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Flame retardant cotton fabrics treated with organophosphorus polymer

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ABSTRACT

Organo-phosphorus compounds was prepared and applied onto cotton fabrics as flame retarding agent. methacryloloxyethylorthophoshor tetraethyl diamidate (MPD) was prepared and its structure was confirmed by IR, NMR and mass spectroscopy. Pyrovatex as commercial flame retardant was used for comparative study. Impregnation method was used as coating for the application of the organophosphorus compounds to cotton fabrics. The major factors affecting the reaction were studied. The results show that the prepared organophosphorus compound can be successfully used as flame retardant for cotton fabrics.

1. Introduction

Cotton is the most important textile fiber because of its comfort and worldwide consumption. However, it ignites easily and is frequently implicated in fire. In fires cotton products, such as apparel, curtains, bedclothes, and upholstered furniture, become quickly engulfed and are difficult to extinguish. Since fire accidents cause injuries and fatalities and also devastate property, considerable efforts have been made to develop flame-retardant cotton. Government regulations, insurance company requirements, building codes, and voluntary standards dictate where and when flame-resistant textiles must be used (Charuchinda, Srikulkit, & Mowattana, 2005). Also in today's litigious environment, textile producers are becoming increasingly concerned with the liability to which they may be exposed if someone accuses their products of causing an injury or fatality. The use of halogen-based flame retardants to reduce the flammability of cotton is one of the most efficient ways of reducing the fire hazard. However, because of their corrosivity, the presence of dioxin, a carcinogen, and suspected smoke toxicity by products such as HBr and HCl, many European countries such as Sweden and Germany have legislated regulations to restrict halogen-based flame-retarded textile products (Holme, 2001). Consequently, public interest concerning environmentally friendly, non-halogen-based flame retardants have been increasing. Phosphorus-based flame retardants have been a major source of interest to replace halogen compounds because of their environmentally friendly by-products and their low toxicity. Also their low production of smoke in fire furthers their appeal. They are highly effective flame retardants for cellulose and cellulose derivatives. These compounds promote dehydration and char formation (Kandola, Horrocks, Price, & Coleman, 1996).

Recently, most of fire retardants finishing of cellulosic textiles have been done by applying organo-phosphorus compounds to textiles to react or polymerize them in and on the fibers. Methods of imparting fire retardants to cotton fabric with phosphorous compounds have been investigated (Abdel-Mohdy, Belyakova, & Gaballa, 2002; Abdel-Mohdy, Khalil, Belyakova, Gaballa, & Yakout, 2002; Abou-Okeil & El-Shafie, 2011; Aly, Hashem, & Abdel-mohdy, 2001).

It is illustrated that presence of nitrogen with phosphorous play a synergistic effect in flame retardance. There is general agreement that acid-forming phosphorous compounds are very effective in preventing flaming. Their action has been attributed to a protective charring at sub flame temperature, which prevents ignition.

The aim of the present work is to prepare and characterize organophosphorus polymer. The obtained polymer will be used as flame retarding agent for cotton fabric.

2. Experimental

2.1. Materials

Mill scoured and bleached plain weaved cotton fabric (169 g/m^2 was supplied by Misr Company for spinning and Weaving), Mehalla Elkobra, Egypt. The fabric was further purified by treatment with a solution containing 2 g/l sodium carbonate and 5 g/l Egyptol for

