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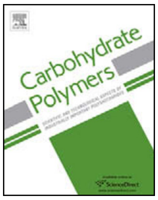

Flame retardant cotton fibers produced using novel synthesized halogen-free phosphoramide nanoparticles

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ABSTRACT

Flame retardant cotton fibers were successfully produced using five new nanosized phosphoramide compounds synthesized by ultrasonic method. The ^{1}H NMR spectra of compounds **1**–**3** illustrate $^3J(\mathrm{H,H})_{cis}$ and $^3J(\mathrm{H,H})_{trans}$ corresponding to the splittings of cis and trans protons present in the $CH{=}CH_2$ bond. Comparing the char lengths of cotton fibers treated with phosphoramides **1**–**5** indicates that the samples with greater degree of grafting (DG) provide smaller char lengths so that the least and the greatest char lengths are observed for the treated fibers with phosphoramides **1** and **5**, respectively. The very close DG and char lengths of compounds **1** and **2** can be described based on their chemical structures containing 4-nitroaniline and 4-chloro-3-trifluoromethyl aniline groups that both can release electrons through their resonance effects to their corresponding P—N bonds and enhance the P—N system synergistic effect. The TGA/DSC analyses on the treated fibers revealed that the maximum weight losses at 800 °C are occurred within the range 43.52% (for fiber treated with **1**) to 56.37 (for fiber treated with **5**) which are all smaller than that of the raw fiber (56.83%). The in vitro antibacterial activity experiments on phosphoramides **1**–**5** displayed the greatest and the least antibacterial activities for compounds **2** and **4**, respectively. Furthermore, when these phosphoramides are applied on the cotton fibers, they also demonstrate the above order for the antibacterial activities.

1. Introduction

Cotton is one of the most important natural fibers employed in the textile industries. However, it is also one of the most flammable fibers with low limiting oxygen index (LOI = 18.4%) and onset of pyrolysis at 350 °C. Improvement of thermal stability of cellulose based textiles is still a challenging issue. Numerous investigations have been conducted in finding innovatory solutions for conferring enhanced and durable flame retardant cotton fibers both at the academic and the industrial levels to achieve the performances of the major industrial target compounds known as Proban® and Pyrovatex® (Alongi et al., 2013a; Weil & Levchik, 2008; Xie, Gao, & Zhang, 2013). To overcome the thermal instability of cotton, surface treatment either with durable (e.g. monomers containing phosphorus and nitrogen along with reactive moiety) or with non-durable (usually inorganic salts containing ammonium, urea, phosphate and poly phosphates) flame retardants are performed (Edwards, El-Shafei, Hauser, & Malshe, 2012; Horrocks, 2011). Indeed, the flame retardants (FRs) are chemicals added to materials both to prevent combustion and to delay the spread of fire after ignition. FRs may have different compositions so that they may contain halogens (bromine and chlorine), phosphorus, nitrogen, metals, minerals based on aluminum and magnesium, or they may be based on borax, antimony trioxide, molybdenum, or the FR may be a nanocomposite.

The most used FRs for rendering cotton fabrics flame retardant were halogen-containing compounds. However, it was established that the halogen-based compounds are not environmentally friendly because they generate toxic gases, which can be endocrine disruptive (Legler & Brouwer, 2003; Rahman, Langford, Scrimshaw, & Lester, 2001), and may cause liver, thyroid, and neuro developmental toxicity. Also, it was demonstrated that they result in liver cancer in laboratory rats and mice (US EPA, 2012). In addition, it was evidenced that they persist in the environment and accumulate in living organisms (Legler & Brouwer, 2003; Rahman et al., 2001; US EPA, 2012). Therefore, the production of the halogenated FRs were

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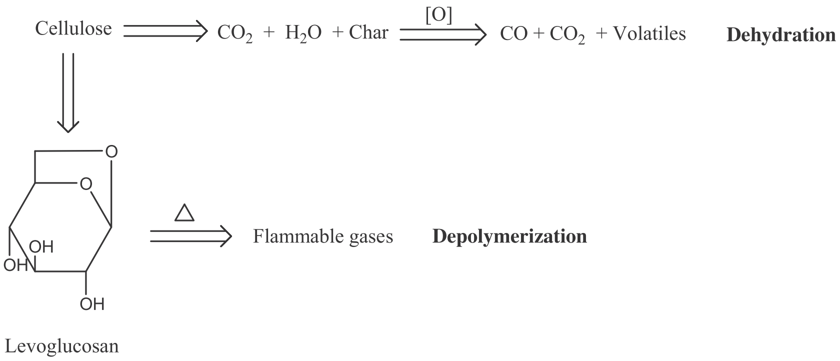


Scheme 1. The proposed mechanisms for the burning/pyrolysis products of cellulose fibers.

banned especially the two major classes including polybrominated diphenyl ethers (PBDEs) and polybrominated biphenyl (PBB) in EU and USA (Legler & Brouwer, 2003; US EPA, 2012).

After the ban on some brominated flame retardants (BFRs), phosphorus flame retardants (PFRs), which were responsible for 20% of the flame retardant (FR) consumption in 2006 in Europe, were replaced as alternatives for BFRs (Andrae, 2007). PFRs can be divided in three main groups, inorganic, organic and halogen containing PFRs. Most of the PFRs have a mechanism of action in the solid phase of burning materials (char formation) while some may also be active in the gas phase. Some PFRs are reactive that are chemically bound to a polymer, whereas others are additives and mixed into the polymer.

Most of the treatments applied in order to confer a flame retardant behavior to many types of fabrics involved a pad-dry process containing familiar organophosphorus compounds particularly those containing P—N bonds (Abou-Okeil, El-Sawy, & Abdel-Mohdy, 2013; Alongi, Colleoni, Rosace, & Malucelli, 2013b; Maki et al., 2000; Wei et al., 2011). These compounds are the most commonly used as flame retardants due to their ability to promote char formation. Many approaches have been developed to deposit a phosphorus-based flame retardant onto cellulose fiber such as the pad/dry/cure technique, graft copolymerization to cellulose, or in situ polymerization of monomer which can form three dimensional network in or on fibers (Horrocks, 1983; Tsafack & Levalois-Grutzmacher, 2006). The char residue acts as a barrier to protect the fabric from attack of oxygen and radiant heat of fire and it can also reduce smoke emission (Duquesne et al., 2004; Granzow, 1978; Green, 2000; Price et al., 2000; Wang, Cheng, Tu, Wang, & Chen, 2006).

The phosphorous–nitrogen (P—N) containing flame retardants have been widely studied (Hebeish, Waly, & Abou-Okeil, 1999). Such systems attracted much attention because of their appropriate thermal stability, low toxicity, and superior performance, due to the synergistic effect of P—N (Lewin, 1999; Pandya & Bhagwat, 1981). The P—N synergism is not a common phenomenon and depends on the nitrogen containing compound and polymer nature (Levchik, 2006). Some theories have been presented for the P—N synergism (Cullis, Hirschler, & Tao, 1991; Gaan, Sun, Hutches, & Engelhard, 2008) and elucidated that P—N compounds reduce the formation of flammable volatiles and catalyze char formation.

Current industrial flame retardant finishing treatments for cotton fabrics exploit the phosphorus–nitrogen synergism (Proban-Rhodia, Pyrovatex). It was shown that upon cellulose pyrolysis at high temperatures, phosphorus compounds can phosphorylate the C(6) of the glucose monomer, avoiding the source of fuel formation as levoglucosan and promoting the dehydration process that is a competitive route to depolymerization (Scheme 1) (Broido, Evett, & Hodges, 1975). In the P—N compounds, the FRs may be converted into phosphorus acid amides that also catalyze the dehydration and carbonization of cellulose thereby the amounts of combustible gases at reduced temperatures are decreasing and the formation of a carbonaceous replica of the original textile fiber is improved. It was illustrated that the most effective FRs are those which cause the transformation of the flammable polymer to a carbonaceous char (Davies, Horrocks, & Miraftab, 2000). The charred residue not only reduces the creation of flammable volatiles but also leads in a flame/heat barrier between the ignition source and the fabric inner layers (Horrocks, Kandola, Davies, Zhang, & Padbury, 2005). The enhancement in char formation is feasible both by conventional intumescents and by increasing thermal barrier properties through nanoparticles (White, 2004).

Functional coating methods are considered as alternative flexible ways to conventional finishing techniques because they are independent of fabric type and necessitate low amounts of additives as well as allow incorporation/combination of different functionalities (Gulrajani & Gupta, 2011). These methods include layer by layer (LBL) assembly, immobilization of enzymes, nano coating and using plasma for deposition of functional molecules. The layer by layer (LBL) assembly was developed to fabricate thin composite films on solid surfaces by sequential adsorption of oppositely charged polycations and polyanions to build a series of polyelectrolyte multilayer films on the substrate (Dvoracek, Sukhonosova, Benedik, & Grunlan, 2009; Everett, Jan, Sue, & Grunlan, 2007; Jang, Rawson, & Grunlan, 2008). Both free and immobilized enzymes can be used to treat the fibers but immobilized enzymes are permanently attached to the textiles. Therefore, the free enzyme is lost after its first use but the immobilized enzyme continues to catalyze the anticipated reactions repeatedly (Banerjee, Pangule, & Kane, 2011; Tasso et al., 2009). The nano coatings based on zinc, silver and titanium dioxide nanoparticles have extensively been applied on the fabrics to produce anti UV, antimicrobial and self cleaning textiles (Kathirvelu, D'Souza, & Dhurai, 2009). Usually, pad/dry/cure, thermal, radiation or chemical methods have been utilized to fix these nanoparticles on textiles. It was found that nano coating through LBL is a chemically mild alternative to other processes in order to produce ultra-thin, transmissive and stable coatings. Plasma can also be applied on textiles for surface activation, to perform polymerization on the surface or for deposition of compounds containing different functionalities. In the plasma enhanced chemical vapor deposition (PECV) technique, the plasma functionalizes the substrate surface before chemical vapor deposition (Alongi, Tata, & Frache, 2011). In a recent work, LBL assembly of branched polyethylenimine and Laponite clay was examined and it was shown that these clay-based assemblies endow flame-resistant behavior to cotton fabric by creating a protective sheath (~10 μm diameter) around each individual microfiber (Li, Schulz, & Grunlan, 2009).

In this work, using ultrasonic method, nanoparticles of five novel phosphoramides were synthesized and characterized by multinuclear NMR, FT-IR, fluorescence, UV–vis spectroscopy, XRD and FE-SEM microscopy. The flame retardancy abilities of these compounds were evaluated quantitatively by their grafting to the cotton fibers. Also, the antibacterial properties of the phosphoramides and the treated cotton fibers with these phosphoramides were evaluated against the Gram-positive *Staphylococcus aureus* and the Gram-negative *Escherchia coli* bacteria and greater antibacterial effects were observed against Gram-positive bacteria.

