

RESEARCH PAPER

Synthesis of a Novel Flame Retardant Containing Phosphorus-Nitrogen Cotton by Grafting Poly Diethyl (Acryloyloxy) Ethylthiophosphoramidate onto Cotton via Atom Transfer Radical Polymerization, and Its Polymer/Clay Nanocomposite

Saber Ghasemi Karaj Abad ¹, Elham Eslamian ¹, Mojtaba Abbasian ², Mehdi Hosseinzadeh ^{3*}, Esmail Vessally ⁴, Solmaz Esmaeily Shoja ⁴

¹ Department of Chemistry, Payame Noor University, P. O. Box: 19395-3697 Tehran- Iran

² Department of Chemical Engineering, University of Bonab, Bonab, Iran

³ Marand Faculty of Technical and Engineering, University of Tabriz, Tabriz, Iran

⁴ Lab. of Materials, Faculty of Engineering, Islamic Azad University, Bonab branch, Bonab, Iran

ARTICLE INFO

Article History:

Received 09 July 2022

Accepted 13 September 2022

Published 01 October 2022

Keywords:

Atom transfer living radical polymerization

Clay

Cotton fabric

Flame retardant

Nanocomposite

Poly diethyl (acryloyloxy)

ethylthiophosphoramidate

ABSTRACT

In this research, a novel strategy for preparation of a flame retardant cotton fabric with a covalently attached diethyl (acryloyloxy) ethylthiophosphoramidate (DEAETPN) through surface initiated ATRP was investigated. Initially, new phosphorus containing flame retardant monomer (nitrogen and sulfur (DEAETPN) was prepared by reacting (2-hydroxy-ethyl)-thiophosphoramidic acid O, O'-diethyl ester with α -chlorophenyl acetyl chloride as an initiator. The initiator for ATRP using our novel method was covalently linked onto the cotton surface fibers. For this purpose, the surface of cotton fibers based-cellulose was modified with 3-aminopropyl triethoxysilane - a silane coupling agent. This functionalized cotton was then reacted with α -chlorophenyl acetyl chloride to prepare the Cotton-APTES-Cl macroinitiator. The metal-catalyzed radical polymerization of DEAETPN with macroinitiator was carried out in the presence of CuBr / 2, 2'-bipyridine (BPY) catalyst system in THF solvent at 70°C to obtain poly (DEAETPN) segments grafted chlorinated cotton. Finally, the resulting nanocomposite obtained from Cotton-g-P (DEAETPN) graft polymer with montmorillonite modified in Carbon tetrachloride (CCl₄) was prepared by a solution intercalation method. The chemical structure of all prepared compounds was confirmed by different techniques such as spectroscopy: FT-IR, ¹HNMR, TEM, and SEM. The compound thermal behavior was also evaluated by DSC and TGA.

How to cite this article

Ghasemi Karaj Abad S, Eslamian E, Abbasian M, Hosseinzadeh M, Vessally E, Esmaeily Shoja S. Synthesis of a Novel Flame Retardant Containing Phosphorus-Nitrogen Cotton by Grafting Poly Diethyl (Acryloyloxy) Ethylthiophosphoramidate onto Cotton via Atom Transfer Radical Polymerization, and Its Polymer/Clay Nanocomposite. J Nanostruct, 2022; 12(4):898-913. DOI: 10.22052/JNS.2022.04.012

* Corresponding Author Email: mh_1268@yahoo.com



INTRODUCTION

In recent decades, the latest research in the field of materials around the world has focused mainly on the making of nanomaterials, nanocomposites, and the improvement of their properties. [1, 2]. Polymer-based nanocomposites are a new generation of materials that contain a polymer matrix and a small number of improved nanometers. Furthermore, the materials-based polymer–clay nanocomposite has been widely investigated in the last few years [3-6]. Polymer-clay nanocomposites have been significantly used in various industrial and research fields compared to similar pure polymers and conventional compounds due to their desirable mechanical, physical and chemical properties. [7, 8]. Nanometer (nm) improvers' expands polymer properties due to their high ratio of length to diameter, very small size, and very high levels compared to typical ones. The final products have lower weight, high mechanical strength, more effortless processability, and higher thermal tolerance compared to typical composites [9]. On the other hand, Cotton is one of the plentiful biodegradable, bio-molecular, and renewable natural materials available for making polymers for various applications. It is possible to achieve functionalized polymers using a surface modification of cotton today that is of utmost importance. Cotton surface characteristics such as absorption, high-level humidity and strong stability have increased the usage of this natural polymer [10]. However, one of the drawbacks of these fibers is their high flammability. One way to reduce flammability is using flame-retardant material. This is done by different flame-retardant materials such as halogen, phosphorus, nitrogen compounds, etc. Each of these materials uses a special mechanism that increases the product's resistance to flame. Therefore, the polymers which contain nutrients such as phosphorus and nitrogen appear to show special properties with high performance in flame retardancy [11-14]. The most common method of combining the functionality of the polymer involves graft polymerization or reactions after grafting. In the past, cotton cloth flame retardant had been prepared using the phosphorylation reaction.

Textile and clothing products are extensively utilized throughout the world. Among the multiple textile materials, one of the most popular materials utilized for textiles and clothing is cotton

fabric. Cotton is used to obtain reinvigorated cellulose fibers, which also have several textile performances. Functionalized cotton fibers have great potential for making textiles with numerous techniques and excellent added value by improving the surface. [15-18]. Once improved with polymers, cotton fibers could be utilized on sports clothes with developed thermal or elastic features, water-proof, oil-water separating fabrics, or self-cleaning. Furthermore, its application in certain conditions has been restricted due to its easy combustion and combustibility in the atmosphere. Various techniques have been used for prepare textile fibers such as, co-monomers or flame retardant additives in synthetic fibers, a surface graft of copolymers, nanocomposite technology, etc. [19-23].

Preparation of monomers is of special importance and in comparison with other grafting techniques, grafting using the living radical polymerization method can have many benefits such as grafting control degree and the reduction of the homo-polymer making. This technique mainly displays a stabilizer iniferter on the surface of the polymer and uses it to graft the copolymer [24–26]. Despite having many advantages, this method is not used much due to low reactivity with polymers, which leads to reduced phosphorus in the polymer. The act also, after grafting, the polymer structure will face chemical defects. In addition to the functionalized polymer creating desirable properties, molecular weight control has been considered in recent years. Therefore, controlled radical polymerization has gotten much attention in recent years. Polymerization using iniferters (a new method for radical polymerization) is free. Iniferters not only act as a starter, but also as a transfer agent, retarders and terminator.

Controlled/living radical polymerization (CLRP) represents a correct pathway for synthesizing controlled graft copolymers with predesigned molecular weight (MW) and narrow molecular weight dispensation ($PDI = (M_w)/(M_n)$). Nevertheless. It was found in multiple architectonics and beneficial end-functionalities [27].

On the other hand, copolymers generally show very different physicochemical properties from their homopolymer mixtures. From this perceptual viewpoint, RDRP (reversible deactivation radical polymerization) is usually well-known as CRP

(controlled radical polymerization) techniques. These techniques consisting of: nitroxide-mediated polymerization (NMP) [28-31], reversible addition of fragmentation chain transfer (RAFT) polymerization [32-35], and atom transfer radical polymerization (ATRP) [36-39], have been well-confirmed as a fundamental and essential factor for the preparation of graft copolymers with narrow dispersity, complex macromolecular architectonics and controlled molecular weight. As a result, ATRP has historically been the foremost among these techniques, representing perhaps the simplest RDRP technology. Thus, the polymerization degree and the basic structure of the prepared polymer and its molecular weight could be controlled by applying iniferters [40]. In 1995 Matyjaszewski and Sawamoto [41], independently introduced the ATRP technique. This method prepares an alternative and easy technique to precisely control the polymerization of different monomers under different reaction situations and makes it possible to synthesize well-defined copolymers. In this polymerization, a metal complex primer affects the initiator and separates halide into the homogenous form followed by creating polymerization radical's initiators and the metal halide complex. [42].

In this present research, as stated, a modern monomer containing nitrogen, phosphorus and sulfur diethyl (acryloyloxy) ethylthiophosphoramidate (DEAETPN) was prepared. Then, it is polymerized and grafted onto cotton fabric (Cellulose) to obtain Cotton-*g*-P (DEAETPN) through the ATRP method. Modified MMT (O-MMT) was produced after treatment with hexadecyl trimethylammonium chloride salt. Finally, Cotton-*g*-P (DEAETPN) / O-MMT nanocomposite in CCl_4 was successfully prepared by solution interpolation method. The structure of the produced nanocomposite was investigated using FT-IR, TGA, DSC, SEM, and TEM techniques.

MATERIALS AND METHODS

Materials

Cotton with the chasing characteristics 125 g/m², tops and termination 35/in and 55/in respectively, simple texture (1/1), number of yarn in weft and warp 282/m and 252/m respectively were applied. 3-aminopropyl triethoxysilane (APTES) was prepared by means (Merck Co) and utilized as a received. Required Toluene was reflux under sodium metal and benzophenone until the

appearance of dark blue color and then distilled under argon gas. Dichloromethane density: 1.33 g/cm³ and molar mass: 84.93 g/mol and Diethyl Amin with density: 707 g/cm³ and molar mass: 73.14 g/mol were dried by calcium hydride over 24 hours and filtered and purified by distillation at low-pressure. Triethylamine (TEA) was also dried over magnesium sulfate for 24 hours and then filtered using low pressure distillation. The rest of the materials were acquired from Merck Company and then were purified according to the standard methods. α - Chloro phenyl acetyl chloride, bpy (2, 2' bipyridine), and CuBr were utilized as received. Hexadecyl trimethyl ammonium chloride salt was provided from Merck Co. (Germany, Darmstadt). Na⁺-MMT was provided from Southern Clay Products (Gonzales, USA, TX) under the commerce Company (Cloisite NaC) with a cation exchange volume of 95 meq 100 g⁻¹ and the idealized chemical formula $\text{Na}_{0.33} [\text{Mg}_{0.33} \text{Al}_{11.67} \text{Si}_4 \text{O}_{10} (\text{OH})_2]$. All other chemical materials and solvents were acquired from Sigma-Aldrich and purified according to the literature.