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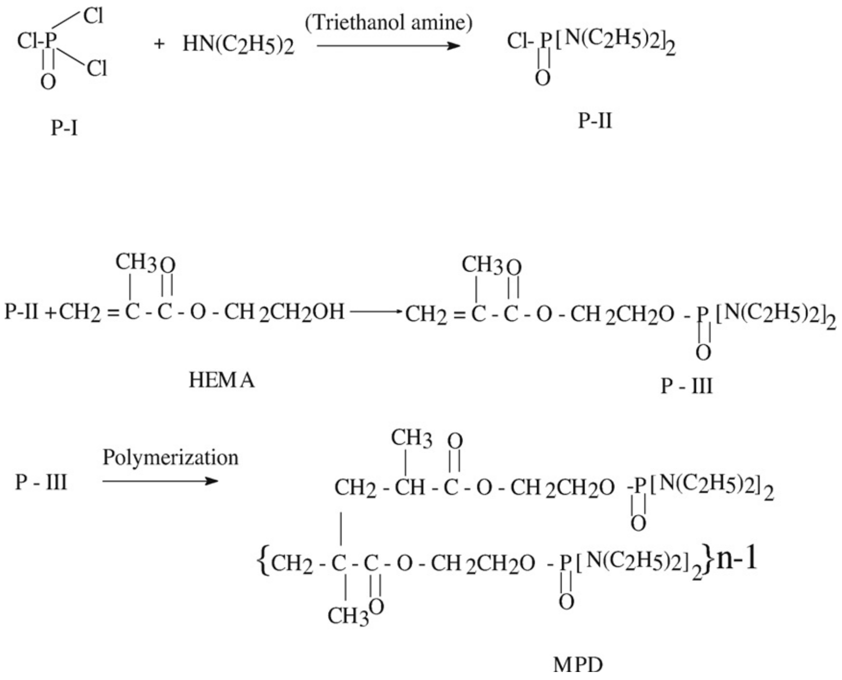

Scheme 1.

2 h. at boiling. After that the fabric was washed thoroughly with distilled water and left to dry in open air.

Pyrovatex was kindly supplied by CibaGeigy, Switzerland. Ployvinylacetate emulsion, Natural rubber emulsion, Styrene butadiene acrylate copolymer emulsion and vinyl acrylate/butylacrylate copolymer emulsion are of commercial grade chemicals were used as binders. Arkofix NG-ET (reactant crosslinking agent), was kindly supplied by Calriant. Phosphorusoxychloride, Diethylamine and hydroxyethylmethacrylate are of laboratory grade chemicals. Egyptol (nonionic detergent) is kindly supplied by the Egyptian Company of Starch and Yeast, Egypt.

2.2. Methods

2.2.1. Preparation of methacryloyloxyethylorthophosphorotetraethyl-diamidate polymer (MPD)

Bis-(N,N-diethyl) aminochlorophoshine oxide (P-II) was prepared by the reaction of phosphorusoxychloride with diethylamine in a 1:2 ratio at −20 °C in the presence of triethanolamine (TEA) (Abdel-Mohdy, 2003) as shown in Scheme 1.In accordance P-II was reacted with hydroxyethylmethacrylate (HEMA) in presence of TEA at 0 °C–5 °C to produce methacryloyloxyethylorthophosphortetraethyldiamidate (P-III) monomer. methacryloyloxyethylorthophosphortetraethyldiamidate (P-III) polymer (MPD) was prepared by the bulk polymerization process in presence of benzoyl peroxide as initiator. No solvent was used, the monomer acts as solvent.

2.2.2. Fabric treatment

Uniform impregnation was carried out by dissolving 1–5 g of the flame retardant agent (pyrovatex) and dispersion of 1–5 g of MPD in 100 ml of water solution containing 2 g of binder and 2 g of crosslinker. The additives are thoroughly mixed using homogenizer DIAX 900, heidolph instrument, Germany. The fabric was dipped in the prepared solution for 5 min and squeezed to 100% pick up, then allowed to dry at 100 °C, then cured at 150 °C for 5 min. The cured samples were washed to remove unreacted materials, and then dried at room temperature.

2.3. Analysis

Physical and mechanical tests were carried out on the Textile Division at the National Research Center in Cairo. All samples are conducted by tests after conditioning the fabric for 24 h under the standard atmospheric conditions (20 ± 2 °C temperature, 65 ± 2% relative humidity). All Physical and mechanical tests were accepted for the fabrics before and after treatment.

2.4. Tensile strength and elongation

Tensile strength and elongation for both warp and weft direction was measured according to ASTM No. D-5035 (2006).

2.5. Air permeability

Air permeability was measured according to ASTM No. D-737 (1996).