2. Experimental

2.1. Materials

All materials were purchased from Merck and Sigma–Aldrich companies and were used as received. They are phosphorus pentachloride, 4-nitroaniline, 4-chloro-3-trifluroroaniline, benzamide, allylamine, formic acid, Muller Hinton agar, methanol, CCl_4, distilled water. The mercerized cotton fabrics were prepared from Yazdbaft textile industries, Yazd, Iran. The two bacteria including one gram positive *S. aureus* and one gram negative *E. coli* were prepared from Pasteur Institute of Iran.

2.2. Measurements

The ^{1}H, ^{13}C and ^{31}P spectra were recorded on a Bruker Avance DRS 500 spectrometer. ^{1}H, ^{13}C and ^{31}P chemical shifts were determined relative to internal $Si(CH_3)_4$ and 85% H_3PO_4 as external standards, respectively. Fourier-transform infrared (FT-IR) spectra were recorded on a Bruker spectrometer. Elemental analysis was performed using a Heraeus CHN-O-RAPID apparatus. Melting points were obtained with an Electrothermal instrument. The field-emission scanning electron microscopy (FE-SEM) micrographs were taken from Zeiss instrument, under vacuum, accelerated at 5, 10, 15 kV. To identify the phases and crystallinity of samples, X-ray diffraction analyses were obtained with an INEL EQUINOX 3000 X-ray diffractometer using Cu K_α radiation ($\lambda = 1.5406$ Å) in the 2θ range of 5–80°. The thermal stability of the phosphoramide grafted cotton fibers and raw fiber were evaluated by thermo gravimetric analysis (TGA) and differential thermal analysis (DTA) in an air atmosphere with heating rate of 10 °C/min up to 800 °C on a TG-DTA SDTA 851e instrument.

The burning test was used to compare the flammability characteristics of treated and untreated samples. A fabric sample of size 100 mm × 100 mm was mounted in a sample holder. The flame from a Terrill burner was placed at a distance of 2 cm from the bottom of sample. The flame was introduced to the sample for 12 s. After the flame was removed, the sample was observed for char length for both treated and untreated cotton.

2.3. Synthesis

2.3.1. N-4-nitrophenyl-N′,N″-diallyl phosphoric triamide (**1**)

To a solution of N-4-nitrophenyl phosphoramidic dichloride (Gholivand, Shariatinia, & Pourayoubi, 2005) (10 mmol, 2.55 g) in acetonitrile, allylamine (40 mmol, 2.28 g) was added dropwise and the reaction flask was placed in an ultrasonic bath at 0 °C for about 1 h. Then, the precipitate was filtered, washed with distilled water and dried. Yield: 71%. M.p. = 146 °C. Anal. Calc. For $C_{12}H_{17}N_4O_3P$: C, 48.65; H, 5.78; N, 18.91%. Found: C, 48.64; H, 5.77; N, 18.90%. $^{31}P\{^1H\}$ NMR (121.49 MHz, $CDCl_3$): $\delta = 8.83$ (s). ^{1}H NMR (300.13 MHz, $CDCl_3$): $\delta = 3.43$ (m, 4H, CH_2), 4.03 (m, 1H, CH), 4.80 (m, 1H, CH), 4.94 (d, $^3J(H,H)_{trans} = 10.2$ Hz, 1H, $=CH_{trans}$), 5.11 (d, $^3J(H,H)_{cis} = 17.2$ Hz, 1H, $=CH_{cis}$), 5.25 (d, $^3J(H,H)_{trans} = 10.5$ Hz, 1H, $=CH_{trans}$), 5.34 (d, $^3J(H,H)_{cis} = 17.3$ Hz, 1H, $=CH_{cis}$), 5.78 (ddd, $^2J(PNH) = 10.5$ Hz, 1H, $NH_{allylamine}$), 5.89 (ddd, $^2J(PNH) = 10.7$ Hz, 1H, $NH_{allylamine}$), 6.57 (d, $^3J(H,H) = 9.2$ Hz, 2H, Ar—H), 7.91 (d, $^3J(H,H) = 9.2$ Hz, 2H, Ar—H), 8.14 (d, $^2J(PNH) = 8.8$ Hz, 1H, $NH_{nitroaniline}$). ^{13}CNMR (75.47 MHz, $CDCl_3$): $\delta = 42.77$ (d, $^2J(P,C) = 7.8$ Hz, $-CH_2$), 114.49 (s, $=CH_2$), 116.46 (s, ortho-C), 116.57 (d, $^3J(P,C) = 6.8$ Hz, ortho-C), 125.02 (s, meta-C), 137.59 (d, $^3J(P,C) = 6.8$ Hz, $CH_{allylamine}$), 139.17 (s, meta-C), 150.56 (s, ipso-C), 150.66 (s, para-C). FT-IR (KBr, cm^{-1}): 3483 (NH), 3374, 3154, 2920, 1628 (C=C), 1596 (NO_2), 1595, 1499, 1477, 1426, 1338 (NO_2), 1307, 1178 (P=O), 1111, 1037 ($P-N_{allylamine}$), 995 ($P-N_{nitroaniline}$), 912, 844, 779, 752, 693, 666, 632, 533, 452, 421. UV–vis (100 ppm in methanol): $\lambda(max) = 203$, 219, 335 nm. Fluorescence (200 ppm in methanol): $\lambda(max) = 490.5$ nm.

2.3.2. N-4-chloro-3-trifluroro-phenyl-N′,N″-diallyl phosphoric triamide (**2**)

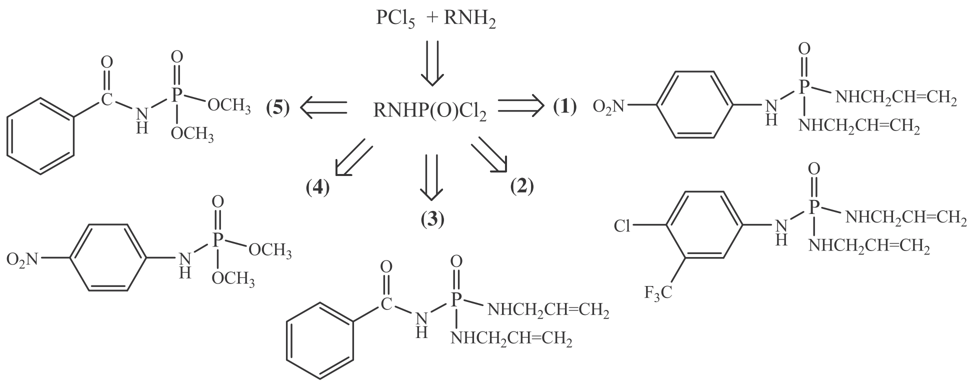
To a solution of N-4-chloro-3-trifluroro-phenyl phosphoramidic dichloride [33] (10 mmol, 3.12 g) in acetonitrile, allylamine (40 mmol, 2.28 g) was added dropwise and the reaction flask was placed in an ultrasonic bath at 0 °C for about 1 h. Then, the solution was evaporated at room temperature and the precipitate was filtered, washed with distilled water and dried. Yield: 65%. M.p. = 99 °C. Anal. calcd. For $C_{13}H_{16}N_3OPClF_3$: C, 44.14; H, 4.56; N, 11.88. Found: C, 44.12; H, 4.55; N, 11.87%. $^{31}P\ \{^1H\}$ NMR (121.49 MHz, d_6-DMSO): $\delta = 9.49$ (s). ^{1}H NMR (300.13 MHz, d_6-DMSO): $\delta = 2.96$ (m, 2H, CH), 3.57 (m, 4H, $-CH_2$), 5.08 (d, $^3J(H,H)_{trans} = 10.2$ Hz, 2H, $=CH_{trans}$), 5.17 (d, $^3J(H,H)_{cis} = 18.1$ Hz, 2H, $=CH_{cis}$), 5.83 (ddd, $^2J(PNH) = 10.6$ Hz, 2H, $NH_{allylamine}$), 6.14 (d, $^2J(PNH) = 6.1$ Hz, 1H, $NH_{aromatic}$), 7.20 (d, $^3J(H,H) = 8.4$ Hz, 1H, Ar—H), 7.29 (d, $^3J(H,H) = 8.4$ Hz, 1H, Ar—H), 7.36 (s, 1H, Ar—H). ^{13}C NMR (75.47 MHz, d_6-DMSO): $\delta = 42.86$ (s, $-CH_2$), 113.95 (s), 114.35 (s, $=CH_2$), 115.91 (d, $^2J(P,C) = 6.5$ Hz, ipso-C), 119.62 (s), 121.91 (d, $^3J(P,C) = 6.6$ Hz, ortho-C), 131.08 (s), 131.56 (s), 137.70 (d, $^3J(P,C) = 6.2$ Hz, $CH_{allylamine}$), 143.02 (s, CF_3). FT-IR (KBr): $\nu = 3408$ (NH), 2921 (CH), 2607, 1621 (C=C), 1570, 1541 (NO_2), 1482, 1437, 1397 (NO_2), 1322, 1258, 1206, 1182 (P=O), 1134, 1114, 1086, 1038 ($P-N_{allylamine}$), 991 ($P-N_{aromatic}$), 937, 885, 831, 768, 747, 727, 672, 617, 600, 524, 470 cm^{-1}. UV–vis (100 ppm in methanol): $\lambda(max) = 205$, 248, 298 nm. Fluorescence (200 ppm in methanol): $\lambda(max) = 492.5$ nm.

2.3.3. N-benzoyl-N′,N″-diallyl phosphoric triamide (**3**)

To a solution of N-4-benzoyl phosphoramidic dichloride [33] (10 mmol, 2.38 g) in acetonitrile, allylamine (40 mmol, 2.28 g) was added dropwise and the reaction flask was placed in an ultrasonic bath at 0 °C for about 1 h. Then, the precipitate was filtered, washed with distilled water and dried. Yield: 55%. M.p. = 102 °C. Anal. Calc. For $C_{13}H_{18}N_3O_2P$: C, 55.91; H, 6.50; N, 15.05%. Found: C, 55.88; H, 6.49; N, 15.04%. $^{31}P\{^1H\}$ NMR (121.49 MHz, $CDCl_3$): $\delta = 10.29$ (s). ^{1}H NMR (300.13 MHz, $CDCl_3$): $\delta = 3.43$ (m, $J = 8.1$ Hz, 2H, CH), 3.64 (m, 4H, $-CH_2$), 5.04 (d, $^3J(H,H)_{cis} = 17.1$ Hz, 2H, $=CH_{cis}$), 5.21 (d, $^3J(H,H)_{trans} = 10.2$ Hz, $=CH_{trans}$), 5.83 (ddd, $^2J(PNH) = 10.0$ Hz, 2H, $NH_{allylamine}$), 7.43 (t, $^3J(H,H) = 8.2$ Hz, 2H, Ar—H), 7.51 (t, $^3J(H,H) = 8.2$ Hz, 1H, Ar—H), 8.00 (d, $^3J(H,H) = 8.2$ Hz, 2H, Ar—H), 9.10 (d, $^2J(PNH) = 10.4$ Hz, 1H, $NH_{benzamide}$). ^{13}C NMR (75.47 MHz, $CDCl_3$): $\delta = 42.47$ (d, $^2J(P,C) = 7.5$ Hz, $-CH_2$), 114.37 (s, $=CH_2$), 127.99 (s, meta-C), 128.29 (s, ortho-C), 132.04 (s, para-C), 133.72 (d, $^3J(P,C) = 8.1$ Hz, ipso-C), 137.61 (d, $^3J(P,C) = 8.1$ Hz, $CH_{allylamine}$), 168.05 (s, C=O). FT-IR (KBr, cm^{-1}): 3254 (NH), 3085, 2928 (CH), 2850 (CH), 1647 (C=O), 1601 (C=C), 1580, 1498, 1455, 1427, 1272, 1205, 1170 (P=O), 1124, 1097, 1037 ($P-N_{allylamine}$), 992, 924 ($P-N_{benzamide}$), 893, 850, 794, 710, 670, 534, 466, 420. UV–vis (100 ppm in methanol): $\lambda(max) = 203$, 230, 275 nm. Fluorescence (200 ppm in methanol): $\lambda(max) = 329.0$ nm.