Characterization

FT-IR spectra were recorded using the device S-8400FTIR- SHIMADZU model. Solid samples were completely powdered and mixed with potassium Brummer and came under pressure, then the resulting KBr tablet was placed in a holder in the spectrometer. The spectroscopy of ¹HNMR on Bruker Spectrospin Avance 400 was done at 25 °C. The specimen for the NMR spectroscope was obtained by dissolving about 10 mg of specimens in 1 mL of deuterated proton-less solvents DMSO or CDCl_3 , and the chemical material change in ppm units were reported with tetramethylsilane (TMS) as the central standard. The thermal particularity of the prepared specimens was studied by a thermogravimetric analyzer (TGA-PL STA 1640 apparatus (Polymer Laboratories, UK, Shropshire)). The TGA experiences were performed under N_2 flow and heated 25 through 700 °C at the rate of 10 °C/min⁻¹. DSC is a thermoanalytical technique was carried out using NETZSCH (Germany, Selb), DSC 200 F₃ Maia; the specimens were well kept warm and then cooled a few minutes to remove thermal stability, and then heated again and the temperature was raised to about 400 °C. X-ray diffraction (XRD) (Siemens, Germany) spectrum was prepared by utilizing a Siemens D 5000, X-ray generator (CuK α irradiance with $\lambda=1.5406$) with

a 2 θ scan range of 20-80°C at room temperature. The whole test was conducted under N₂, flowing at a pour rate of 50 mL/min⁻¹. The scanning electron microscope (SEM) specimen was performed utilizing a LEO 1430 VP to characterize the morphology of the synthesized nanocomposite. Transmission electron microscopy (TEM) synthesized nanocomposite was done by means of LEO906 ZEISSALMAN with a 100 kV at an operation voltage of 15.00 kV. The layered structure of O-MMT and its dispersion condition were seen with a (VEGA//TESCAN KX5000 apparatus) scanning electron microscope (China, Shanghai). Afterward, the specimen was reheated up to 200 °C at a rate of 10 °C /min⁰¹. According to XRD, all examine were applied under N₂ flowing at a pour rate of 50 mL/ min⁰¹.

Preparation of monomer

The monomer was prepared in two stages with the use of ethanolamine as a starting material.

(A) Stage 1: Preparation of 2-hydroxyethyl-thiophosphoramidic acid diethyl ester

Regarding the first stage, to a 100 ml two-necked flask equipped with a magnetic stirrer, and reflux condenser for about (2. 37 g, 0.02 mol) sodium carbonate (Na₂CO₃), 1.11 ml dichloromethane (CH₂Cl₂) as a solvent, and (0.01 mol, 0.6 ml) of ethanolamine (ETA) was poured. The resulting mixture was stirred for 30 minutes under argon gas pressure. Then (0.01 mol, 1.66 ml) of Diethylthiochlorophosphate and 1.11 ml CH₂Cl₂ through hopper increasing (within 20 minutes) was added drop by drop to the mixture. The reaction mixture was stirred for seven hours at room temperature. After the specified time, since the reaction product was two fuzzy, the separation of the aqueous phase and the organic phases was done using a separating funnel as follows: Firstly, 10 ml of distilled water was added to the solution. After stirring the solution, ultimately, the aqueous phase and organic phase were separated from each other (because the density of CH₂Cl₂ was more than water, so the organic phase was heavier than the aqueous phase). Therefore, the obtained aqueous phase was also extracted using CH₂Cl₂ (10 × 4 ml). The organic phase extracted from CH₂Cl₂ was first added to the separated organic phase. To further purification, obtained organic phase 4 times were mixed and separated again, respectively, with values of 10 ml of distilled water, 20 ml of HCl (10 × 2 ml), and 5 mL of saltwater.

Finally, to fully absorb the water from the solution, some amount of anhydrous sodium sulfate (until the clear solution) to the mixture was added and stirred. After converting the opaque organic phase to the bright organic phase, a smooth operation was performed and ultimately evaporated using a rotary evaporator solvent to achieve high purity. A material 2- Hydroxyethyl- thiophosphoramidic acid, O, O, diethyl ester, which is pale yellow and sticky, was produced. [43].

(B) Stage 2: synthesis of Diethyl (acryloyloxy) ethylthiophosphoramidate (DEAETPN)

In the second step, triethylamine (TEA) (0.01 mol, 1.3925 ml) and 11.26 ml of CH₂Cl₂ were poured into a 100 ml three-necked flask equipped with a magnetic stirrer, reflux cooler and funnel step, then 0.009 mol of the obtained material from the previous step, (2- hydroxyethyl) - thiophosphoramidic acid O, O- diethyl ester) was also added to the contents of the flask under zero ° C (the balloons were placed into an ice water bath) and also under nitrogen gas that entered into the balloon by salty gas (0.8 mol, 0.72 ml), Acryloyl Chloride was added into the balloons drop by drop. After Acryloyl Chloride was added completely, the ice water bath, and salt gas were removed and the reaction mixture was under nitrogen gas to reflux for 4 hours and got hot to the laboratory temperature, then the obtained precipitate is three-ethylene amino hydrochloride was removed by the filtration. The material after the deposition was two phases that separated from each other by the funnel in this way. Firstly, for the separation of the two phases, 10 ml of water was added to the reaction mixture, then the separated organic phase was mixed with the values of 20 ml HCl 1N (10 × 2 mL), 10 ml of distilled water, and 5 ml of mixed saltwater respectively and the organic phase was extracted for 4 times, then to further purification, 10 ml of diethyl ether was added and completely, the organic phase was separated, after that a small amount of waterless sodium sulfate was added to remove its water completely. Finally, to achieve a high degree of purity, the resulting oily substance was placed in a rotary evaporator. The final obtained substance is diethylene (acryloyloxy) ethylthiophosphoramidate which is a colorless liquid (Fig. 1) [43].

The Preparation of Resistant Cotton against Fire_ The Synthesis of Functionalized Cotton with 3-aminopropyl triethoxysilane (APTES) over Flame

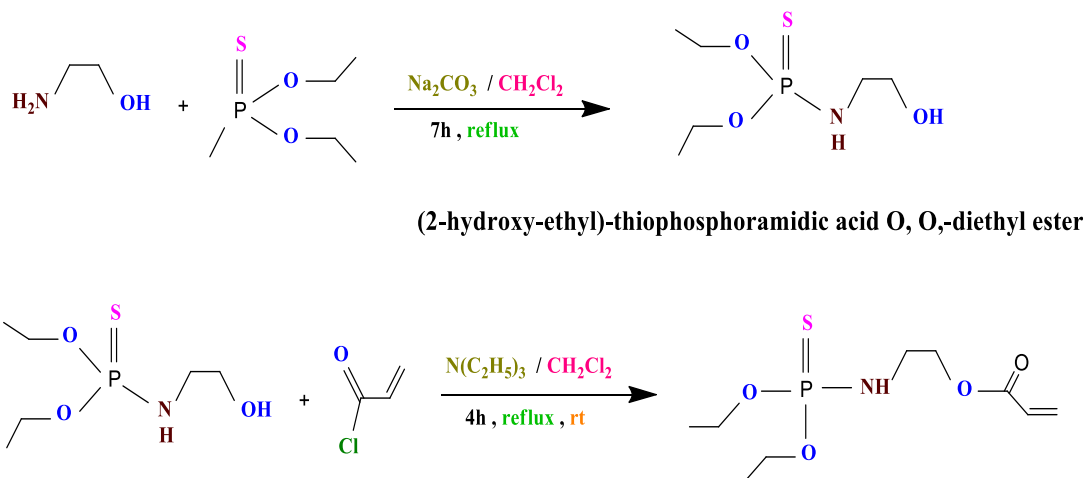


Fig. 1. Synthesis of diethyl (acryloyloxy) ethylthiophosphoramidate (DEAETPA).

and Connecting the Living Radical Polymerization initiator on it

To functionalization of cotton, to a 100 ml two-neck flask which is fitted with an additive funnel and a magnetic stirrer (0.001 mol, 0.234 ml) of APS was mixed up in 50 ml of toluene, under nitrogen gas, 1 gr pristine Cotton was added to the mixture. The resulting mixture was stirred with a magnetic stirrer under nitrogen gas for 30 minutes, and then the mixture was cooled to zero degrees centigrade; after that, just a drop, (0.001 mol, 0.142 ml) of α - Chloro Phenyl Acetyl Chloride was added to the flask. The reaction was stirred at the same temperature for 1 hour, and then the reaction went forward overnight with soft stirring. Finally, the obtained suspension was centrifuged, and the obtained white deposit with ice ethanol was washed and dried under a vacuum oven.