2.6. Water permeability

Water permeability was measured according to ASTM No. D-461 (1993).

2.7. LOI

ASTM, Standard Test Method for Measuring the Minimum Oxygen Concentration to Support Candle–Like Combustion of Plastics (Oxygen-Index): ASTMD 2863.81

2.8. N%

Nitrogen percentage (N%) was measured using micro Kjeldhal method.

2.9. Roughness

Roughness was measured using the surface roughness measuring instrument (surfcorder) SE1700α (Kosakalab, Japan).

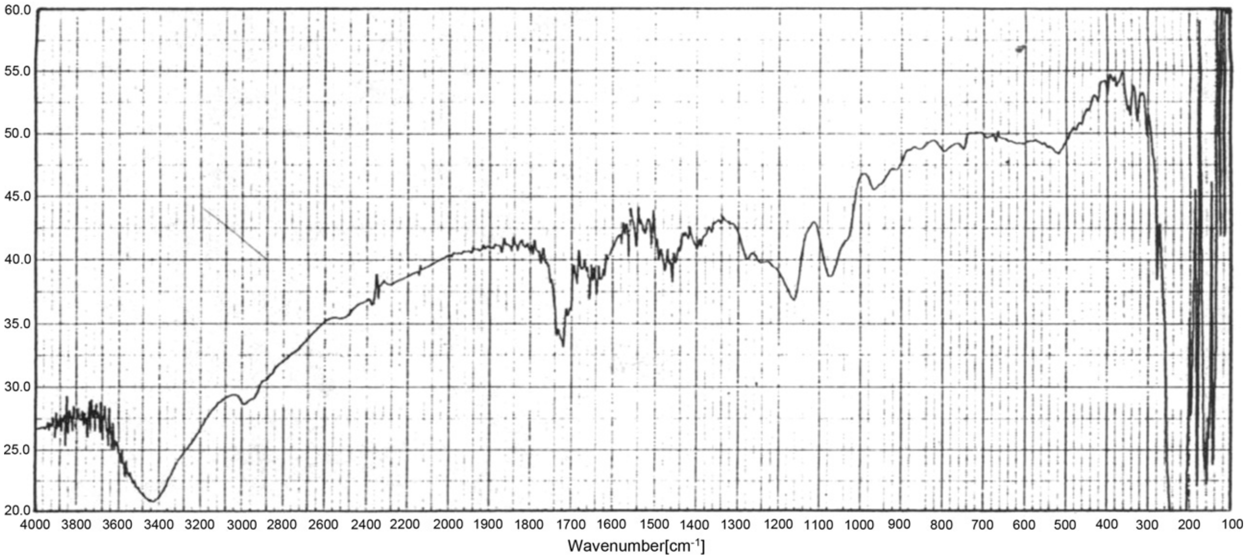

Fig. 1. Shows the I.R. spectra, (in KBr) cm^{-1} for the compound (MPD).

2.10. FTIR

FTIR spectroscopy was recorded on a Jasco FT/IR-300 E.

2.11. ^{1}H NMR

^{1}H NMR was obtained on a Jeol nuclear magnetic resonance (NMR) EX-270.

2.12. Mass spectrum

Mass spectrum was measured using Finnegan Mat SSQ 700, England.

2.13. TGA

Thermal gravimetric analysis (TGA) was carried out using Perkin–Elmer 7DX Thermo Gravimetric Analyzer, USA.

3. Results and discussion

3.1. Characterization of MPD

The structure of MPD was characterized by FTIR, ^{1}H NMR and mass spectroscopy. An FTIR spectrum (Fig. 1) shows the absorption peaks at 3400, 2970, 1720 and 1240 cm^{-1} which is attributed to OH, CH_2, CO and PO, respectively. Mass spectrum (Fig. 2) revealed fragments at 58 (100%), 72 (40%), 86 (62%), and 191 (10%) assigned to glycoxal, 2-methyl propanaldehyde, α-methylacrylate and orthophosphorotetraethyldiamidate respectively. ^{1}H NMR shows that (Fig. 3) the product has an olefinic protons which appeared as singlets at δ 6.2 ppm along with three sets of multiplets at δ 3.6, δ 4.0 and δ 4.3 ppm assignable to N—CH_2, O—CH_2 and CH_2—O—P=O, respectively.