2.3.4. N-4-nitrophenyl-dimethyl phosphoramidic acid ester (**4**)

A solution containing N-4-nitrophenyl phosphoramidic dichloride [33] in methanol was placed in an ultrasonic bath at



Scheme 2. The preparation pathway of phosphoramides **1**–**5**.

0 °C for about 1 h. Then, the precipitate was filtered, washed with distilled water and dried. Yield: 53%. M.p. = 159 °C. Anal. Calc. For $C_8H_{11}N_2O_5P$: C, 39.03; H, 4.50; N, 11.38%. Found: C, 39.01; H, 4.49; N, 11.37%. $^{31}P\{^1H\}$ NMR (121.49 MHz, DMSO): $\delta = 3.59$ (s), 3.49 (s). ^1H NMR (300.13 MHz, DMSO): $\delta = 3.67$ (d, ^3J(POCH) = 11.4 Hz, 6H, OCH_3), 7.17 (d, ^3J(H,H) = 9.1 Hz, 2H, Ar—H), 8.14 (d, ^3J(H,H) = 9.1 Hz, 2H, Ar—H). ^{13}CNMR (75.47 MHz, DMSO): $\delta = 53.30$ (d, ^2J(P,C) = 5.4 Hz, OCH_3), 116.77 (d, ^3J(P,C) = 4.9 Hz, ortho-C), 116.88 (d, ^3J(P,C) = 5.3 Hz, ortho-C), 125.50 (s), 126.40 (s), 140.71 (s), 147.94 (d, ^2J(P,C) = 8.8 Hz, ipso-C). FT-IR (KBr, cm^{-1}): 3450 (NH), 3151, 3120, 3035, 2987, 2949, 2919, 2874, 2850, 1781, 1609, 1596 (NO_2), 1521, 1498, 1447, 1402, 1383, 1343 (NO_2), 1299, 1263, 1229, 1181 (P═O), 1123, 1111, 1084, 1045, 957 ($P—N_{nitroaniline}$), 858 (P—O), 819, 749, 690, 659, 624, 589, 538, 518, 498, 432. UV–vis (100 ppm in methanol): λ(max) = 204, 222, 317 nm. Fluorescence (200 ppm in methanol): λ(max) = 400.0 nm.

2.3.5. *N-benzoyl-dimethyl phosphoramidic acid ester (**5**)*

A solution containing N-4-benzoyl phosphoramidic dichloride [33] in methanol was placed in an ultrasonic bath at 0 °C for about 1 h. Then, the precipitate was filtered, washed with distilled water and dried. Yield: 49%. M.p. = 117 °C. Anal. Calc. For $C_9H_{12}NO_4P$: C, 47.17; H, 5.28; N, 6.11%. Found: C, 47.14; H, 5.28; N, 6.10%. $^{31}P\{^1H\}$ NMR (121.49 MHz, DMSO): $\delta = 2.15$ (s). ^1H NMR (300.13 MHz, DMSO): $\delta = 3.73$ (d, ^3J(POCH) = 11.6 Hz, 6H, OCH_3), 7.47 (t, ^3J(H,H) = 8.1 Hz, 2H, Ar—H), 7.62 (t, ^3J(H,H) = 8.1 Hz, 1H, Ar—H), 7.93 (d, ^3J(H,H) = 8.1 Hz, 2H, Ar—H), 9.99 (d, ^2J(PNH) = 9.2 Hz, 1H, $NH_{benzamide}$). ^{13}CNMR (75.47 MHz, DMSO): $\delta = 53.81$ (d, ^2J(P,C) = 5.7 Hz, OCH_3), 128.30 (s), 128.48 (s), 132.58 (s), 132.72 (s), 168.25 (s, C═O). FT-IR (KBr, cm^{-1}): 3431 (NH), 3350, 3143, 3053 (CH), 3002, 2952, 2889, 2852, 1793, 1682 (C═O), 1646, 1598, 1579, 1502, 1456, 1432, 1277, 1242, 1186 (P = O), 1106, 1043, 938 ($P—N_{benzamide}$), 902 (P—O), 860, 811, 777, 716, 670, 617, 514, 469, 442, 423. UV–vis (100 ppm in methanol): λ(max) = 203, 231, 274 nm. Fluorescence (200 ppm in methanol): λ(max) = 365.0 nm.

2.4. *Application of monomers*

In this study, three concentrations of monomers **1**–**5** (25%, 50%, 75% o.w.f.) were used for grafting to the cotton fabrics. The thermal initiator was potassium persulphate (KPS) ($K_2S_2O_8$) 5% along with Mohr's salt (ammonium iron(II) sulfate, $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$) 1% for preventing homopolymerization and promoting free radical graft polymerization of the monomer on the substrate. For each monomer, the application recipe includes monomer, thermal initiator (KPS) and Mohr's salt. Each monomer was dissolved in methanol (CH_3OH). The thermal initiator (5%) and Mohr's salt (1%) were dissolved in distilled water separately and the two solutions were pad applied separately on a 100 mm × 100 mm swatch of cotton fabric at pick up of 85–90%. Then, the cotton sample was dried and padded with a monomer solution. The cotton sample was allowed to dry and finally, the treated samples were cured at 121 °C for 3 min in a muffle furnace with a heating rate of 5 °C/min. The washing durability up to 5 accelerated washes for 30 min was evaluated using a non-ionic detergent at 35 °C. The degree of grafting was calculated using the following formula (1) where W_g and W_0 are the weight of sample after and before grafting, respectively.

$$\text{Degree of grafting(DG)} = \frac{W_g - W_0}{W_0} \times 100 \qquad (1)$$

2.5. *In vitro antibacterial activities*

The in vitro antibacterial activities of the phosphoramides **1**–**5** and treated cotton fibers with five different concentrations of these phosphoramides (25%, 50%, 75% o.w.f.) were evaluated by the filter paper disk method (Shariatinia & Nikfar, 2013). In these experiments, the Gram-positive *Staphylococcus aureus* and the Gram-negative *Escherchia coli* bacteria were examined and greater antibacterial effects were observed against Gram-positive bacteria. The bacteria were cultured in nutrient agar medium and used as inocula. The phosphoramides were dissolved in ethanol and the Whatmann filter paper disks (diameter 6.5 mm) were soaked into the phosphoramides solutions to adsorb them. The disks were then air-dried to remove the surface solvent and placed on the surface of a sterilized agar nutrient medium that was inoculated with the test bacterium. For the phosphoramides treated fibers, 0.004 g of each sample was directly placed on the agar medium. The thickness of the agar medium was kept equal in all Petri dishes. Next, the disks were incubated at 37 ± 1 °C for 24 h. The zones of growth inhibitions were measured indicating the inhibitory activities of the samples on the growth of the bacterium. The average of three diameters was calculated for each assay.

3. Results and discussion

3.1. *Spectroscopic and microscopic study*

In this study, five new phosphoramides were synthesized (Scheme 2) and characterized by FT-IR, multinuclear NMR, UV–vis and fluorescence spectroscopy. A summary of the NMR and FT-IR data of compounds **1–5** are given in Table 1. The phosphorus chemical shift, $\delta(^{31}P)$, moves to down field from compounds **1** (8.83 ppm) to **3** (10.29 ppm). This down field shift shows the most electron withdrawing of substituents on the phosphorus atom in **3** resulting in the most deshielded phosphorus atom. Also, comparing the $\delta(^{31}P)$ of molecules **4** and **5** with their analogous phosphoramides **1** and **3** confirms that replacements of allylamine with methoxy groups lead to much shielded phosphorus atoms. Moreover, the

Table 1
The summary of the NMR and FT-IR spectra of phosphoramides **1–5**.

Compound	$\delta(^{31}P)$ (ppm)	$^3J(H,H)_{cis}$ (Hz)	$^3J(H,H)_{trans}$ (Hz)	$^2J(PNH)$ (Hz)	$^3J(POCH)$ (Hz)	$^2J(P,C)$ (Hz)	$^3J(P,C)$ (Hz)	$\nu(P{=}O)$ (cm^{-1})	$\nu(P{-}N)$ (cm^{-1})	$\nu(P{-}O)$ (cm^{-1})
1	8.83	17.2, 17.3	10.2, 10.5	10.5[a], 10.7[a], 8.8[b]	–	7.8[a]	6.8[b], 6.8[a]	1178	1037[a], 995[b]	–
2	9.49	18.1	10.2	10.6[a], 6.1[b]	–	6.5[b]	6.6[b], 6.2[a]	1182	1038[a], 991[b]	–
3	10.29	17.1	10.2	10.0[a], 10.4[b]	–	7.5[a]	8.1[b], 8.1[a]	1170	1037[a], 924[b]	–
4	3.59, 3.49	–	–	–	11.4	5.4[a], 8.8[b]	4.9[b], 5.3[b]	1181	957	858
5	2.15	–	–	9.2[b]	11.6	5.7[a]	–	1186	938	902

[a] Aliphatic.
[b] Aromatic.

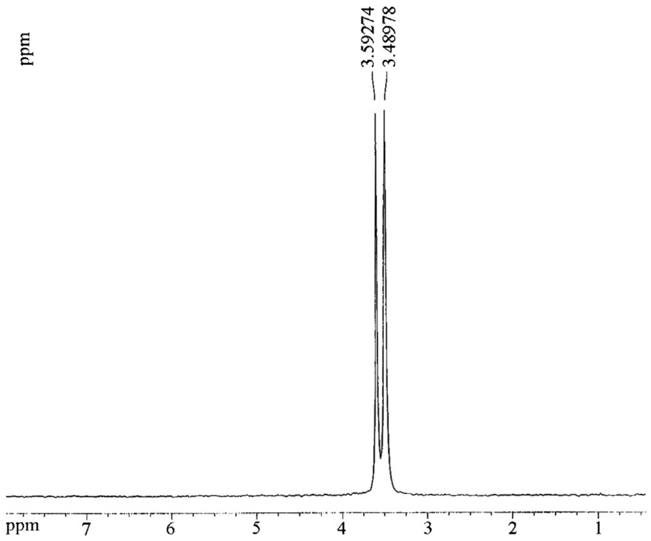


Fig. 1. The ^{31}P NMR spectrum of **4** indicating two peaks in a 1:1 ratio.