Achieving Fire-resistant Asbestos by Metal-Catalyzed Radical Polymerization

In a 100 ml two-neck flask which is equipped with a magnetic stirrer, a reflux condenser, and a thermometer, the amount of 1 ml distilled water, 2 ml of methanol, 1.0 gr of 2, 2 -Biperiden (bpy), and 0.001 mol of synthesized monomer diethyl (acryloyloxy) ethylthiophosphoramidate (DEAETPN) was poured, respectively. Then the amount of 0.275 gr of APTES-Cotton-Cl was added to the flask. After stirring the reaction mixture for 10 minutes under nitrogen gas, the amount of 0.03 gr of copper chloride (CuCl) (I) under nitrogen gas was slowly added to the mixture,

stirring operation continued in the same state for 5 minutes. The contents of the reaction flask were contained in a 37 °C water bath. The reaction continued at the same temperature for 7 hours under nitrogen gas with gentle stirring. After the specified time, the suspension was completely red due to the presence of residual copper in the polymer. Therefore, to remove the impurities and achieve the desired product, a smoothing action was done until white sediment was washed with a large amount of acetone and distilled water. In the end, the produced white precipitate, that is, the asbestos, was dried in a vacuum [44]. Fig. 2 displays the overall strategy for functionalizing cotton surface and the polymerization reaction.

Reactions related to the preparation of nanocomposite

Surface modification of pristine montmorillonite

The amount of 3 gr of MMT was added slowly to a half-liter beaker containing 100 ml of deionized water (DIW) stirred by a magnetic stirrer. After an hour of stirring, it was placed in the ultrasonic device for 10 minutes. Subsequently, along with this phase, a 3% solution by weight - the weight of hexadecyltrimethylammonium chloride rectifier (with a density of 0.89 cm³ / gr) was prepared. The content of MMT was poured into a 250 ml two-neck flask, and the rectifier was added to the stirring mixture drop by drop. Suspension inside the balloon was stirred vigorously for 24 hours at 60 °C. Finally; the obtained mixture was rinsed several times with deionized water until all

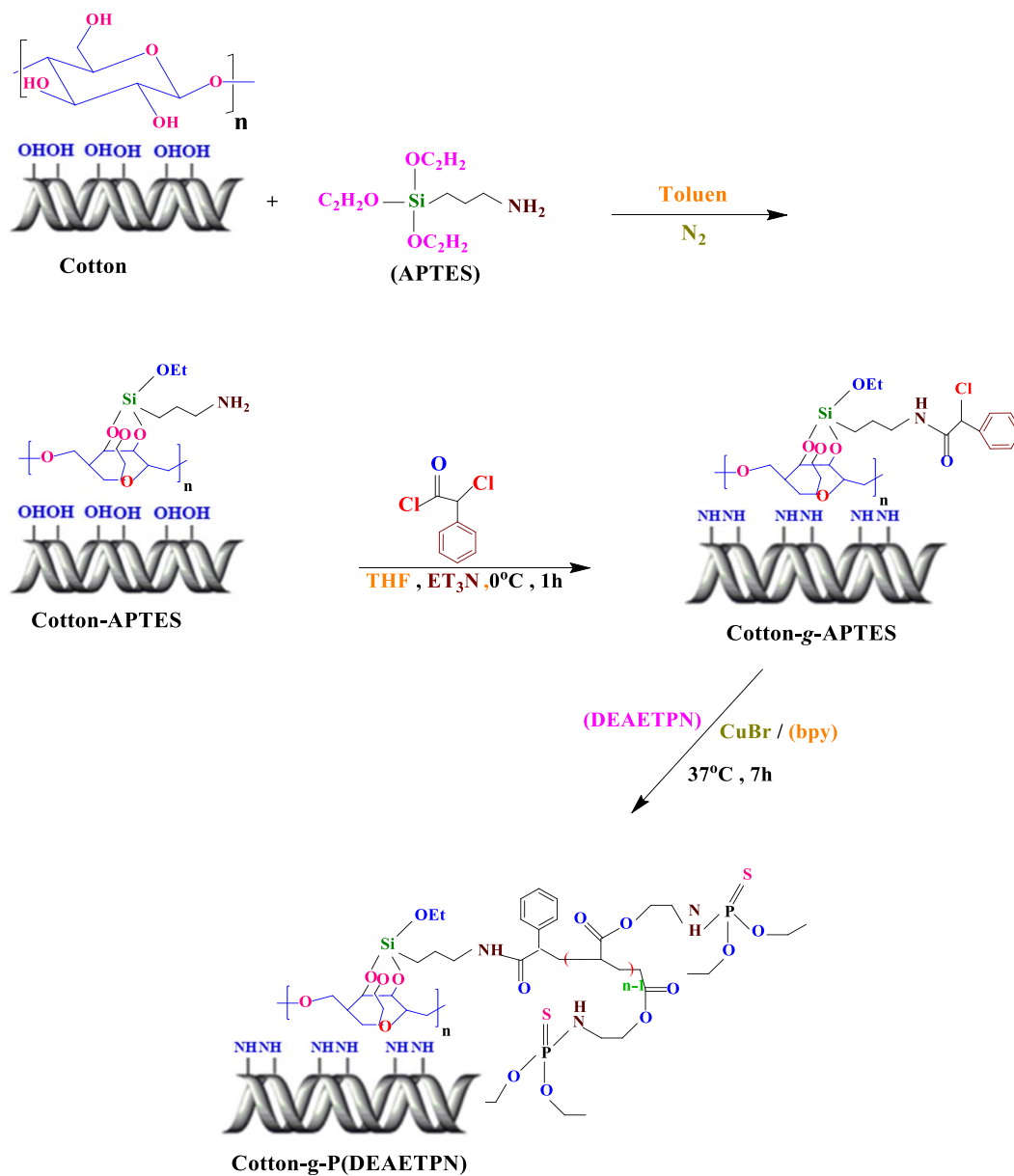


Fig. 2. Schematic illustration of the synthesis of Cotton-g-P (DEAETPN).

additional chloride anions (Cl^-) were completely emitted, which was ensured using the silver nitrate test (AgNO_3). Finally, using ethanol, the rectified MMT, was rinsed and dried under a vacuum at 60°C .

Preparation of Cotton-g-P (DEAETPN) / O-MMT nanocomposite via solution polymerization method

Preparation of nanocomposite is provided

by mixing in the solution phase. Rectified MMT (0.05 g, 5 wt. %) was stirred in a 200 ml beaker of 40 ml of fresh and dry CCl_4 for 1 hour at room temperature with a magnetic stirrer, then was put for 10 minutes in the ultrasonic. The 4.0 gr of the obtained polymer was stirred separately in 40 ml of dry CCl_4 , and the rectified MMT suspension was added drop by drop to the mixture of the beaker and was put in Ultrasound for 15 minutes. The obtained mixture was vigorously stirred in

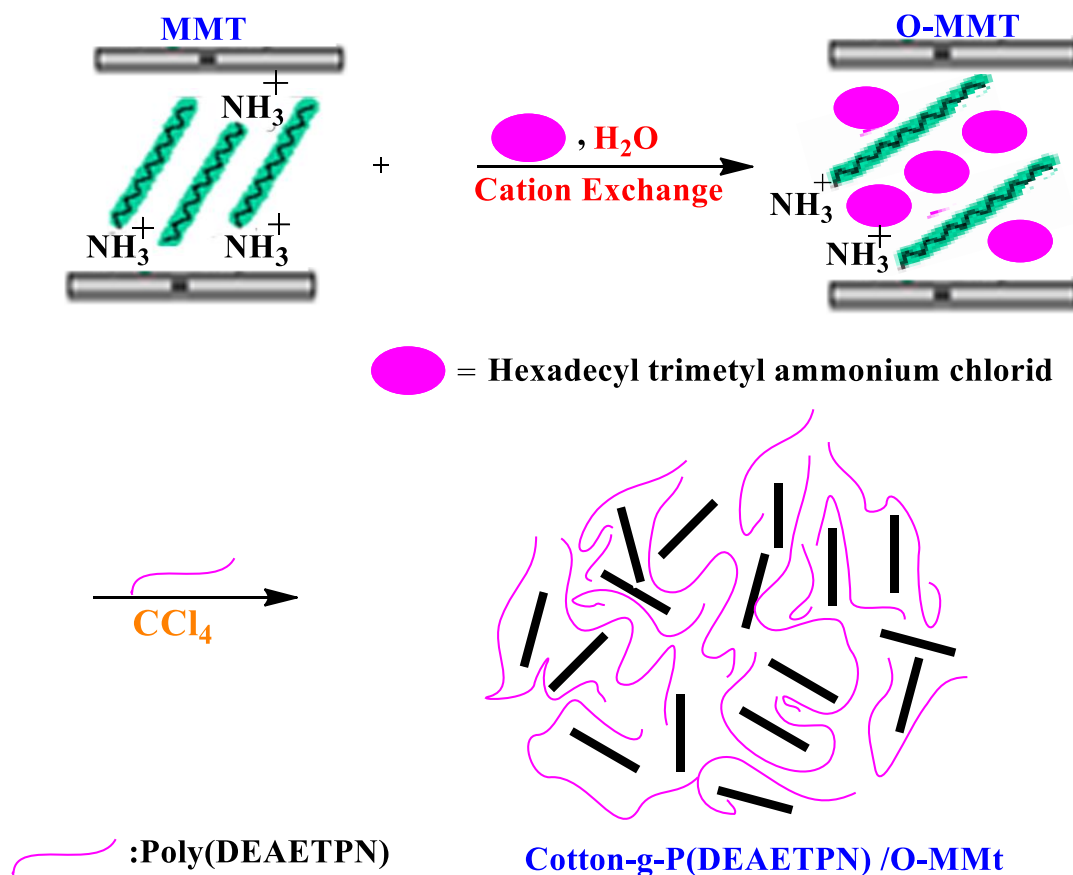


Fig. 3. Preparation of Cotton-g-P (DEAETPN) /O-MMT nanocomposite through solution polymerization.

acidified precipitated methanol at 60 ° C for 24 hours, the mixture was re-precipitated in acidified methanol, then refined and dried under a vacuum oven at 60 ° C (Fig. 3).

