leaded to an irregular difference in the flammability resistance suggesting that the cross linking between Phosphorous-PMMA/modified MMT nanocomposite flame retardant and cellulose has changed irregularly [35].

It is clear from this study that the blank cotton fiber was consumed by the bright flame quickly and left a few black ashes after burning for 48 s and afterglow for 90 s ,whereas, for treated samples, neither after flame nor afterglow appeared, which indicates that the phosphorous-PMMA/modified MMT nanocomposite has a certain flame-retardant effect. After burning, the char length and black area of the treated cotton samples were smaller than those of the untreated sample [34].



Fig. 6. The photograph related to horizontal flame test of different samples of phosphorous-PMMA/modified MMT nanocomposite CF (P1-P5) with different concentration of phosphoric acid.

Treated samples (cotton 100%)					
Sample	% phosphoric acid	Rate of burning (mm2/sec.)			
Blank(100 % cotton)	00 %	80			
P1 (3 %)	3 %	70.8			
P2 (5 %)	5 %	65			
P3 (7 %)	7 %	15			
P4 (9 %)	9 %	60			
P5 (11 %)	11 %	30			

Table (2): Rate of burning of untreated and treated samples using different concentration of phosphoric acid.



Fig. 7.The rate of burning of untreated and treated samples using different concentration of phosphoric acid.

3.6. LOI %

The values of LOI (%) of untreated and treated CF were determined by Standard method of ASTM D2863-97 [24]. The results represented graphically in **Fig. (8)** and cited numerically in **Table (3)** showed clearly that the LOI of untreated cotton fabric had a smaller value compared to those of the treated samples. Thus, it seems that the resistance of treated CF samples for burning was enhanced due to phosphoric acid. The values of LOI of the treated CF samples increased from 23.7-31.2 % by increasing the phosphorus percentage from 3-11 % respectively. The increase of LOI % values indicates the decrease in the flammability of treated cotton [36].

Table (3) The LOI value (%) of the untreated and treated cotton fabric samples using different concentrations of phosphorous-PMMA/modified MMT nanocomposite.

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Sample code	LOI value (%)			
Blank cotton 100%	17.1			
P1 (3 %)	23.7			
P2 (5 %)	24.5			
P3 (7 %)	27.4			
P4 (9 %)	29.1			
P5 (11 %)	31.2			



Fig. 8. LOI value % of treated and untreated cotton fabric using different concentration of phosphoric acid (P1-P5).

3. 7. Tensile strength test

The application of phosphorous-PMMA/modified MMT nanocomposite may affect fabric properties, like strength and bending rigidity. The tensile strength for treated and untreated cotton fabric is collected in **Table (4)**. We concluded that the tensile strength of treated CF samples is slightly increased in the sample of concentration 11 % of phosphoric acid (P5). The increasing in tensile strength support the the cross linking between phosphorous-PMMA/modified MMT nanocomposite

fire retardant and cellulose [22,37]. Table (4) Tensile strength for untreated, treated CF with different concentrations of phosphorous-PMMA/modified MMT nanocomposite.

Samples	Tensile strength in warp Direction (N/mm²)	Tensile strength in weft Direction (N/mm ²)
Blank (100%cotton)	110	100
P1 (3 %)	98	90
P2 (5 %)	100	95
P3 (7 %)	108	98
P4 (9 %)	115	103
P5 (11 %)	120	110

4. Conclusion

- Poly (methyl methacrylate) (PMMA) was prepared by free radical addition polymerization in the presence of high-power ultrasound and montmorillonite (MMT) clay modified by Cetyl Trimethyl Ammonium Bromide (CTAB).

- The phosphorous-poly (methylmethacrylate) (PMMA)- modified Montmorillonite (MMT) clay nanocomposites with different concentrations of phosphoric acid were synthesized to investigate the fire retardant performance with cotton fabrics.

- The FT-IR spectra confirmed the chemical structure of the prepared phosphorous-PMMA/modified MMT nanocomposite, treated and untreated cotton fabric.

- The morphology of the prepared material showed nanospheres from SEM and TEM images. The EDX elemental mapping spectra proved the presence of phosphate in the prepared materials.

- The thermogravimetric analysis (TGA) of the prepared material supported the chemical structure and the thermal degradation behavior. Also, DSC analysis of the prepared material indicated the exothermic reaction.

- The results showed a good flame retardant of the prepared phosphorous-PMMA/modified MMT nanocomposites used for treating cotton fabrics with more durability.

- The data revealed that increasing the concentration of phosphoric acid led to increase the flammability resistance, limiting oxygen index (LOI%) and tensile strength more than that of untreated cotton fabric and all treated samples showed a lower burning rate than that of the untreated one.

5. References

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