^{31}P NMR spectrum of **4** reveals two peaks in a 1:1 ratio reflecting the presence of two isomers in the solution state for this molecule (Fig. 1). This can be attributed to the existence of a chiral phosphorus center within the molecule due to non symmetrical orientation of the two OCH_3 moieties relative to each other.

The ^1H NMR spectra of compounds **1–3** Exhibit $^3J(H,H)_{cis}$ and $^3J(H,H)_{trans}$ coupling constants about 10.5 and 17.0–18.0 Hz, respectively. These are produced due to the splittings of cis and trans protons present in the $CH{=}CH_2$ bond. The $^2J(PNH)_{aliphatic}$ coupling constant within the range 10.0–10.6 Hz are measured for the splitting of the amino proton of allylamine group with the ^{31}P nucleus. It is seen in the ^1H NMR spectrum of **1** that all of the protons signals of the two allylamine moieties are appeared separately that can be due to the presence of non symmetric P atom in this molecule. The $^2J(PNH)_{aromatic}$ coupling constants are observed for the compounds **1**–**3** and **5** equal to 6.1, 8.8, 10.4 and 9.2 Hz, respectively. Comparing the $^2J(PNH)_{aromatic}$ of molecules **3** and **5** both containing $C_6H_5C(O)NHP(O)$ moiety illustrates a smaller value in **5**. This means that substitution of the allylamine with methoxy results in a less interaction between the $NH_{aromatic}$ proton and the P atom. The $^3J(POCH)$ coupling constants of 11.4 and 11.6 Hz are observed for the splittings of the methoxy protons with the P atoms in compounds **4** and **5**, respectively.

The ^{13}C NMR spectrum of **1** indicates six separated signals for the carbon atoms of nitroaniline ring but one set of peaks for the two allylamine groups. This splitting pattern in the ^{13}C NMR spectrum further validates the presence of a chiral phosphorus in the molecule as mentioned above. The $^2J(P,C_{aliphatic})$ coupling constant is measured for the splitting of the $-CH_2$ carbon atom with the P nucleus equal to 7.8 and 7.5 Hz in compounds **1** and **3**, respectively. The methoxy carbons in molecules **4** and **5** couple with their related phosphorus atoms to give $^2J(P,C_{aliphatic})$ values of 5.4 and 5.7 Hz, respectively. The $^3J(P,C_{aliphatic})$ values are also detected for molecules **1–3** for the splitting of $=CH_2$ carbon atom with the P nucleus equal to 6.8, 6.6 and 8.1 Hz, respectively. The two $^3J(P,C_{aromatic}) = 4.9$, 5.3 Hz are present in the ^{13}C NMR spectrum of **4** due to the existence of six non equivalent carbon atoms of the nitroaniline ring. Comparing the ^{13}C NMR spectra of compounds **1** and **4** illustrates that in both of them a similar result is observed (six non equivalent carbon atoms for the nitroaniline ring) that can be related to the effect of nitroaniline ring on the molecular spatial orientation. In molecule **4**, the ipso carbon atom also splits with the P atom with a $^2J(P,C_{aromatic}) = 8.8$ Hz.

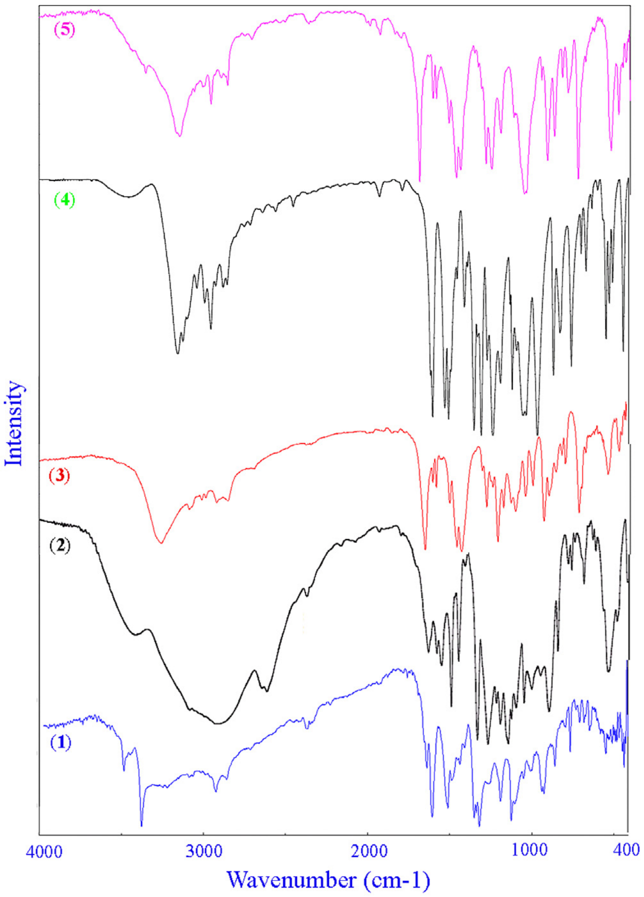
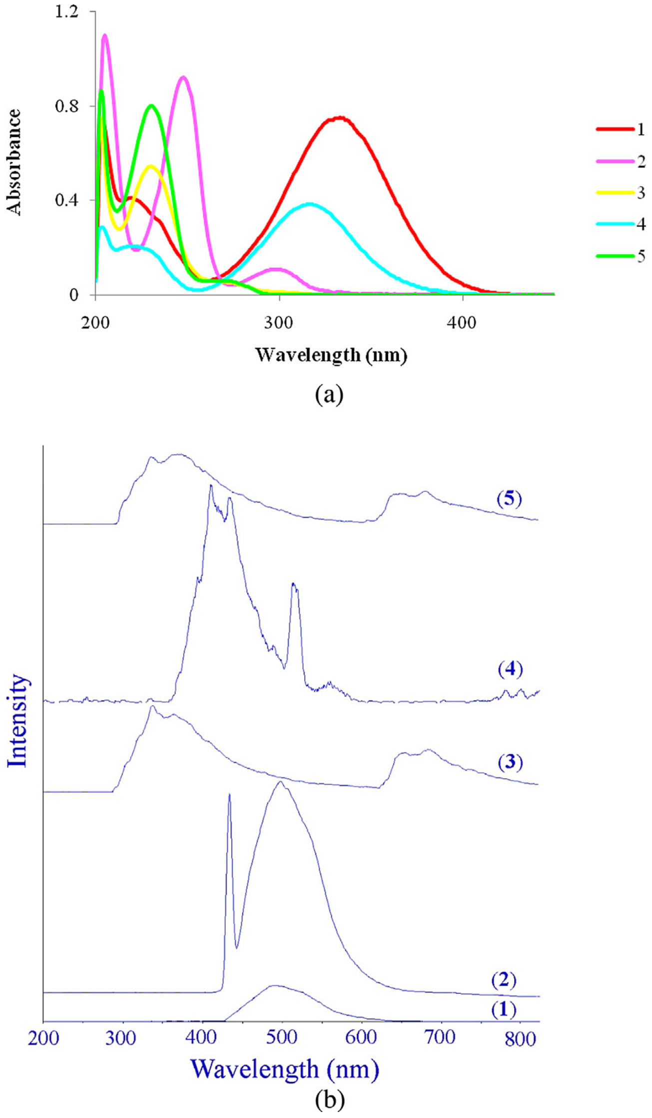


Fig. 2. The FT-IR spectra of phosphoramides **1**–**5**.

The FT-IR spectra (Fig. 2) demonstrate that the ν(P=O) value decreases from **1**, **2** (1178, 1182 cm^{-1}) to **3** (1170 cm^{-1}) exhibiting almost comparable P=O bonds in **1**, **2** but its weakening in **3**. The $\nu(P—N)_{aliphatic}$ values in compounds **1–3** (~1037 cm^{-1}) are greater than the $\nu(P—N)_{aromatic}$ (~990, 924 cm^{-1}). Comparing the ν(C=O) of compounds **3** (1647 cm^{-1}) and **5** (1682 cm^{-1}) displays a stronger C=O bond for **5** that is owing to its stronger PN bond created by the preferred resonance form C(O)—N=P(OH) than C(OH)=N—P(O). The P—N bond in **4** is stronger than in **5** indicating replacement of nitroaniline with benzamide causes weakening of the P—N bond. An opposite trend is observed for their P—O bonds than is associated with the effect of the P—N bonds.

A summary of the UV–vis and fluorescence spectra of compounds **1–5** and also their crystal/particle sizes are presented in Table 2. The UV–vis spectra of compounds **1**–**5** display three maximum absorption wavelengths at 203–205, 222–248, and 274–335 nm (Fig. 3a) that can be related to the $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$ transitions. The fluorescence spectra of compounds **1–5** are presented in Fig. 3b showing the λ(max) of emission signals appear at ~490 nm in **1**, **2** but it shifts to 329 nm in **3** (blue shift) leading to increasing the band gap from ~2.52 eV in **1**, **2** to 3.77 eV in **3**. Therefore, replacement of benzamide with both nitroaniline and 4-chloro-3-trifluoroaniline causes enhanced band gaps for the phosphoramides. A blue shift is seen for the λ(max) of emission from **1** to **4** while a red shift is detected from **3** to **5**. The band gaps (E_g) measured for compounds **4** and **5** are 3.10 and 3.40 eV, respectively. The phosphoramide **2** presents the highest emission intensity among compounds **1–3**. Also, the emission intensities of molecules **4** and **5** are very much lower than those of their analogs **1** and **3**.



(a)

(b)

Fig. 3. The (a) UV–vis and (b) fluorescence spectra of phosphoramides **1**–**5**.

The nanoparticles of compounds **1–5** were prepared by ultrasonic irradiation method and their FE-SEM micrographs are shown in Fig. 4 indicating the spherical morphology for the particles that are 25–45 nm in size. Comparing the average particle sizes of these molecules in Table 2 with their related bang gaps reveal that when the particle size decreases the band gap is increased. The XRD patterns in Fig. 5 reveal sharp peaks due to high crystallinity with the sharpest peaks for compounds **1**, **3–5** appear at 2θ values of 9.62°, 8.78°, 14.58° and 16.73°, respectively. The Debye-Scherrer equation ($d = 0.9\,\lambda/\beta\cos\theta$) (Klug & Alexander, 1954) was used to evaluate the average crystallite sizes where d is the average crystallite size, λ is the X-ray wavelength, β is the full width at half maximum (FWHM) and θ is the diffraction angle. The crystal sizes of these phosphoramide were measured from the XRD diagrams within the range 32.8–93.4 nm (Table 2).

3.2. Flame retardancies of phosphoramides grafted cotton fibers

The flame retardant cotton cellulose fabrics treated with phosphoramides **1**–**5** were obtained and their various properties were evaluated by FT-IR, degree of grafting, vertical burning test, FE-SEM microscopy, TGA/DSC analyses and antibacterial activities. The FE-SEM micrographs of the burnt treated cotton fabrics were also

Table 2
The summary of the UV–vis and fluorescence spectra of phosphoramides **1**–**5** and their average crystal/particle sizes from the XRD patterns and FE-SEM images.