RESULTS AND DISCUSSION

Study of FT-IR and ¹HNMR

The FTIR spectrum of (2-hydroxy-ethyl)-thiophosphoramidic acid *O,O'*-diethylester (a), and Diethyl (acryloyloxy) ethylthiophosphoramidate (b) are shown in Fig. 4. The characteristic absorption peaks owing to stretching vibration of –OH group at 3356 cm⁻¹, C=O group stretch vibration at 1772 cm⁻¹, stretch vibration of -CH symmetric and asymmetric group at 2935 cm⁻¹ and 2995 cm⁻¹, stretch vibration of (POC) bond at 900-1250 cm⁻¹ and stretch vibration of (P=S) bond at 600 cm⁻¹. Also, the spectrum of FT-IR poly (DEAETPN) (b) represented characteristic absorption peaks owing to stretch vibration of NH group at 3356 cm⁻¹, stretch vibration of C=C at 1400 cm⁻¹, C-O stretch

vibration at 1200 cm⁻¹, the absorption peak of C = O at 1745 cm⁻¹.

On the other hand, the surface modification of Cotton treated with APTES has been extensively utilized. To get evidence that APTES chemically was connected to Cotton, the spectroscopy of FT-IR for verification was initially applied to recognize the qualitative combination of the Cotton. The FT-IR spectrum of pristine cotton (a), and (Cotton-APTES-Cl) macroinitiator (b), poly (DEAETPN)(c), and Cotton-g-P (DEAETPN)/O-MMT nanocomposite (d) are seen in Fig. 5. The FT-IR spectrum of pristine cotton displays the characteristic absorption peaks owing to the stretch vibration of C–O at 1158 cm⁻¹, stretch vibration of C–H at 2885 cm⁻¹, the asymmetric shaking of the –CH₂ at 1452 cm⁻¹, and the wagging vibration of the –C–H at 886 cm⁻¹. Furthermore, the strong peak marked at 3347 cm⁻¹ corresponds to the stretch vibration of OH groups. The presentation of APTES onto the cotton surface is verified by the peaks at 1055 cm⁻¹ and 850 cm⁻¹,

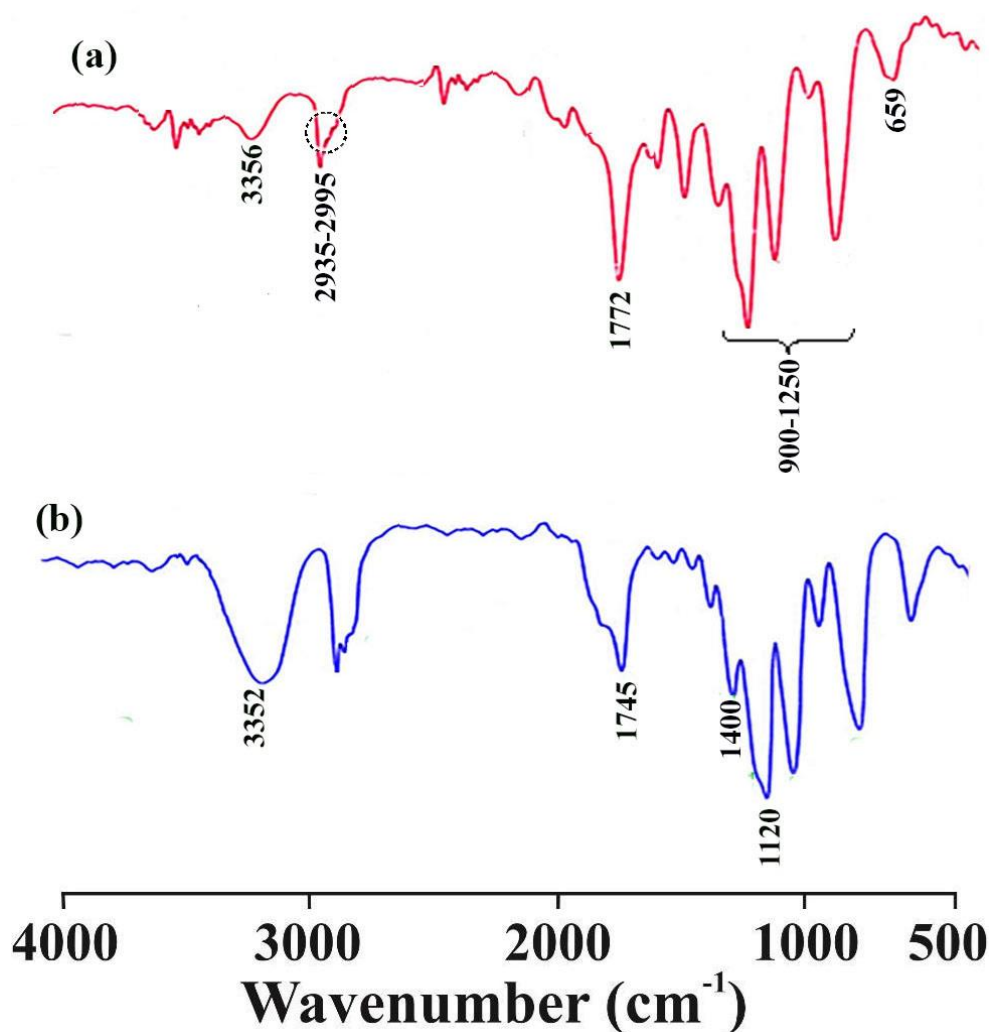


Fig. 4. The FT-IR spectrum of (2-hydroxy-ethyl)-thiophosphoramidic acid *O, O'*-diethyl ester (a) and diethyl (acryloyloxy) ethylthiophosphoramidate (DEAETPA) (b).

which belonged to the stretch vibration of Si–O and Cotton–O–Si. The reaction of APTES–Cotton with (α -chlorophenyl acetyl chloride) procreates macroinitiator in which the showing of APTES half is demonstrated with the band at 3452 cm^{-1} is attributed to the stretch of the second kind amines (NH). The absorption band at 1567 cm^{-1} exhibited, CH_2 groups. Furthermore, the peak at 1768 cm^{-1} is attributed to the stretch vibration of the C=O group. The band at 600 cm^{-1} is related to the C–Cl, the aromatic group, and the ATRP initiator has become manifest at 3137 cm^{-1} . In the FT-IR spectra of poly (DEAETPN), the stretch vibration of the N–H group was seen at 3402 cm^{-1} as well as the presence of aliphatic groups attached

to the amide group was observed. The stretch vibration of the P = S bond at 668 cm^{-1} could be observed. Furthermore, the invisibility of the peak at 1628 cm^{-1} belonged to the polymerization of $\nu\text{ C=C}$ (A) in the acrylic units. In the FT-IR spectra of Cotton-g-P (DEAETPN)/O–MMT nanocomposite, the whole addition to the peaks appeared in the produced polymer peak, indicating the arrival of clay nanoparticles to the matrix polymer, the stretch vibration of Si–O–Si bond appeared in the area of 1050 cm^{-1} . Description of the other peaks has been brought.

Fig. 6 shows the $^1\text{H-NMR}$ spectrum of (2-hydroxy-ethyl)-thiophosphoramidic acid *O, O'*-diethyl ester, diethyl (acryloyloxy)