3.2. Characterization of treated fabrics

Cotton fabrics were independently treated with four binders, namely, polyvinyl acetated emulsion, natural rubber emulsion, Styrene butadiene acrylic copolymer and vinyl acetate/butylacrylate copolymer. Treatment of cotton fabric with

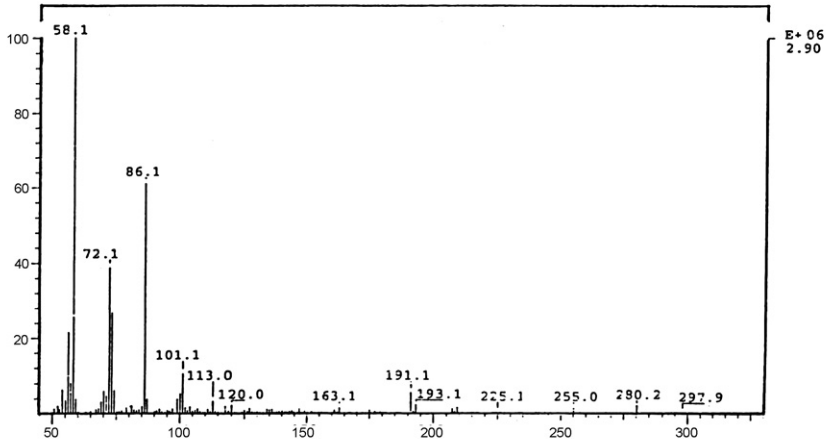

Fig. 2. Shows the mass spectra (% rel. Int.) for the compound (MPD).