Compound	Maximum wavelengths of absorbtions[a] (nm)	λ(max) of emission (nm)	Max intensity of emission	Δ*E* (eV)	Average particle size from FE-SEM (nm)	Crystal size from XRD (nm)
1	203 (0.74), 219 (0.41), 335 (0.75)	490.5	174.84	2.53	45	32.8
2	205 (1.10), 248 (0.92), 298 (0.11)	492.5	635.22	2.52	40	–
3	203 (0.75), 230 (0.55), 275 (0.05)	329.0	131.86	3.77	25	68.1
4	204 (0.28), 222 (0.21), 317 (0.38)	400.0	50.52	3.10	35	53.8
5	203 (0.86), 231 (0.80), 274 (0.06)	365.0	92.50	3.40	30	93.4

[a] The numbers in parantheses are the intensities.

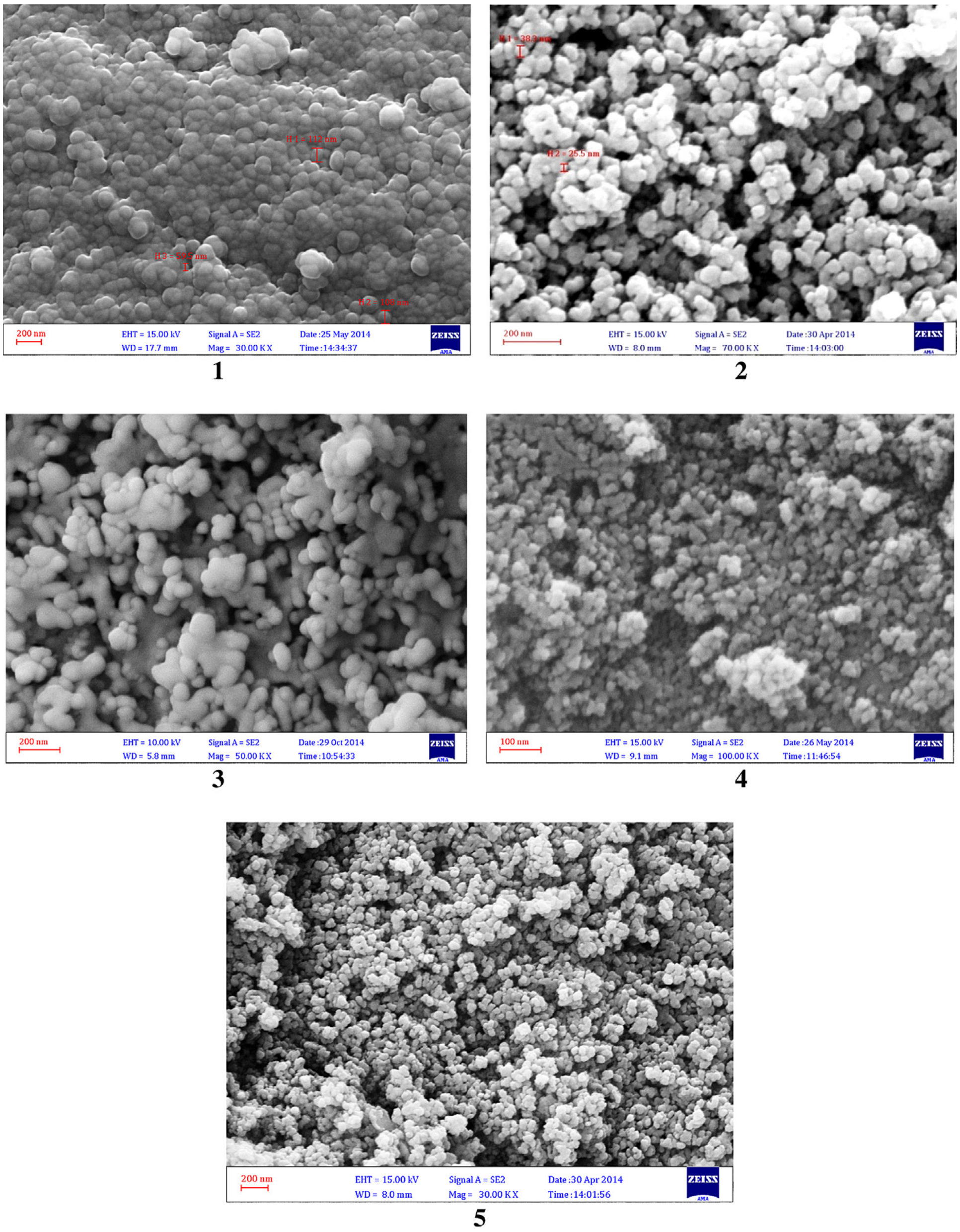


Fig. 4. The FE-SEM micrograph of nanoparticles of phosphoramides **1**–**5**.

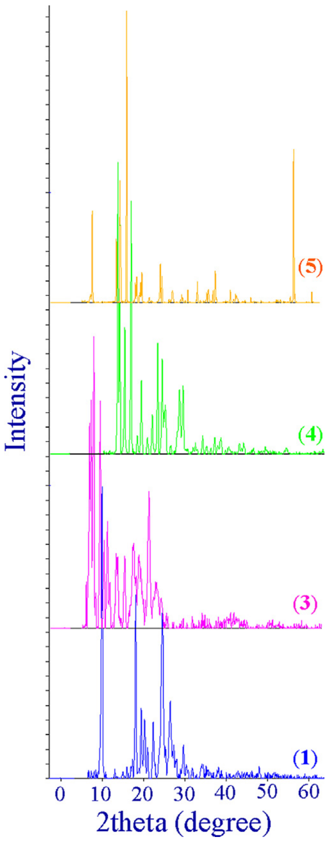


Fig. 5. The XRD patterns of phosphoramides **1**, **3**–**5**.

obtained to compare the effects of different phosphoramides on the produced flame retardant fibers.

The FT-IR spectra of treated cotton fibers with phosphoramides **1**–**5** in Fig. 6 evidently reveal that there are some new peaks around 1600–1750 cm^{-1} that are related to the existence of carbonyl, ester and/or carboxylic acid bonds created upon grafting the phosphoramides to the fibers. It is well known that the cotton fiber is almost pure cellulose that is a linear polysaccharide with long chains consisting of β-D-glucopyranose units joined by β-1,4-glycosidic linkages (Scheme 3) (Gurgel, Junior, Gil, & Gil, 2008; Qin, Soykeabkaew, Xiuyuan, & Peijs, 2008). In one repeating unit of cellulose molecule, there are one methylol and two hydroxyl groups as functional groups. Therefore, it is seen that the grafting of phosphoramides to the cellulosic fibers can create C=O/C—O bonds.

Table 3 shows the degree of grafting (DG) obtained for each monomer at three concentrations. It is seen that the DG is increased by increasing the monomer concentration. Among monomers **1**–**3** including allylamine groups connected to the phosphorus atom and have unsaturated C=C bonds with the ability to graft to the cotton fabrics, compound **1** presents the greatest DG and phosphoramide **3** reveals the least DG. The phosphoramides **4** and **5** that do not contain unsaturated bonds in their structures for polymerization and grafting to the fibers were also synthesized and examined on the cotton fibers to evaluate their ability to make flame retardant fibers. It is obvious that the DG of compound **4** is greater than that of compound **5**. The DG of compounds **1**–**5** changes within the order **1** > **2** > **3** > **4** > **5**.

Vertical flame test was performed to compare and evaluate the flammability of the treated and untreated cotton samples. The results of the char lengths for each of the treated and un-treated cotton samples are given in Table 3. Fig. 7 exhibits the digital photographs of vertical burning tests results on cotton fibers treated with phosphoramides indicating their char lengths. The char length for the raw cotton fiber was zero while the treated fibers present measurable char lengths. The reason for such burning behaviors is linked to the lower decomposition temperatures of the treated samples. The lower decomposition temperature for the treated cotton is combined with less available fuel due to the presence of flame retardant material that causes the flame to propagate quickly in search of combustible fuel (Hobart & Rowland, 1978). This behavior was observed during the burning test for the fabrics treated with the phosphoramides **1**–**5**. For the treated cotton, the flame runs through the whole sample very quickly. Nevertheless, the main discrepancy between the treated and untreated cotton was the afterglow so that there is no afterglow for the treated samples at all. The untreated cotton fabric burns vigorously with much stronger flame and the flame is higher from the surface of the sample with high heat of combustion and there is absolutely no char. However, for the treated samples, the flame is weak with very little heat of combustion and significant char formation. The increase in the char for the treated cotton fabrics is very high so that the burnt samples kept their structural integrity.

It is expected that the char lengths of the treated fibers decrease with increasing in their degrees of grafting. Comparing the char lengths of cotton fibers treated with phosphoramides **1**–**5** illustrates that the samples with greater DGs provide smaller char lengths so that the least and the greatest char lengths are measured for the treated fibers with phosphoramides **1** and **5**, respectively. The reason for the very close DGs and char lengths of compounds **1** and **2** can be described based on their chemical structures containing 4-nitroaniline and 4-chloro-3-trifluoromethyl aniline groups, respectively. The two groups can release electrons through their

Table 3
The degree of grafting of cotton fibers treated with three concentrations of phosphoramides and the char lengths of the burnt treated fibers.

Sample	Concentration (% o.w.f.)	Raw fiber weight (g)	Degree of grafting (%)	Char length (mm)	Degree of grafting after washing (%)	Char length after washing (mm)
1 + fiber	25	1.5	11.85	8	6.42	11
2 + fiber	25	1.5	11.57	9	5.97	12
3 + fiber	25	1.5	10.45	11	4.52	14
4 + fiber	25	1.5	9.12	12	5.14	15
5 + fiber	25	1.5	7.68	14	3.15	16
1 + fiber	50	1.5	16.28	5	10.62	7
2 + fiber	50	1.5	15.97	7	10.33	9
3 + fiber	50	1.5	15.14	8	9.38	10
4 + fiber	50	1.5	14.71	9	8.97	11
5 + fiber	50	1.5	12.35	11	7.72	12
1 + fiber	75	1.5	22.42	3	16.39	5
2 + fiber	75	1.5	21.98	4	16.14	6
3 + fiber	75	1.5	20.92	5	15.42	7
4 + fiber	75	1.5	19.46	6	14.56	8
5 + fiber	75	1.5	17.57	8	13.24	10