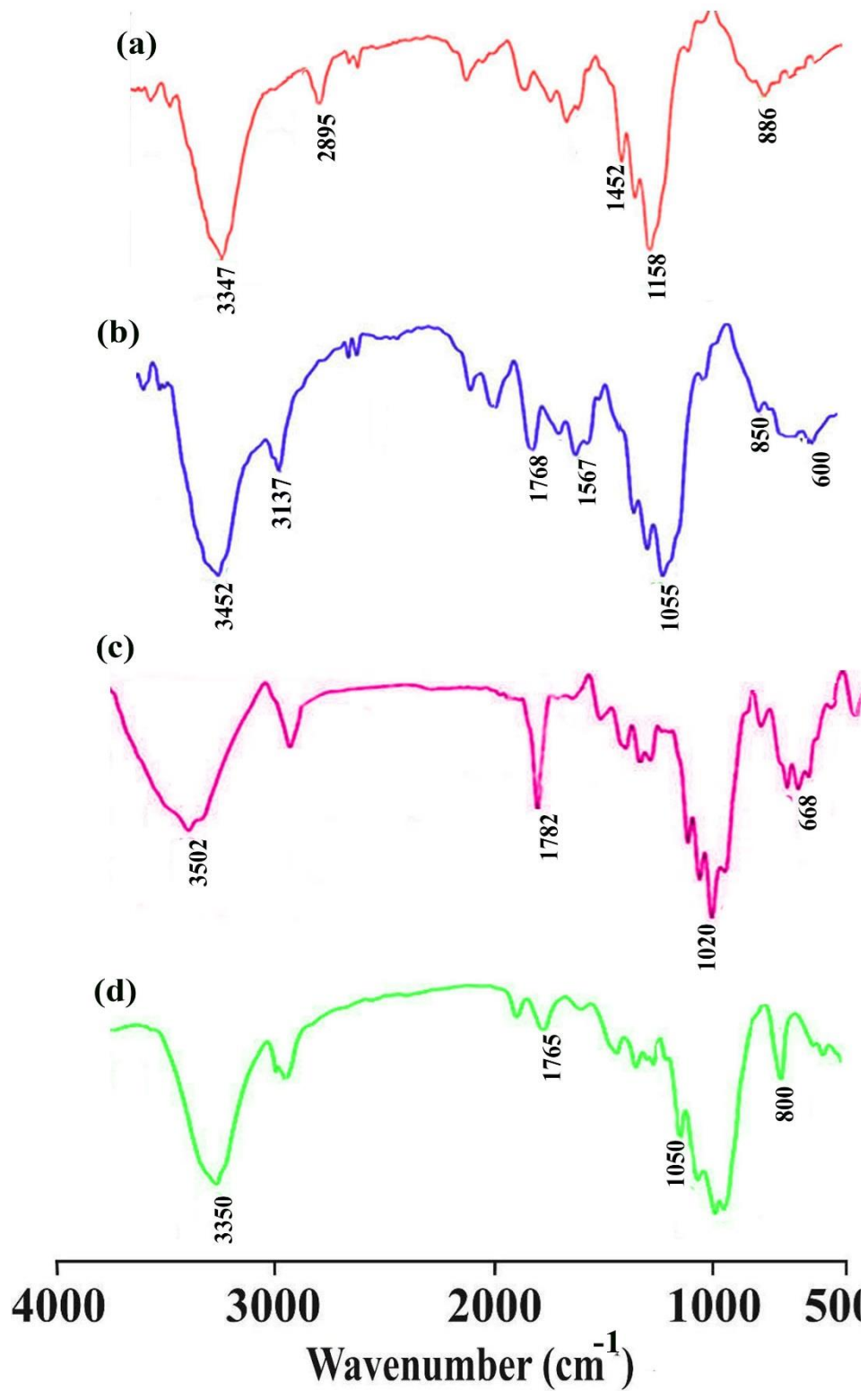


Fig. 5. The spectrum of FT-IR pristine Cotton (a) and Cotton-APTES-Cl (b) Poly (DEAETPN) (c) and Cotton-g- Poly (DEAETPN) / O-MMT nanocomposite (d).

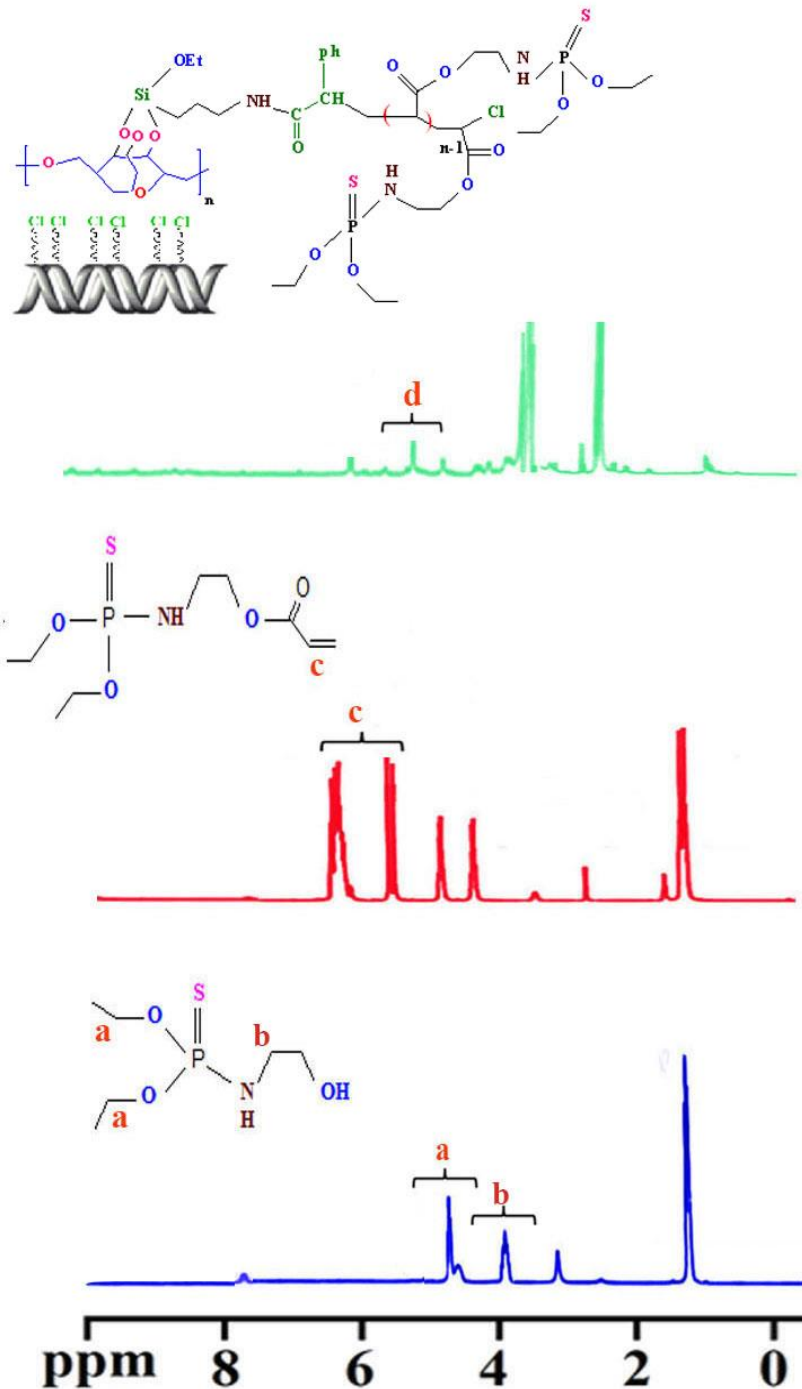


Fig. 6. The ^1H NMR spectra of (2-hydroxy-ethyl)-thiophosphoramidic acid O, O'-diethyl ester, diethyl (acryloyloxy) ethylthiophosphoramidate (DEAETPN) and Cotton-g-P (DEAETPN).

ethylthiophosphoramidate (DEAETPN), and Poly (DEAETPN) grafted onto cotton fabric. In the ^1H NMR spectrum, the invisibility of bands between

δ 5.37 and 6.12 that attributed to C=C was appeared. The peaks observed at δ 1.20 - δ 3.90 ppm correspond to the CH_2 protons conjugated to

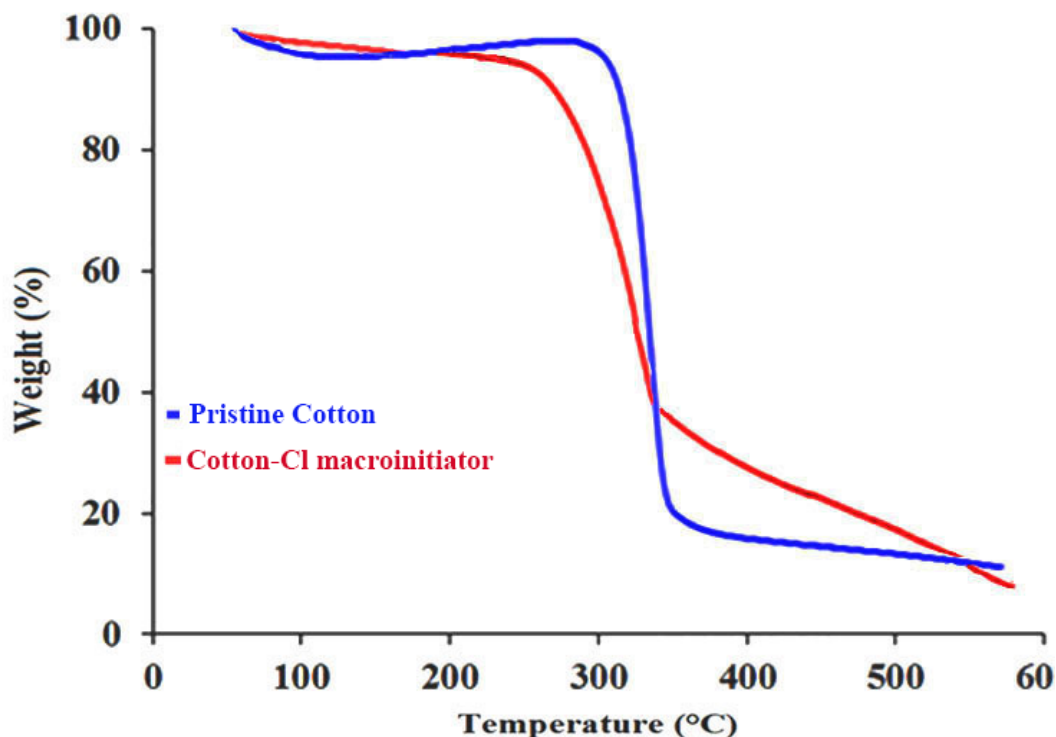


Fig. 7. TGA curves of the pristine cotton and Cotton-APTES-Cl macroinitiator

the OH and N-H group. The peaks observed at δ 4.30 ppm related to methylene protons appended to groups are CH₂OPS. The peak regarding benzene ring manifested with a very poor severity in ¹H NMR that indicated polymerization was chiefly performed using infesters. Some shift in the value of other bands in the ¹H NMR has appeared.