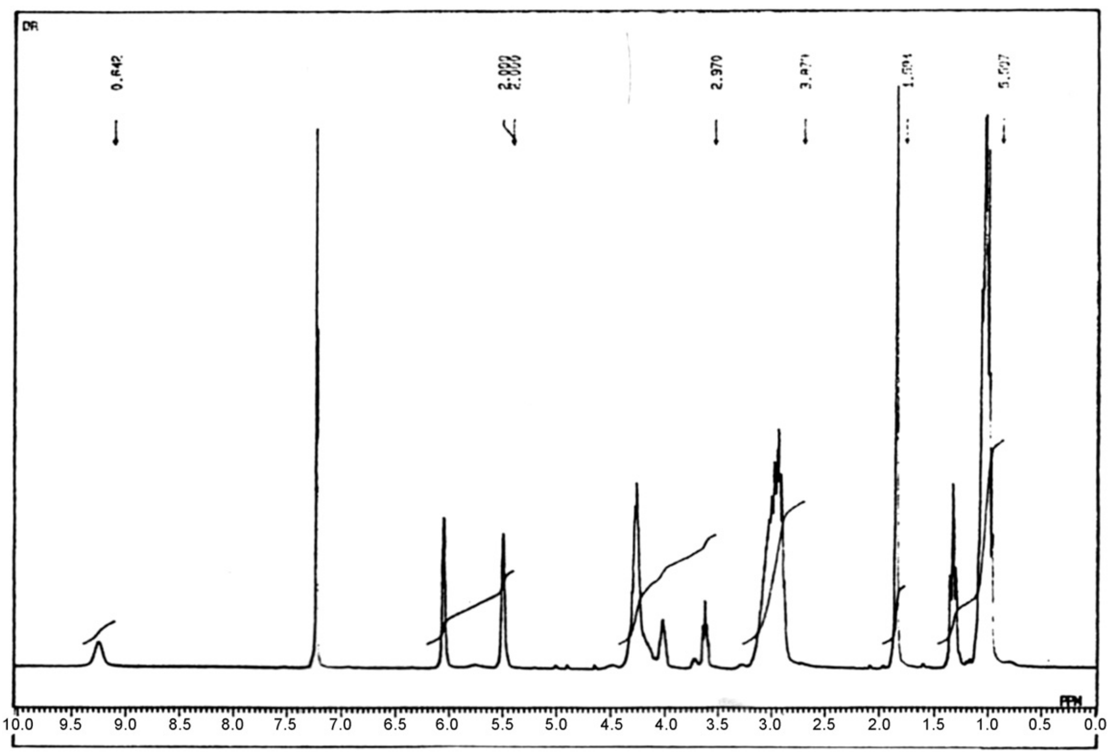

Fig. 3. Shows the ^{1}H NMR spectra for the compound (MPD) (in CDCl3, Sppm).

Table 1
Effect of type of binder on the properties of cotton fabric.

Binder type	Tensile strength (Kgf)		Elongation (%)		Water permeability (cm^3\cm^2\s)	Air permeability (cm^3\cm^2\s)	Roughness μm	LOI
	Warp	Weft	Warp	Weft				
Untreated	23	14.2	11	24	0.6154	13.71	17.22	17
Vinyl acetate emulsion	37.4	26.2	13	32	0.5435	1.604	15.63	17.4
Natural rubber emulsion	31	31	10	40	0.408	3.823	16.36	17.3
Styrene butadiene/acrylic acid copolymer	35.3	26	14	33	0.388	1.88	15.68	17.3
Vinyl acrylate/butyl acrylate copolymer	36	29.3	12	28	0.385	1.95	16.36	17.3

Aqueous dispersion solution, (binder) 2%, crosslinker, 2%, emulsifier, 1%, 100% pick up, then allowed to dry at 100 °C, then cured at 150 °C for 5 min and then dried at room temperature.

Table 2
Effect of pyrovatex concentration on the properties of cotton fabric.

Pyrovatex %	Tensile strength (Kgf)		Elongation (%)		Water permeability (cm^3\cm^2\s)	Air permeability (cm^3\cm^2\s)	Roughness μm	N%	LOI
	Warp	Weft	Warp	Weft					
2	61	55	15	17	0.662	38.17	15.01	0.33	18
3	60.5	52.5	15	22	0.617	39.06	15.16	0.38	18
4	52	52	16	24	0.617	35.5	15.9	0.48	18.5
5	51	44	13	28	0.571	29.37	15.37	0.58	18.3

Aqueous dispersion solution, (binder) 2%, crosslinker, 2%, emulsifier, 1%, 100% pick up, then allowed to dry at 100 °C, then cured at 150 °C for 5 min and then dried at room temperature.

Table 3
Effect of MPD concentration on the properties of cotton fabric.

MPD %	Tensile strength (Kgf)		Elongation (%)		Water permeability (cm^3\cm^2\s)	Air permeability (cm^3\cm^2\s)	Roughness μm	N%	LOI
	Warp	Weft	Warp	Weft					
2	70	52	17	31	0.578	22.24	15.33	0.48	18.7
3	71.5	49	15	28	0.550	24.4	15.43	0.48	18.6
4	71.5	46.5	10	27	0.54	20.4	12.98	0.58	19
5	61.5	40	10	25	0.521	15.47	12.80	0.77	19

Aqueous dispersion solution, (binder) 2%, crosslinker, 2%, emulsifier, 1%, 100% pick up, then allowed to dry at 100 °C, then cured at 150 °C for 5 min and then dried at room temperature.