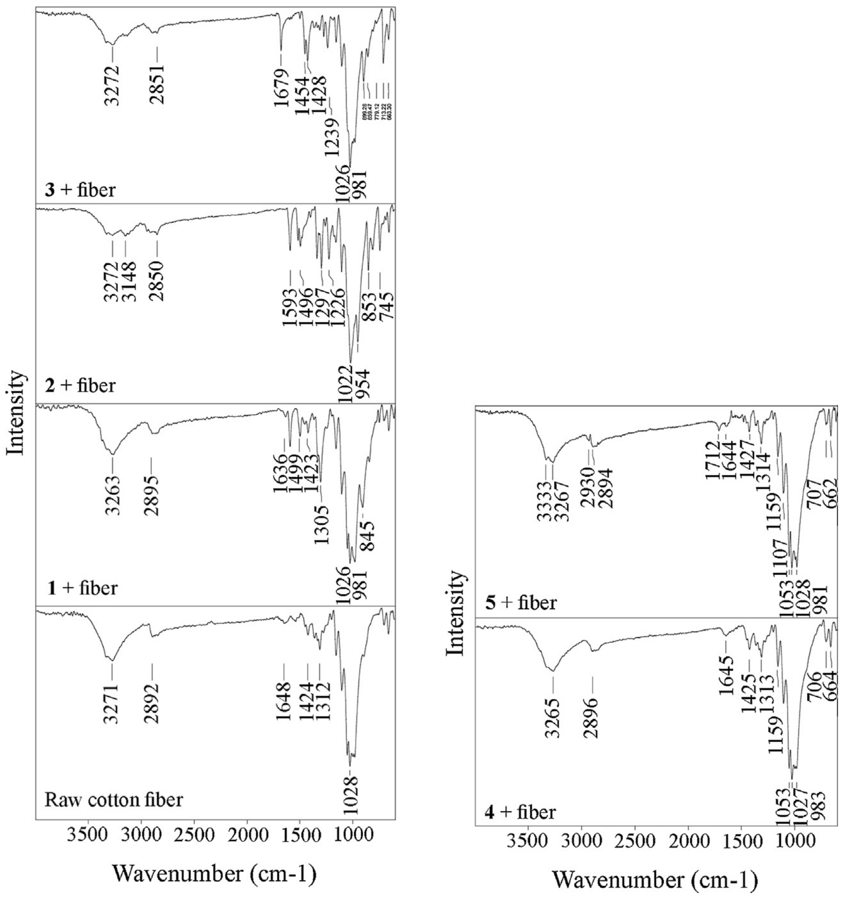
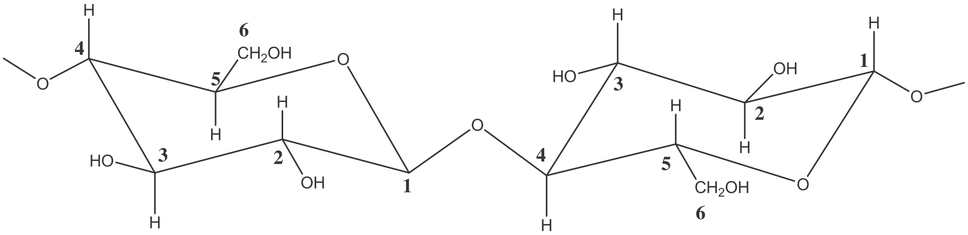


Fig. 6. The FT-IR spectra of cotton fibers treated with phosphoramides **1**–**5**.

resonance effects to their corresponding P—N bonds and enhance the P—N system synergistic effect. The benzamide substituent in compounds **3** and **5** has a more electron withdrawing property relative to the 4-nitroaniline and 4-chloro-3-trifluoromethyl aniline groups, thus could not strengthen the P—N bond similar to these functionalities. This subject is confirmed by the FT-IR spectra indicating weaker $P—N_{benzamide}$ bond than the $P—N_{nitroaniline}$ and $P—N_{4\text{-chloro-3-trifluoromethyl aniline}}$. It is noteworthy that the presence of weaker $P—N_{amide}$ bonds than the $P—N_{amine}$ has always been confirmed by both the FT-IR spectra and X-ray crystallography of the previously reported phosphoramides (Gholivand et al., 2005).

The char lengths after washing the treated fabrics were enhanced for all cases and the fibers with higher DGs revealed smaller increase in the char length. The reduction in the flame retardancy and DGs of the fibers is also reported by other researchers (Cheema, El-Shafei, & Hauser, 2013). It is evident that the covalent bonds formed between the phosphoramide monomers and cellulose fibers are stable and do not break by washing. Therefore, the reason can be washing and removing the intercalated/entrapped unreacted monomers or even homopolymers (formed during the padding method) within the fibers.

It is known that the chemical action of heat on cotton fibers plays a key role when their combustion is considered (Horrocks, 1983). In fact, cellulose degrades upon heating by two competitive routes including depolymerization and dehydration (Scheme 1) so that the former induces the creation of levoglucosan that subsequently pyrolyzes and giving rise mainly to low molecular weight, highly flammable species. The pyrolysis products are oxidized in the presence of oxygen and the highly exothermic character of the combustion causes more cellulose to pyrolyze. On the other hand, dehydration produces a carbonaceous residue called as char. The equilibrium between these processes depends on the heating rate (Alongi, Camino, & Malucelli, 2013c). The roles of any flame retardant on the cellulosic fabrics are removing the heat, reducing the gas generation and combustible, promoting the char formation, preventing oxygen access to the flame and interfering with the oxidation of flammable species. Consequently, the ideal flame retardant candidates for cotton are compounds capable of



Scheme 3. The chemical structure and atom-numbering of cellulose.

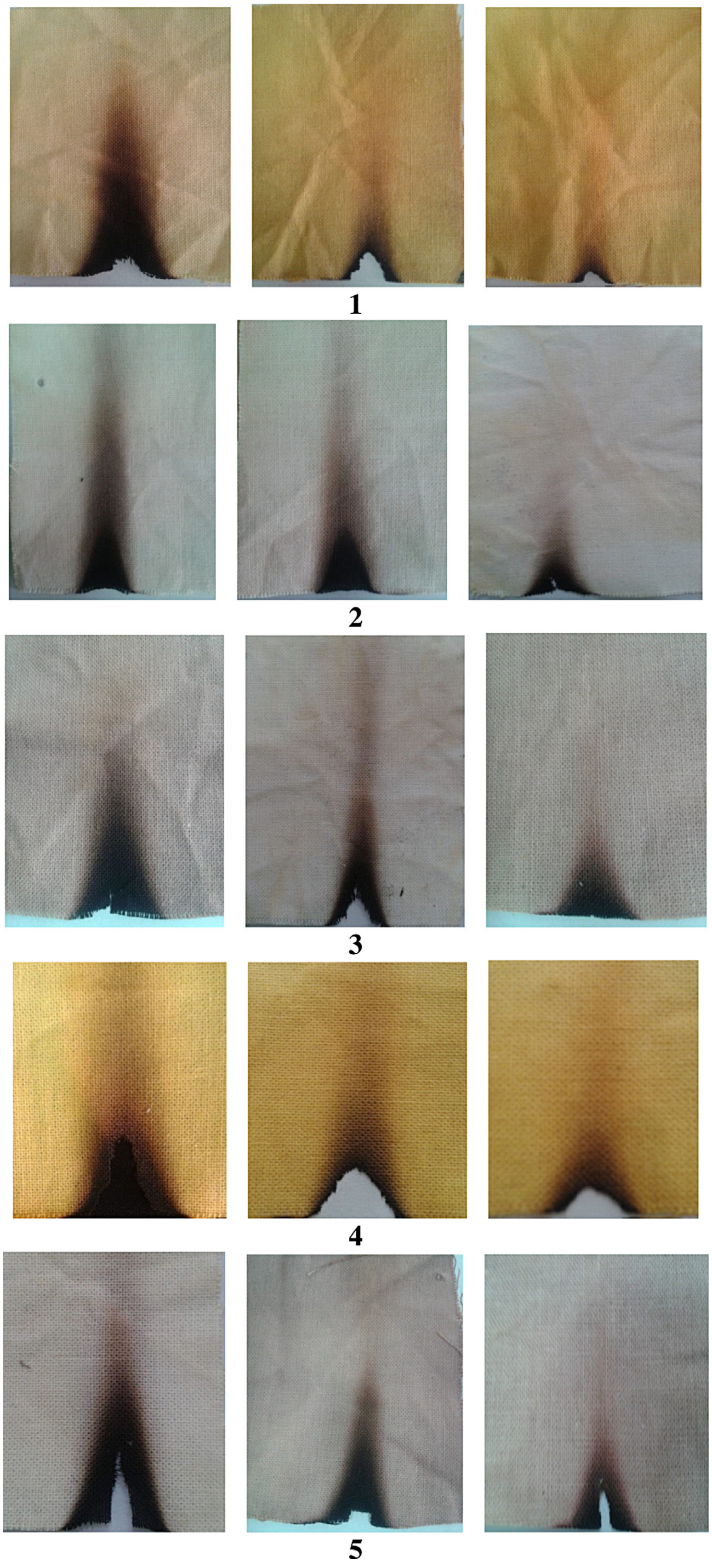
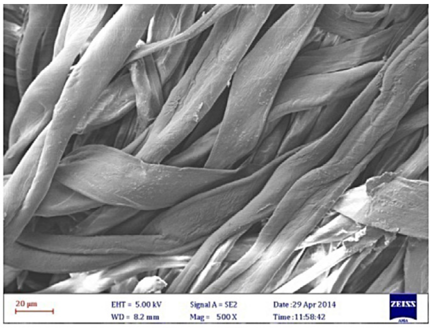
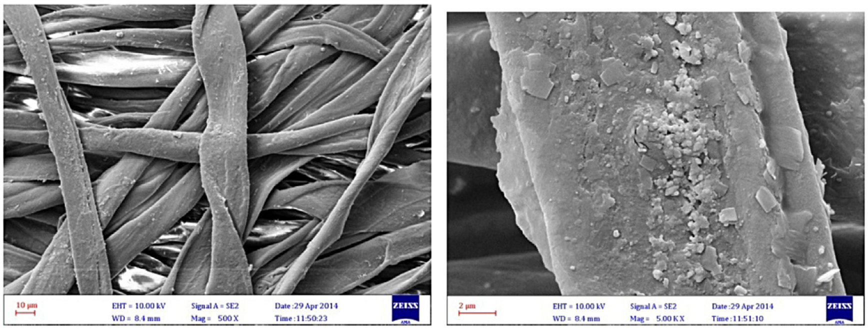


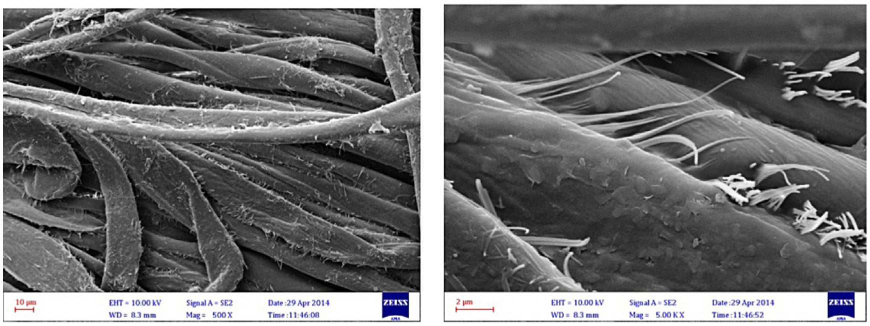
Fig. 7. The digital photographs of vertical burning tests results indicating the increasing in the char lengths of phosphoramides treated cotton fibers. In each series, the concentration of phosphoramide in increased from 25% to 50% and 75%, o.w.f. from left to right, respectively.