Characterization of O-MMT

The FT-IR and XRD spectra of the pristine MMT and O-MMT, according to relevant reference, were accomplished [29].

Study of TGA and DSC analysis

The thermal behaviors of pristine cotton (Cotton-APTES-Cl), poly (DEAETPN), and Cotton-g-P (DEAETPN) / O-MMT nanocomposite were studied through TGA and DSC. Fig. 7 displays the TGA of pristine cotton and (Cotton-APTES-Cl). According to the data, Cotton disintegrates in the range of 300-400°C, with an approximately 85% loss in volume [45], while disintegration in the range of 250 and 350°C for (Cotton-APTES-Cl) leads to weight loss in the range of 4–46 %.

The remaining weight of the composition at a temperature of 400 °C is about 50%. Due to the reduction of pristine cotton in the temperature range of 300-400 °C, the thermal stability of (Cotton-APTES-Cl) compared to pristine cotton by approximately 92% was increased.

The TGA was utilized to verification of thermal behavior happening in the period of heating under N₂ pour for poly (DEAETPN), and its polymer/clay nanocomposite, as shown in Fig. 8. the significant disintegration of the obtained nanocomposite was happening in one stage around 260–320 °C, and after that the weight-loss rate gradually reduced. The remaining at 600 °C for the Cotton-g-P (DEAETPN) / O-MMT nanocomposite approximately is 15 wt.%. The disintegration of nanocomposite in one stage may result from a strong interfacial interaction between the polymer chain and O-MMT. According to Fig. 8, we can conclude in the TGA curve of Cotton-g-P (DEAETPN)/ O-MMT nanocomposite that the weight-loss near 400 °C is a conclusion of poly (DEAETPN) chains disintegration that was covalently attached to the surface of clay

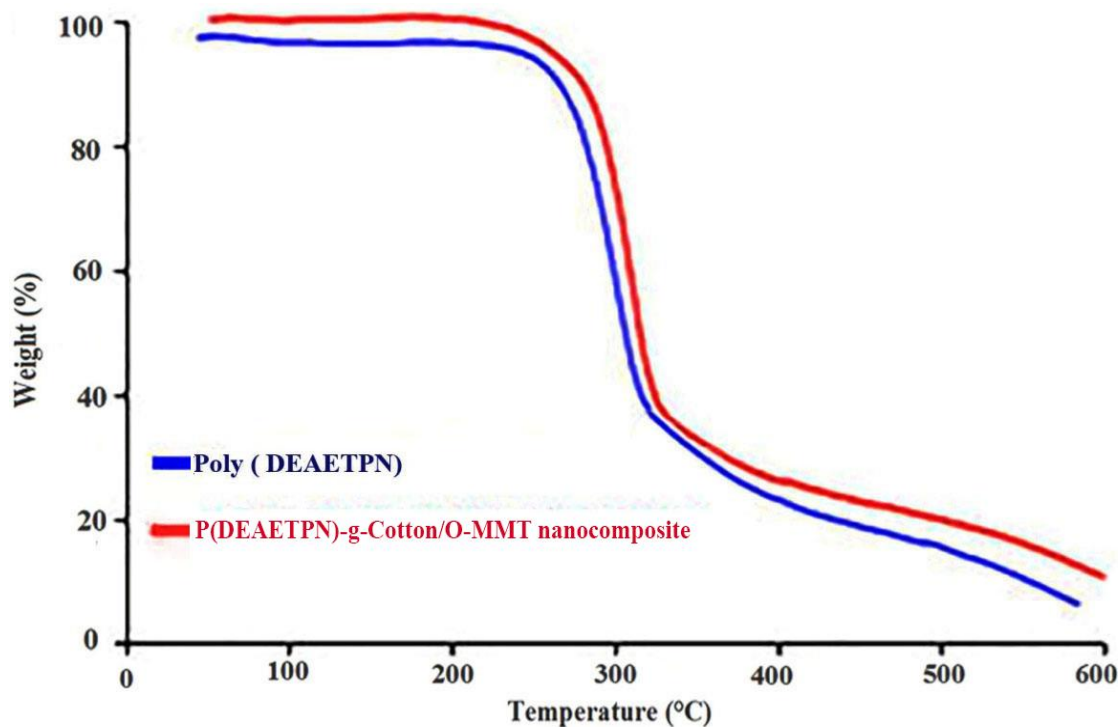


Fig. 8. TGA curves of the poly (DEAETPN) and Cotton-g-P (DEAETPN)/ O-MMT nanocomposite (3 wt %).

nanoparticles. Higher disintegration temperature of Cotton-g-P (DEAETPN)/ O-MMT nanocomposite (298 °C) compared to pure poly (DEAETPN) (265 °C) demonstrated that any noncovalent polymer was absorbed on the surface of clay nanoparticles. These data (TGA curve) show that in a stagnant space, the existence of O-MMT nanoparticles has a considerable consequence on the thermal degradation of poly (DEAETPN). The result of TGA is that the thermal stability of pristine polymer is less than that of the prepared nanocomposite.

DSC thermograms of the pristine cotton, (Cotton-APTES-Cl), poly (DEAETPN), and Cotton-g-P (DEAETPN) / O-MMT nanocomposite are shown in Fig. 9. Cotton gives important changes in the temperature range of 150 - 180 °C. Therefore, the endothermic peak observed at 175°C, assigned to the gradual destruction of pristine cotton and glass transition temperature (T_g) at 120 °C corresponding to pristine Cotton (Fig. 9 (a)). in the DSC trace of (Cotton-APTES-Cl), thermal transmission at about 45°C is assigned to solvent evaporation and the amount of moisture (Cotton-APTES-Cl). The endothermic peak seen at 180 °C belongs to the T_g of the (Cotton-APTES-Cl) (Fig. 9 (b)). On the other hand, in the DSC curves

of poly (DEAETPN) and Cotton-g-P (DEAETPN) / O-MMT nanocomposite, the thermogram of poly (DEAETPN) showed an endothermic peak at nearly 117 °C that was attributed to T_g . The T_g value of the Cotton-g-P (DEAETPN) / O-MMT nanocomposite (3 wt. %) is 147 °C, which is higher than those of pure poly (DEAETPN). In Fig. 9 (c), the endothermic peak observed at 40 °C is related to the evaporation solvent and the moisture content of the polymer. The DSC curve of Cotton-g- P (DEAETPN) / O-MMT nanocomposite displayed just one endothermic stage based on T_g at 147 °C. Therefore, intense interfacial attaching between the O-MMT nanoparticles and polymer matrix leads to an enhancement of T_g in the prepared nanocomposite. Nevertheless, the layers of O-MMT are dispersed in the polymer chains, homogeneously and intense interfacial powers are created between the polymer chains and clay layers, resulting in an enhancement of T_g (Fig. 9 (d)).

Morphology analysis

The SEM is a type of electron microscope that represents factual images of a specimen by scanning the surface with a concentrated beam