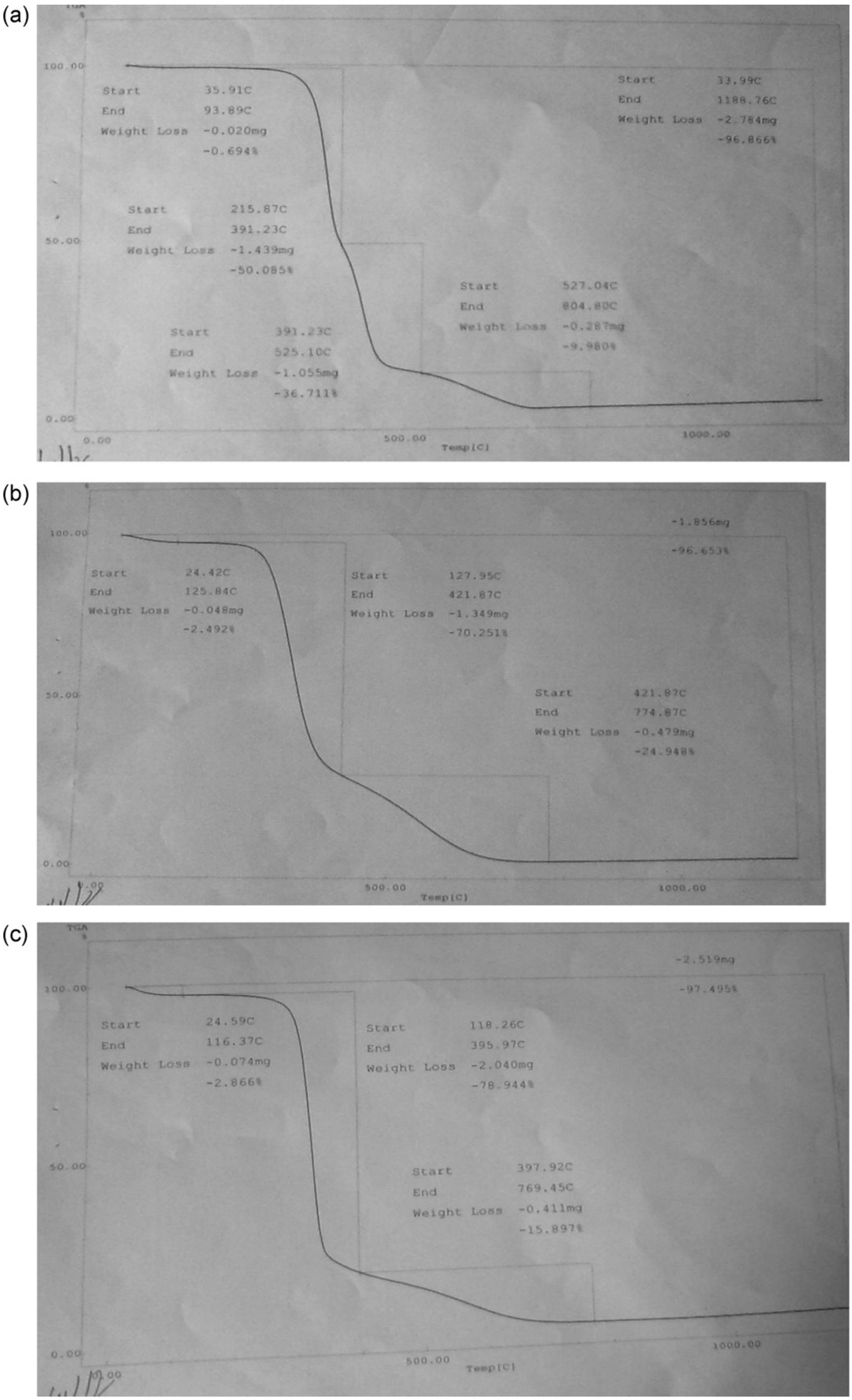

Fig. 4. TGA of (a) untreated cotton fabric, (b) pyrovatex treated cotton fabric and (c) MPD treated fabric.