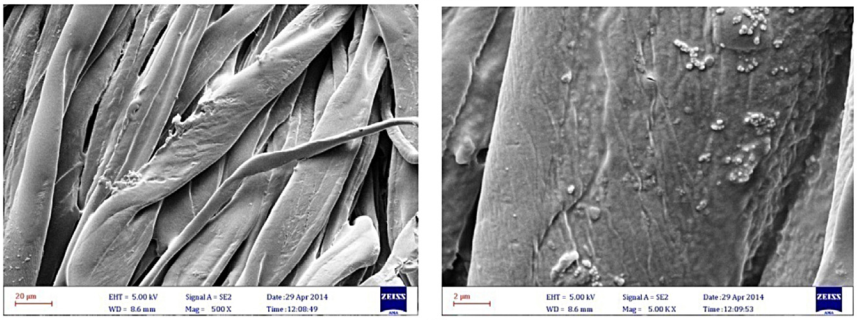
Raw fiber



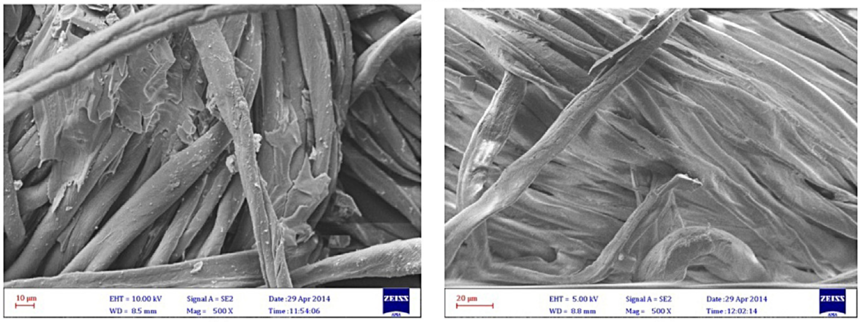
1 + fiber



2 + fiber



3 + fiber



4 + fiber **5** + fiber

Fig. 8. The FE-SEM micrographs of cotton fibers treated with phosphoramides **1**–**5**.

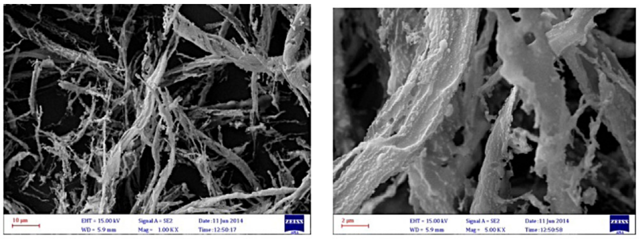
catalyzing the dehydration and thus to act as char former in the condensed phase.

Among many examined flame retardants, compounds containing P—N bonds are considered as efficient and non-toxic materials (Hendrix, Drake, & Barker, 1972a, 1972b). It was suggested that nitrogen in P—N synergistic retardants acts by a nucleophilic attack on the phosphate, creating polymeric species having P—N bonds that are more polar than the already present P—O bonds, and the enhanced electrophilicity of the phosphorus atom increases its ability to phosphorylate the C(6) primary hydroxyl group of cellulose (Horrocks, 1983). As a result, the intramolecular C(6)–C(1) rearrangement reaction forming levoglucosan is blocked. Moreover, the auto-crosslinking of cellulose promotes and consolidates the char formation caused by the action of the same flame retardants.

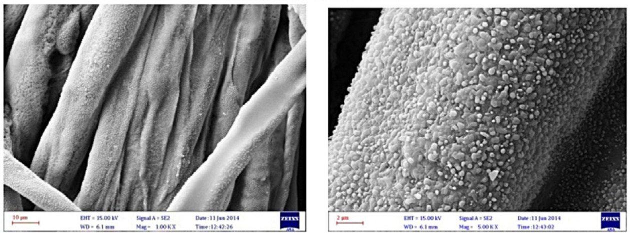
Surface morphology can provide useful information for the substrates undergone any chemical changes on their surfaces. To address any surface changes following the monomer applications, FE-SEM analysis was performed on both treated and untreated cotton samples. The FE-SEM micrographs of treated cotton fibers with phosphoramides **1**–**5** are shown in Fig. 8. It is observed that the FE-SEM micrographs illustrated outstanding differences in the treated and un-treated cotton samples so that the attachment of phosphoramides **1**–**3** on treated cotton samples are clearly approved. It is seen from the FE-SEM images of treated cotton fabrics with the phosphoramides **4** and **5** that the fabrics have become much sensitive to the electron beam under the same FE-SEM imagining conditions and the fibers are destroyed by electron bombardment.

The FE-SEM images of the charred samples were also analyzed to determine the efficiency of each monomer as a flame retardant (Fig. 9). It is seen than the raw cotton fibers become almost completely destroyed by burning but the treated fibers with phosphoramides **1**–**3** maintain their primary forms and do not destroy entirely. Comparing these figures with the char lengths obtained from the vertical burning tests demonstrates that the treated cotton fibers with less char lengths are more stable against destroying than the un-treated fabric. Interestingly, the treated fibers with phosphoramides **4** and **5** are also more stable against decomposition relative to the raw cotton fiber. Moreover, the phosphoramide **4** produces more resistant fabric than phosphoramide **5**. This may be described by enhanced interaction of phosphoramide **4** with the cotton fibers than phosphoramide **5**.

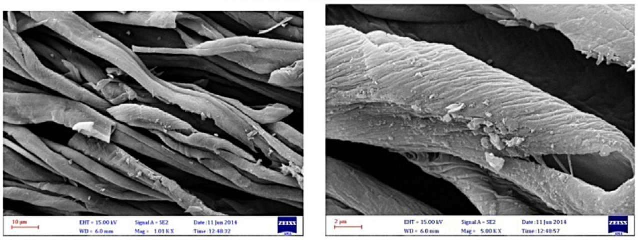
The enhancement in char formation for the cotton fabrics treated with phosphorus-based flame retardants is consistent with the proposed condensed phase mechanism. The presence of phosphorus-based flame retardant changes the pyrolysis pathway of the substrate by lowering the decomposition temperature, ultimately reducing the formation of gaseous combustibles and favors the formation of char. This can also be confirmed by the TGA/DSC results. The TGA/DSC plots of raw cotton fiber and phosphoramides treated cotton fibers are presented in Fig. 10. It was investigated that the chemical processes happening during the pyrolysis of untreated and treated cotton fibers are alike (Franklin & Rowland, 1979). It was shown that for flame retardant treated cotton, pyrolysis products are formed at lower temperatures so that the presence of a flame retardant increases all the pyrolysis processes (dehydration and char formation) at the expense of processes leading to the formation of flammable volatiles that result in flamed combustion.



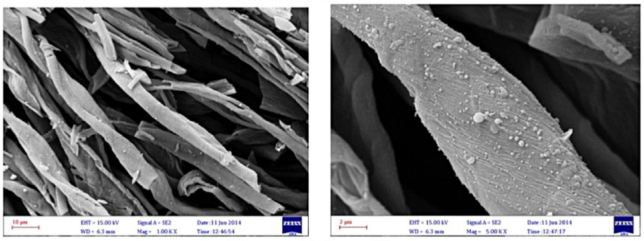
Charred raw fiber



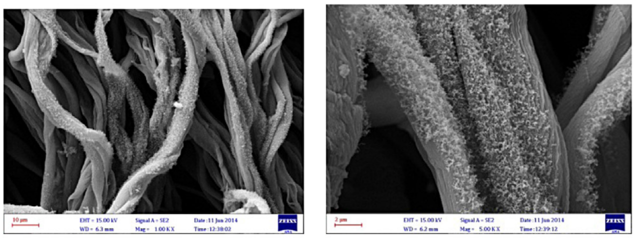
Charred **1** + fiber



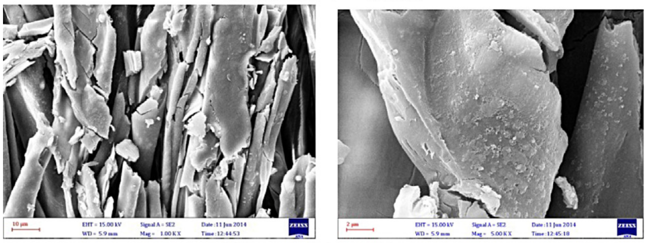
Charred **2** + fiber



Charred **3** + fiber



Charred **4** + fiber



Charred **5** + fiber

Fig. 9. The FE-SEM micrographs of charred cotton fibers treated with phosphoramides **1**–**5**.

Table 4 presents the TGA/DSC results for the raw cotton fiber and the fibers treated with phosphoramides **1**–**5**. The TGA/DSC thermographs of raw cotton fabric reveal two decomposition temperatures at 356.5, 477.2 °C with 36.65, 55.51% weight losses, respectively. Comparing the weight loss percents of un-treated and treated cotton samples with phosphoramids **1**–**5** in the temperature range ~310–325 °C illustrates that in all treated cotton samples, the weight loss percents change from 22.41% to 31.02% that are smaller than that of the raw cotton fiber (35.65%). The first degradation temperatures of treated cotton samples occur at lower temperatures within the range 310.29–328.72 °C compared with that of the un-treated sample (356.5 °C). Moreover, it is clearly observed from

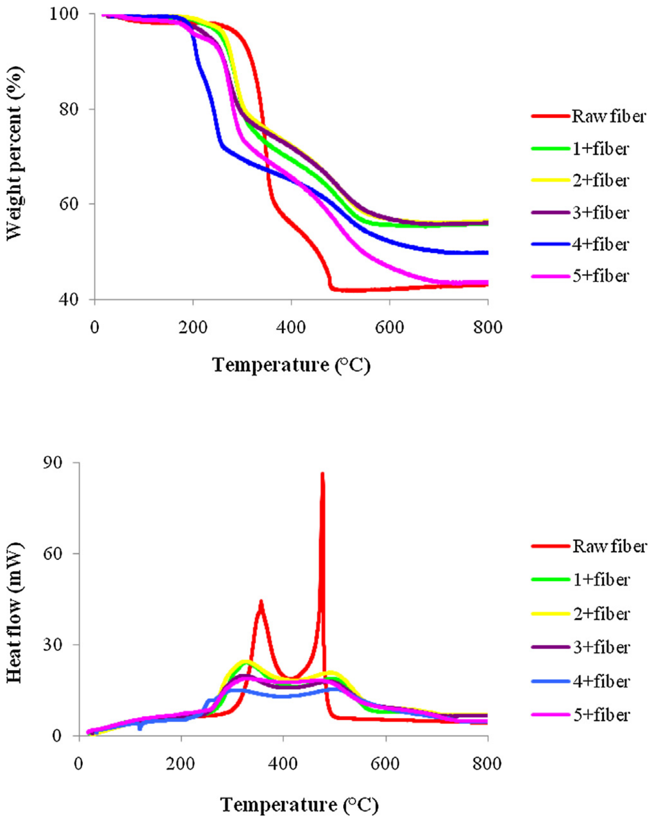


Fig. 10. The TGA/DSC plots of raw cotton fiber and cotton fibers treated with phosphoramides **1**–**5**.

the DSC plots that the weight losses of all five treated fabrics at their two main degradation temperatures around 310–330 °C and 466–500 °C are all about 10% smaller than those of the raw fiber.