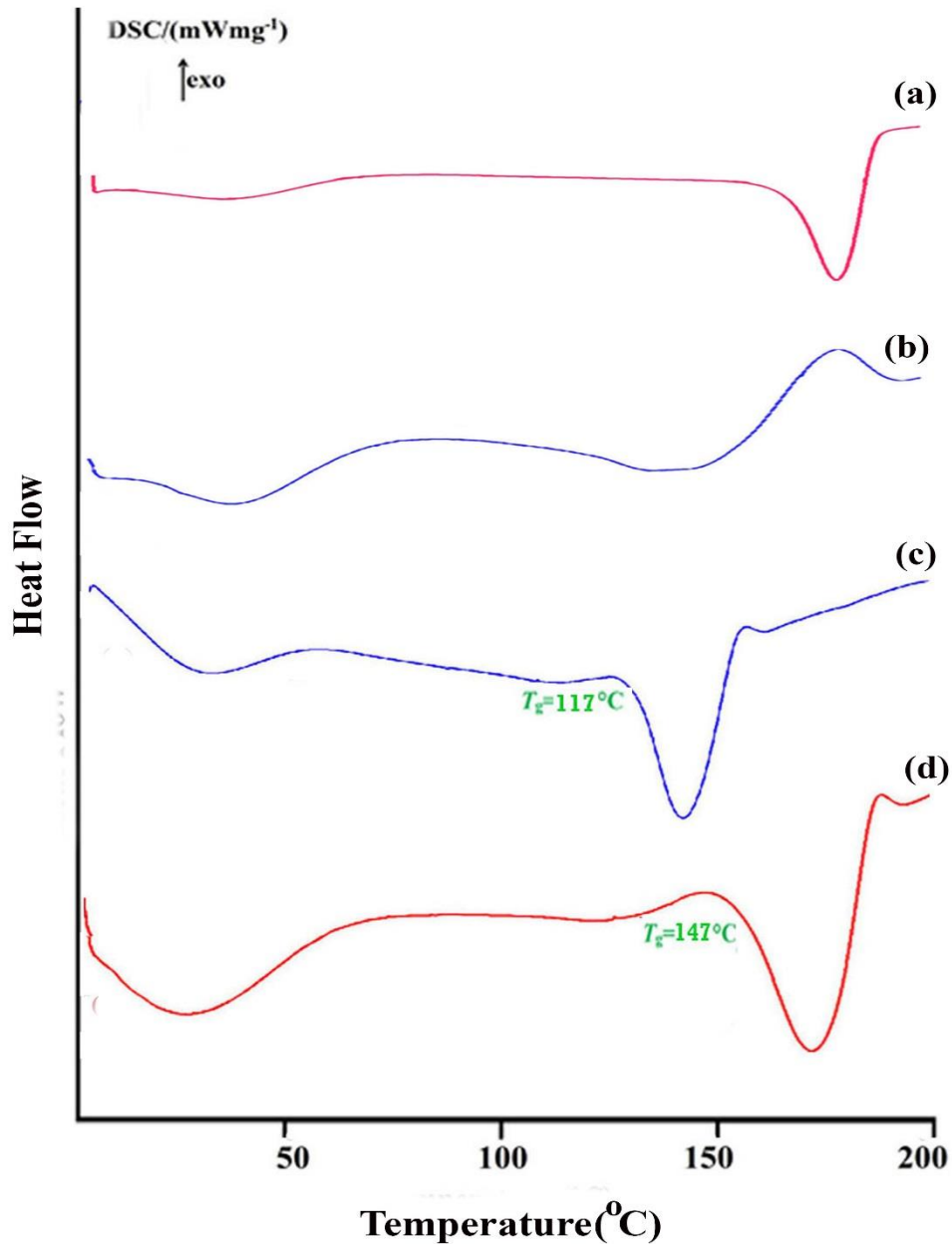


Fig. 9. The DSC traces of the pristine Cotton (a) and Cotton-grafted APTES-Cl (b) poly (DEAETPN) (c) and Cotton-g-P (DEAETPN)/ O-MMT nanocomposite (3 wt. %) (d).

of electrons. The electrons interact with atoms in the specimen, producing different signals that contain information about the dispersion level, the topography of the surface, and the composition of the specimen synthesized Cotton-g-P (DEAETPN)/ O-MMT nanocomposite. One way to study the morphology of nanocomposite is investigated by

SEM images. SEM micrographs of the obtained nanocomposite according to (Fig. 10) show better dispersion, which increases the surface area of the nanoparticles. For this reason, SEM images of the prepared nanocomposite show a disrupted structure. Furthermore, the image indicates a uniform dispersion on the nano-clay surface.

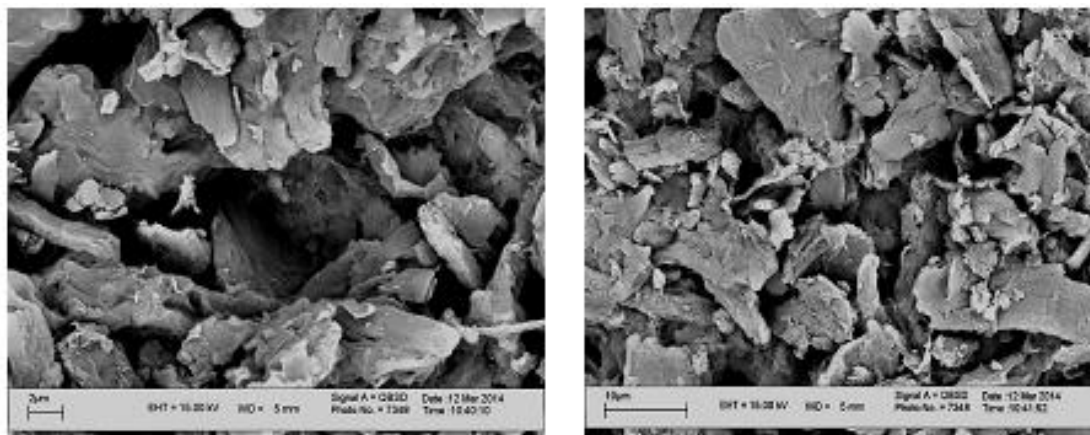


Fig. 10. The SEM images of Cotton-g-P (DEAETPN)/ O-MMT nanocomposite with 2000 nm (a) and 1000 nm (b).

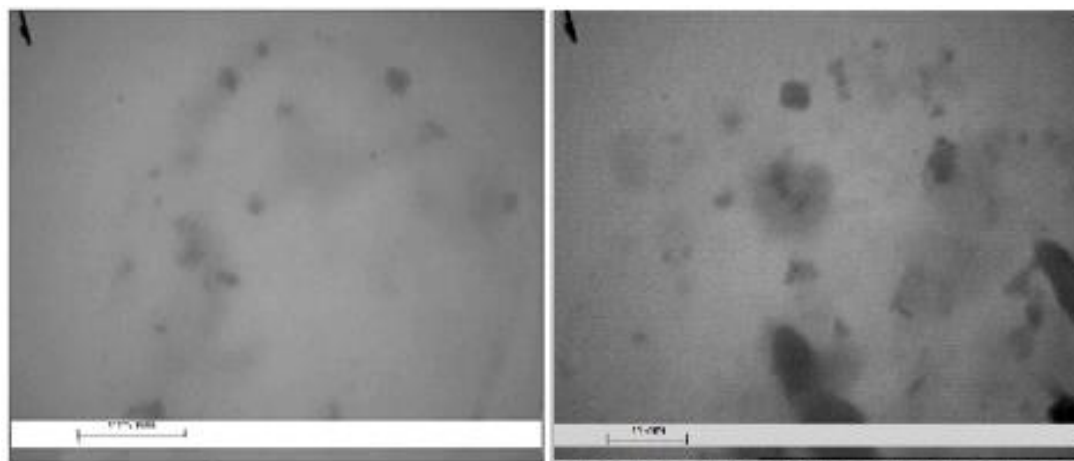


Fig. 11. The TEM images of Cotton-g-P (DEAETPN)/ O-MMT nanocomposite with 336 nm (a) and 260 nm (b).

These are assigned to the polymer chains that can extend from the ATRP agent that is grafted to modify the nanoclay surface.

TEM images are another method to study the morphology of cotton-g-P (DEAETPN)/ O-MMT nanocomposite as shown in Fig. 11. According to Fig. 11, the black lines are the attaching of the O-MMT sheets, but the bright areas display the polymer matrix. The border between the matrix and the filler particles is visible, suggesting that part of the matrix has been influenced by the fillers. Although the silicate layers are not homogeneously distributed in the polymer matrix, these images illustrate that the prepared polymerization is a considerable degree of layers'

silicate exfoliated. The narrow areas demonstrate separated layers of the erased silicate particles and indicate exfoliation. Thus, the unclear area displays that there were still lines that practically had a high aggregation of silicate. This may be originated from the excellent interactions between O-MMT and poly (DEAETPN) onto cotton fabric (Cellulose) matrix.

CONCLUSION

In short, the graft polymerization of Cotton-g-P (DEAETPN)/ O-MMT nanocomposite using the ATRP method was examined. For this purpose, Diethyl (acryloyloxy) ethylthiophosphoramidate, from the nucleophilic reaction of 2-hydroxy-

ethylthiophosphoramidic acid *O*, *O'*-diethyl ester with acryloyl chloride, in the presence of triethylamine with precipitation from the solutions of dichloromethane. First, the Cotton was functionalized with APTES (coupling agent) and then, the amine groups of APTES were reacted with ATRP macroinitiator (α -chlorophenyl acetyl chloride). Then, Diethyl (acryloyloxy) ethylthiophosphoramidate monomers were grafted onto the cotton chain through Cu-Cl and 2, 2'-bipyridine in the solution medium. Thus, Cotton-g-P (DEAETPN)/O-MMT nanocomposite previously modified with hexadecyltrimethylammonium chloride modified a small percentage of its increasing influence in solution synthesis. Health products obtained by ^1H NMR and FT-IR spectra were reviewed and approved. The results of DSC spectroscopy showed an increase in T_g during each phase consisting of cotton synthesis Chlorinated linked poly (DEAETPN) and nanocomposite relevant to the raw cotton. The results obtained from cotton derivatives spectroscopy TGA enhance the thermal stability of nanocomposite than raw cotton found in each stage. TEM observation displayed that the narrow O-MMT leaf-like with about 5 nm density were distributed well in the nanocomposite. Thus, the result of the vigorous interplay between the polymer matrix and O-MMT produced an exfoliated structure.