these binders in presence and absence of flame retardant would verify their contribution, if any, in the flame resistance of the fabric. The treatment would also showed insight on differences in the magnitude of this contribution which is anticipated to rely on the nature of the polymeric binder used. It is seen from Table 1 that the differences could be recorded among the 4 binders used, yet kind and nature of polymer along with handling experience advocate polyvinyl acetate emulsion as the better choice than the other polymers examined for treatment of cotton fabrics. Treatment of cotton fabrics with the finishing formulations containing binder and different fire retardant compounds increases the tensile strength in the warp direction and in the weft directions (Tables 1–3). Most probably, the finishing agents diffuse into the microstructure of cotton cellulose and form a coating layer on the surface of the fabrics. Results of elongations have the same trend as tensile strength which can be explained by the similar way as tensile strength. The results show increment in roughness of the treated fabrics with different finishing formulations in case of pyrovatex, but did not reach the level which affects their comfort properties. In case of MPD the roughness decreased with increasing the concentration of MPD which indicates the smoothness of the produced fabrics, this can be attributed to the nature of long chain MPD which have a good effect on the smoothness of the treated fabrics. It is obvious from the results (Tables 1–3) that the air and water permeability values of the treated fabrics are lower than that of untreated fabrics. The coating of the polymer on the surface of cotton fabrics, acts as a barrier which decreases the number and the size of available pores on the surface of the fabric. This phenomenon reflected on the results of air and water permeability. Also we have another factor which is the hydrophilic and hydrophobic character of the polymer used in the treatment. Obviously increasing the concentration of pyrovatex and MPD leads to increasing the N% (Tables 2 and 3) which is very expected since pyrovatex and MPD are the main source of nitrogen in the formulation.

3.3. LOI

LOI, which is a measure of flammability of the samples, is the minimum amount of oxygen in an oxygen/nitrogen gas stream mixture that supports combustion. Fibers having LOI values of 21 or below ignite easily and burn rapidly in air (containing 20.8% oxygen). Those with LOI values above 21 ignite and burn more slowly and generally when LOI values increase above approximately 26–28, fibers may be considered to be flame retardant. The effect of pyrovatex or MPD on flame retardancy can be assessed by considering the LOI values. In this study, the LOI values, measured at 29 °C and 46% relative humidity, are given in Tables 1–3 and the results were in agreement with the burning behavior. It is seen that the LOI values of 17 of untreated cotton fabrics. In the matter of cotton fabrics treated with pyrovatex in presence of vinyl acetate as binder, it was found that the LOI values were in the range of 18–18.5 depending on the concentration of pyrovatex. Pyrovatex may act as a char-forming flame retardant; however, LOI values increased to only 18.5 due to the absence of phosphoric acid which acts as crosslinking agent. The matter of cotton fabrics treated with the MPD with vinyl acetate as binder, it was found that their LOI values are in the range 18.6–19. It is clear that the LOI of MPD at high concentration (3%–4%) is higher than that of pyrovatex which was 18, this finding confirm that the ability of MPD to act as flame retardant agent of cotton fabric, although seems to needs some adaptation of the formulations by adding some synergistic additives to increase the LOI to over 20.

3.4. TGA

Fig. 4 shows TGA of (a) un treated cotton fabric, (b) cotton fabric treated with pyrovatex, (c) cotton fabric treated with MPD, the decomposition temperature of cotton fabric alone started at 333 °C, and reached 466 °C this is against 286 °C and reached to 421 °C and 307 °C and reached to 395 °C for cotton fabrics treated with pyrovatex and MPD respectively. The treatment of cotton fabric leads to the decrease of decomposition temperature by 50 °C for pyrovatex and only by 20–25 °C for MPD. Also the weight loss decreases from 86% for untreated cotton fabric to 70% and 78 in case of pyrovatex and MPD at decomposition temperature respectively. From the results of TGA it can be concluded that the treatment of cotton fabric with MPD leads to thermal stability of cotton fabric which reflected by the value of weight loss and still the results of MPD comparable with the results of pyrovatex.

4. Conclusion

methacryloyloxyethylorthophosphortetraethyldiamidate (P-III) polymer (MPD) was prepared by the bulk polymerization process in presence of benzoyl peroxide as initiator. This polymer was characterized by FTIR, NMR and mass spectroscopy. MPD was used as flame retardant agent for cotton fabric. From the results obtained it is concluded that MPD can be used as flame retardant for cotton fabric comparing to the commercial product (pyrovatex).

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