The first degradation of sample treated with phosphoramide **4** at 111.06 °C can be attributed to the evaporation of water (moisture) within the fabric. The second degradation of this sample at 184.73 °C may be due to the decomposition of phosphoramide. Similarly, the first degradation of sample treated with phosphoramide **5** at 199.04 °C can be related to the phosphoramide decomposition. There are also third decomposition for all of the treated fabrics at the temperature range 627.02–725.95 °C that are probably owing to the fragmentation of the polymeric bonds within the fabrics.

Table 4
The TGA/DSC results for the raw cotton fiber and the fibers treated with phosphoramides **1**–**5**.

Compound	Degradation T (°C)	Weight loss (%)	Weight loss (%) at 800 °C
Raw cotton fiber	356.5	36.65	56.83
	477.2	55.51	
1 + fiber	327.38	25.01	43.52
	494.81	38.63	
	627.02	44.40	
2 + fiber	324.82	22.41	43.85
	492.87	36.19	
	641.66	43.62	
3 + fiber	321.87	23.13	44.00
	491.51	35.91	
	643.83	43.85	
4 + fiber	111.06	0.5442	50.17
	184.73	1.58	
	310.29	31.02	
	500.64	41.63	
	725.95	50.17	
5 + fiber	199.04	4.06	56.37
	328.72	29.09	
	466.41	40.79	
	648.04	55.13	

Table 5
The inhibition zones (mm) measured for the antibacterial activities of phosphoramides **1**–**5**, raw cotton fiber as well as cotton fibers treated with these phosphoramides.[a]

Sample	Bacterium type	
	E. coli	*S. aureus*
1	10.33 ± 0.45	18.36 ± 0.49
2	14.57 ± 0.44	25.84 ± 0.48
3	12.26 ± 0.50	20.75 ± 0.47
4	9.89 ± 0.48	15.66 ± 0.43
5	10.53 ± 0.46	18.74 ± 0.50
Raw cotton fiber	0	0
1 + fiber	8.61 ± 0.47	16.56 ± 0.47
2 + fiber	11.69 ± 0.52	22.12 ± 0.44
3 + fiber	9.45 ± 0.47	17.23 ± 0.45
4 + fiber	6.78 ± 0.49	12.56 ± 0.51
5 + fiber	7.32 ± 0.47	15.89 ± 0.49

[a] Mean ($n = 3$) ± standard deviation.

The maximum weight losses of treated cotton fabrics with phosphoramids **1**–**5** at 800 °C were measured within the range 43.52% (for fiber treated with **1**) to 56.37 (for fiber treated with **5**) which are all smaller than that of the raw fiber (56.83%). The greater weight loss of the untreated cotton fiber is related to the formation of flammable volatiles but the decrease in the weight losses of treated cotton fabrics is due to the formation of less volatiles and more char. Hence, it can be stated that the treatment with phosphoramids **1**–**5** made cotton fabrics remarkably thermally stable.

Considering the melting points of phosphoramides **1**–**5** and the degradation temperatures in the TGA/DSC diagrams, it is found that for none of the treated fabrics there exist pure phosphoramides within the fibers. This is due to the formation of covalent bonds between monomers **1**–**3** with fibers and entrapments of monomers **4**, **5** within them. Therefore, the interactive mechanism proposed between the intumescents and fibers (Horrocks, Anand, & Hill, 1992; Horrocks, Anand, & Sanderson, 1994) can be accepted here between phosphoramides **4**, **5** and cotton fibers.

3.3. *Antibacterial activity*

The in vitro antibacterial activities of the phosphoramids **1**–**5** and cotton fibers treated with three different concentrations of these phosphoramids (25%, 50%, 75% o.w.f.) were performed against one Gram-positive *Staphylococcus aureus* bacterium as well as one Gram-negative *Escherchia coli* bacterium. Each experiment was repeated for at least three times. The digital photographs of the antibacterial effects against *Escherchia coli* and *Staphylococcus aureus* bacteria for the phosphoramids **1**–**5** and cotton fibers treated with 75% o.w.f. concentration of phosphoramids are indicated in Fig. 11. The inhibition zones (mm) measured for the antibacterial activities of phosphoramides **1**–**5**, raw fibers as well as cotton fibers treated with these phosphoramides are given in Table 5.

It is well known that although the Gram-positive bacteria have a thicker peptidoglycan layer in their cell wall that encases their cell membrane than the Gram-negative bacteria, the Gram-positive bacteria are more receptive to antibiotics than Gram-negative bacteria that is due to the latter's relatively impermeable lipid based bacterial outer membrane. For this reason, all the samples exhibited the least antibacterial activity against the Gram-negative E. coli bacterium. Comparing the inhibition zones of five phosphoramides with each other, it is clear that compound **2** has the greatest antibacterial activity. The antibacterial activities change within the order **2** > **3** > **1** > **5** > **4**. Moreover, when these phosphoramides are applied

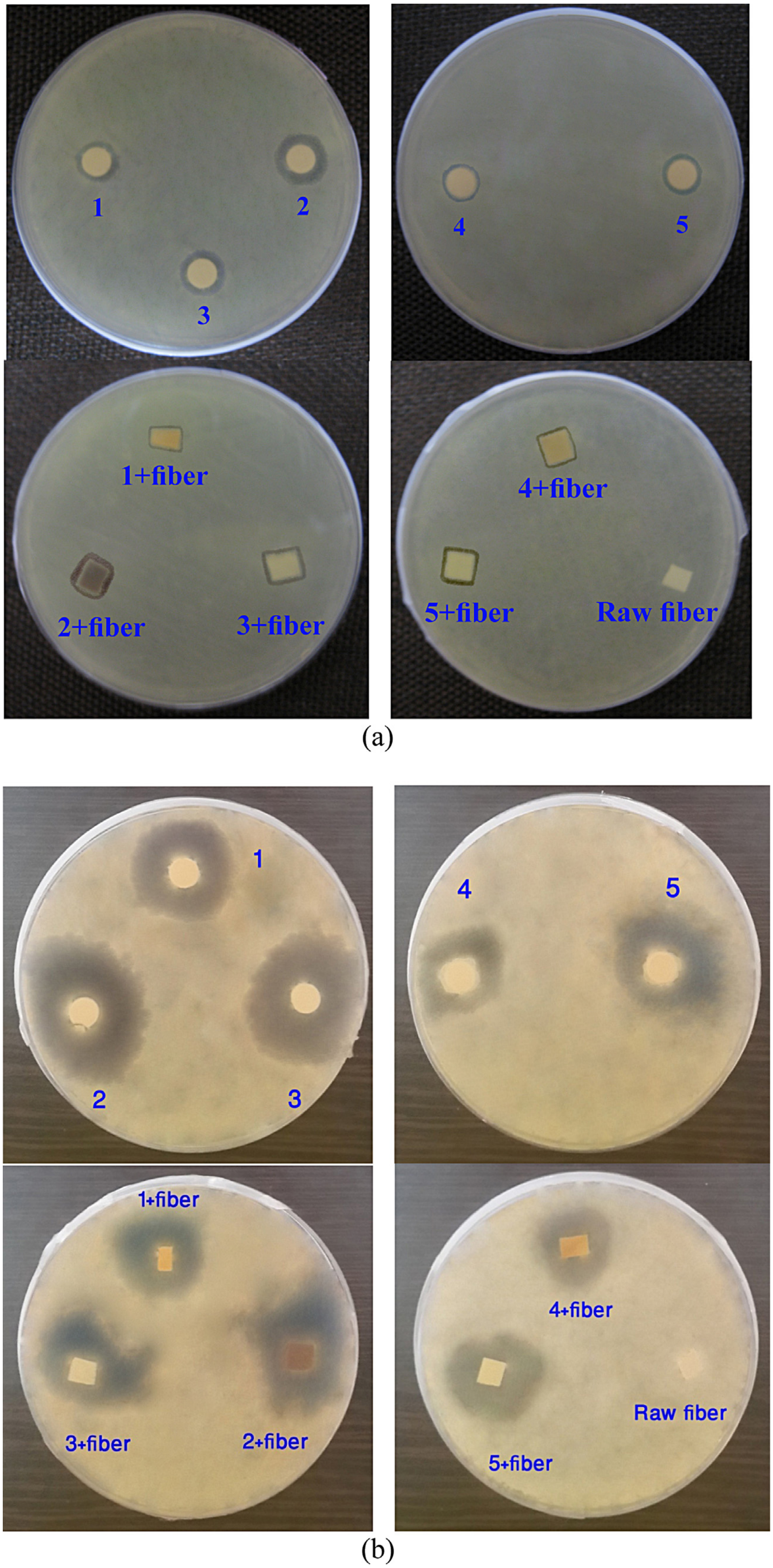


Fig. 11. The antibacterial activities of phosphoramides **1**–**5**, cotton fibers treated with these phosphoramides and raw cotton fiber against (a) *Escherchia coli* and (b) *Staphylococcus auerus* bacteria.

on the cotton fibers, their effect become somewhat smaller but they show the above order for the antibacterial activity. It is also found that the antibacterial effect is increased by increasing the phosphoramid concentration from 25% to 75% on cotton fibers. Therefore, it can be said that these treated fibers can be used as antibacterial fibers in producing hygiene related textiles.

4. Conclusion

In summary, using ultrasonic irradiation, five novel nanosized phosphoramide compounds were synthesized and fully characterized by NMR, FT-IR, fluorescence, UV–vis spectroscopy, XRD and FE-SEM microscopy. These phosphoramides were pad applied on cotton cellulose fibers to make flame retardant fabrics. It was found that among monomers **1**–**3** including allylamine groups connected to the phosphorus atom and have unsaturated C═C bonds with the ability to graft to the cotton fabrics, compound **1** indicated the greatest degree of grafting (DG) but phosphoramide **3** showed the least DG. The greater DG for phosphoramide **4** relative to its analog **5** (both do not contain unsaturated bonds in their structures for polymerization and grafting to the fibers) can be related to the effect of nitroaniline group. The in vitro antibacterial activities against Gram-positive *Staphylococcus aureus* and Gram-negative *Escherchia coli* bacteria were enhanced by increasing the phosphoramide concentration (o.w.f.) from 25% to 75% on cotton fibers. For phosphoramides **1**–**3**, the unsaturated C═C bonds of allylamine groups contribute in the formation of covalent C—O bonds with the OH groups present on the cotton fibers but in case of phosphoramides **4** and **5**, they are entrapped between the fibers and have electrostatic interactions with the functional groups of the fibers. The TGA/DSC analyses revealed lower degradation temperatures for the flame retardant treated cotton fibers than the raw fiber, thus the mechanism of action for the phosphoramides **1**–**5** as flame retardants is increasing all the pyrolysis processes (dehydration and char formation, Scheme 1) at the expense of processes which form flammable volatiles leading to flamed combustion.

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