ACKNOWLEDGEMENTS

The authors thank Tabriz Payame Noor University for supporting this project.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

REFERENCES

- Chen T. Synthesis and characterization of novel segmented polyurethane/clay nanocomposites. *Polymer*. 2000;41(4):1345-1353.
- Ramos J, Millán A, Palacio F. Production of magnetic nanoparticles in a polyvinylpyridine matrix. *Polymer*. 2000;41(24):8461-8464.
- Nazarenko S, Meneghetti P, Julmon P, Olson BG, Qutubuddin S. Gas barrier of polystyrene montmorillonite clay nanocomposites: Effect of mineral layer aggregation. *Journal of Polymer Science Part B: Polymer Physics*. 2007;45(13):1733-1753.
- Shia D, Hui CY, Burnside SD, Giannelis EP. An interface model for the prediction of Young's modulus of layered silicate-elastomer nanocomposites. *PoCom*. 1998;19(5):608-617.
- Fujimori A, Ninomiya N, Masuko T. Structure and mechanical properties in drawn poly(l-lactide)/clay hybrid films. *Polymers for Advanced Technologies*. 2008;19(12):1735-1744.
- Alexandre M, Dubois P. Polymer-layered silicate nanocomposites: preparation, properties and uses of a new class of materials. *Materials Science and Engineering: R: Reports*. 2000;28(1-2):1-63.
- Jancar J, Douglas JF, Starr FW, Kumar SK, Cassagnau P, Lesser AJ, et al. Current issues in research on structure-property relationships in polymer nanocomposites. *Polymer*. 2010;51(15):3321-3343.
- Haldorai Y, Shim J-J, Lim KT. Synthesis of polymer-inorganic filler nanocomposites in supercritical CO_2 . *The Journal of Supercritical Fluids*. 2012;71:45-63.
- Kedzior SA, Zoppe JO, Berry RM, Cranston ED. Recent advances and an industrial perspective of cellulose nanocrystal functionalization through polymer grafting. *Current Opinion in Solid State and Materials Science*. 2019;23(2):74-91.
- Sokker HH, Badawy SM, Zayed EM, Nour Eldien FA, Farag AM. Radiation-induced grafting of glycidyl methacrylate onto cotton fabric waste and its modification for anchoring hazardous wastes from their solutions. *J Hazard Mater*. 2009;168(1):137-144.
- Tsafack MJ, Levalois-Grützmacher J. Flame retardancy of cotton textiles by plasma-induced graft-polymerization (PIGP). *Surface and Coatings Technology*. 2006;201(6):2599-2610.
- Langley JT, Drews MJ, Barker RH. Pyrolysis and combustion of cellulose. VII. Thermal analysis of the phosphorylation of cellulose and model carbohydrates during pyrolysis in the presence of aromatic phosphates and phosphoramides. *J Appl Polym Sci*. 1980;25(2):243-262.
- Hendrix JE, Drake GL, Barker RH. Pyrolysis and combustion of cellulose. II. Thermal analysis of mixtures of methyl α -D-glucopyranoside and levoglucosan with model phosphate flame retardants. *J Appl Polym Sci*. 1972;16(1):41-59.
- Horrocks AR. Developments in flame retardants for heat and fire resistant textiles—the role of char formation and intumescence. *Polym Degradation Stab*. 1996;54(2-3):143-154.
- Harifi T, Montazer M. Past, present and future prospects of cotton cross-linking: New insight into nano particles. *Carbohydrate Polymers*. 2012;88(4):1125-1140.
- Li K, Zhang J, Gong J. Wrinkle-resistant finish of foam technology for cotton fabric. *J Ind Text*. 2013;43(4):525-535.
- Peng H, Yang CQ, Wang X, Wang S. The Combination of Itaconic Acid and Sodium Hypophosphite as a New Cross-Linking System for Cotton. *Industrial & Engineering Chemistry Research*. 2012;51(35):11301-11311.
- Shen D, Yu H, Huang Y. Synthesis of graft copolymer of ethyl cellulose through living polymerization and its self-assembly. *Cellu*. 2006;13(3):235-244.
- Alongi J, Ciobanu M, Malucelli G. Cotton fabrics treated with hybrid organic-inorganic coatings obtained through dual-cure processes. *Cellu*. 2011;18(5):1335-1348.
- Stuart MAC, Huck WTS, Genzer J, Müller M, Ober C, Stamm M, et al. Emerging applications of stimuli-responsive polymer materials. *Nature Materials*. 2010;9(2):101-113.
- Siriviriyannun A, O'Rear EA, Yanumet N. Self-extinguishing cotton fabric with minimal phosphorus deposition. *Cellu*. 2008;15(5):731-737.
- Chang S, Condon B, Graves E, Uchimiya M, Fortier C,

- Esson M, et al. Flame retardant properties of triazine phosphonates derivative with cotton fabric. *Fibers and Polymers*. 2011;12(3):334-339.
23. Li Y-C, Mannen S, Morgan AB, Chang S, Yang Y-H, Condon B, et al. Intumescent All-Polymer Multilayer Nanocoating Capable of Extinguishing Flame on Fabric. *Advanced Materials*. 2011;23(34):3926-3931.
24. Nakayama Y, Miyamura M, Hirano Y, Goto K, Matsuda T. Preparation of poly(ethylene glycol)-polystyrene block copolymers using photochemistry of dithiocarbamate as a reduced cell-adhesive coating material. *Biomaterials*. 1999;20(10):963-970.
25. Hendrix JE, Drake GL, Barker RH. Pyrolysis and combustion of cellulose. III. Mechanistic basis for the synergism involving organic phosphates and nitrogenous bases. *J Appl Polym Sci*. 1972;16(2):257-274.
26. Hattori K, Hiwatari M, Iiyama C, Yoshimi Y, Kohori F, Sakai K, et al. Gate effect of theophylline-imprinted polymers grafted to the cellulose by living radical polymerization. *J Membr Sci*. 2004;233(1-2):169-173.
27. Matyjaszewski K. Macromolecular engineering: From rational design through precise macromolecular synthesis and processing to targeted macroscopic material properties. *Progress in Polymer Science*. 2005;30(8-9):858-875.
28. Mohammad-Rezaei R, Massoumi B, Abbasian M, Eskandani M, Jaymand M. Electrically conductive adhesive based on novolac-grafted polyaniline: synthesis and characterization. *Journal of Materials Science: Materials in Electronics*. 2018;30(3):2821-2828.
29. Karaj-Abad SG, Abbasian M, Jaymand M. Grafting of poly[(methyl methacrylate)-block-styrene] onto cellulose via nitroxide-mediated polymerization, and its polymer/clay nanocomposite. *Carbohydrate Polymers*. 2016;152:297-305.
30. Abbasian M, Bakhshi M, Jaymand M, Karaj-Abad SG. Nitroxide-mediated graft copolymerization of styrene from cellulose and its polymer/montmorillonite nanocomposite. *Journal of Elastomers & Plastics*. 2018;51(5):473-489.
31. Raffei H, Abbasian M, Yegani R. Synthesis of well-defined poly(n-vinylpyrrolidone)/n-TiO₂ nanocomposites by xanthate-mediated radical polymerization. *Iranian Polymer Journal*. 2020;29(5):371-381.
32. Abbasian M, Hasanzadeh P, Mahmoodzadeh F, Salehi R. Novel cationic cellulose-based nanocomposites for targeted delivery of methotrexate to breast cancer cells. *Journal of Macromolecular Science, Part A*. 2019;57(2):99-115.
33. Abbasian M, Razavi L, Jaymand M, Ghasemi Karaj-Abad S. Synthesis and characterization of poly(styrene-block-acrylic acid)/Fe₃O₄ magnetic nanocomposite using reversible addition-fragmentation chain transfer polymerization. *Iranica*. 2019;0(0):0-0.
34. Sofla SFI, Abbasian M, Mirzaei M. Synthesis and micellar characterization of novel pH-sensitive thiol-ended triblock copolymer via combination of RAFT and ROP processes. *International Journal of Polymeric Materials and Polymeric Biomaterials*. 2018;68(6):297-307.
35. Ahmadkhani L, Akbarzadeh A, Abbasian M. Development and characterization dual responsive magnetic nanocomposites for targeted drug delivery systems. *Artificial Cells, Nanomedicine, and Biotechnology*. 2017;46(5):1052-1063.
36. Abbasian M, Seyyedi M, Jaymand M. Modification of thermoplastic polyurethane through the grafting of well-defined polystyrene and preparation of its polymer/clay nanocomposite. *Polymer Bulletin*. 2019;77(3):1107-1120.
37. Muthusamy S, Charles J. In situ synthesis and characterization of polyaniline/prussian blue/zinc oxide nanocomposite. *Polymer Bulletin*. 2018;76(1):119-137.
38. Mohammad-Rezaei R, Massoumi B, Eskandani M, Abbasian M, Jaymand M. A new strategy for the synthesis of modified novolac resin and its polymer/clay nanocomposite. *Express Polymer Letters*. 2019;13(6):543-552.
39. Massoumi B, Abbasian M, Mohammad-Rezaei R, Farnudiyani-Habibi A, Jaymand M. Polystyrene-modified novolac epoxy resin/clay nanocomposite: Synthesis, and characterization. *Polymers for Advanced Technologies*. 2019;30(6):1484-1492.
40. Kaur I, Rajneesh M, Vibha D. Flame-retardant Cotton Fabric Through Graft Copolymerisation. *Def Sci J*. 2007;57(2):249-258.
41. Wang J-S, Matyjaszewski K. Controlled/"Living" Radical Polymerization. Halogen Atom Transfer Radical Polymerization Promoted by a Cu(I)/Cu(II) Redox Process. *Macromolecules*. 1995;28(23):7901-7910.
42. Sumerlin BS, Tsarevsky NV, Louche G, Lee RY, Matyjaszewski K. Highly Efficient "Click" Functionalization of Poly(3-azidopropyl methacrylate) Prepared by ATRP. *Macromolecules*. 2005;38(18):7540-7545.
43. Kaur I, Verma SK. Living radical polymerization and grafting of diethyl (acryloyloxy) ethylthiophosphoramidate onto cotton fabric to impart flame retardancy. *Surface and Coatings Technology*. 2010;205(7):2082-2090.
44. Sato M, Kawata A, Morito S, Sato Y, Yamaguchi I. Preparation and properties of polymer/zinc oxide nanocomposites using functionalized zinc oxide quantum dots. *European Polymer Journal*. 2008;44(11):3430-3438.
45. El-Khouly AS, Takahashi Y, Takada A, Safaan AA, Kenawy E, Hafiz YA. Characterization and thermal stability of cellulose-graft-polyacrylonitrile prepared by using KMnO₄/citric acid redox system. *J Appl Polym Sci*. 2010:NA-NA.