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ORIGINAL RESEARCH

Preparation and flame retardant properties of cotton fabrics treated with resorcinol bis(diphenyl phosphate)

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Abstract A flame-retardant agent, resorcinol bis(diphenyl phosphate) (RDP), was synthesized with resorcinol, phenol and phosphorus oxychloride under a catalytic action of magnesium chloride. Synthesized RDP was applied to cotton fabrics with a bridging agent of urea-formalin resin (UFR) to endow them with flame retardancy. The vertical flammability tests were performed, revealing that cotton fabrics treated with 25% RDP and 15% UFR could exhibit the most reasonable flame retardancy. Here, other properties of cotton fabrics, such as mass increment, color change, resistance to washing and hand feeling, were found to be almost unspoiled. The suitable heat-treating condition for temperature and duration was determined to be 160 °C and 2 min. The results of scanning electron micrography, energy dispersive X-ray and Fourier transform infrared spectroscopy showed that RDP was strongly bonded to cotton fiber with a successful bridging action of UFR. Thermogravimetric analysis confirmed that the coated cotton fabrics possessed flame retardant properties.

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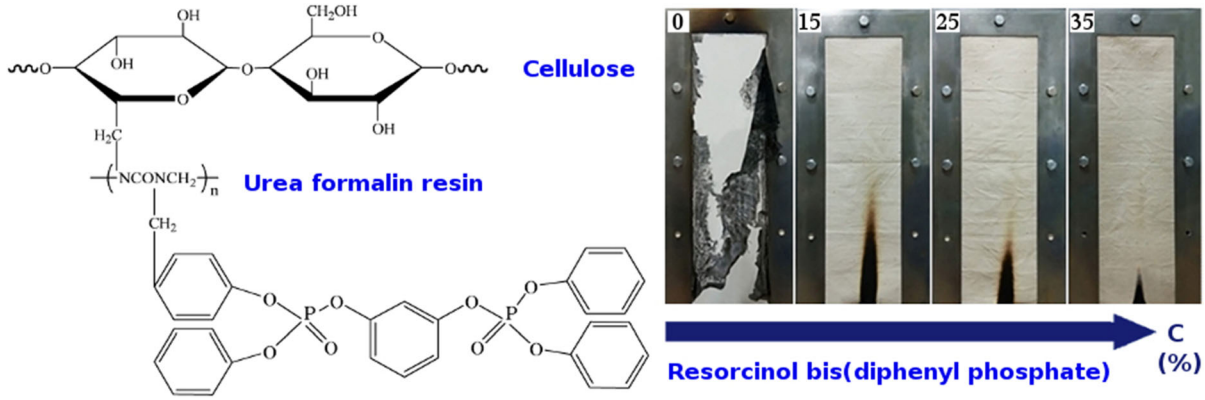
Graphic abstract



Keywords Flame retardancy · Resorcinol bis(diphenyl phosphate) · Cotton fabrics · Urea-formalin resin · DFT calculation

Introduction

Fire is essential for the preservation of human life. If not properly managed, however, it causes severe problems such as accidental deaths, civilian injuries and property loss. Therefore, it is necessary to develop efficient flame-retardant agents for combustible materials like textile, wood and plastic to inhibit ignition and flame propagation. In this context, considerable attention has been devoted to the development of flame-retardant textiles, which are highly flammable and widely used in the manufacture of clothes and soft furnishings. Among various textile materials, cotton is a natural polymeric fiber, and extensively used in wearing, protective garments and hospital textiles. Since it is particularly susceptible to flame or heat flux, numerous flame-retardant agents have been explored to improve cotton with flame resistance (Salmeia et al. 2016; Alongi and Malucelli 2015).

The flame retardation or inhibition of cotton fabric is mainly achieved by coating the surface of fabric with flame-retardant layers without changing the mechanical properties of the cotton fabrics (Chen et al. 2015). Most flame-retardant agents for cotton can be classified into halogen-, boron-, nitrogen-, phosphorus-, silicon-based compounds, mineral, nano-metric materials and biomacromolecules (Chang et al. 2014). Among these, in spite of excellent flame retardancy, halogen- and boron-based agents have been forbidden to use due to release of toxic materials during combustion (Stieger et al. 2014). When applied to cotton fabric, silicon-based compounds have been reported to show good flame resistance by forming a physical barrier on the surface (Yan et al. 2018; Laufer et al. 2011), but do not give cotton fiber a self-extinguishing function. For more cost-effective and eco-friendly flame retardants, researches have been performed with bio-materials including deoxyribonucleic acid (DNA) Alongi et al. (2013), biomacromolecules (Malucelli and Barbalini 2019) and citric acid (Taherkhani and Hasanzadeh 2018), and epoxy resin (Carja et al. 2014). Furthermore, nano-metric materials have also been reported to exhibit good flame retardancy, revealing that dispersion at nanoscale is essential to achieve the reasonable thermal performance (Jing et al. 2018). However, it was also found that nano-materials did not have sufficient vertical flame-retardancy (Pan et al. 2015).

For the environmental concerns, phosphorus-containing compounds, which are a typical type of reactive-type flame retardants, have been developed as a promising alternative to the halogenated agents (Li et al. 2019; Suryaprabha and Sethuraman 2018; Jia et al. 2017; Xu et al. 2017; Zheng et al. 2016; Guo et al. 2016; Shi and Wang 2016; Wagner et al. 2016; Grancaric et al. 2015; Gao et al. 2015; Su et al. 2014; Wang et al. 2013). Halogen-free organic phosphates can be directly bonded to the flame-retardant segments. They exhibited better flame retardancy in combination with superhydrophobicity and transparency, compared to the additive-type flame retardants (Chen et al. 2015; Li et al. 2019; Zheng et al.

2016). When igniting and burning, the phosphate groups can generate phosphoric acid, which catalyzes the dehydration of cellulose. The amount and position of phosphorus atoms in the phosphorus-containing compounds were found to be mainly related with the flame-retardant effect (Yan et al. 2018; Wang et al. 2013). Furthermore, considerable research attention has been paid to phosphorus-nitrogen (Jia et al. 2017; Grancaric et al. 2015; Su et al. 2014; Wang et al. 2013) or -sulfur (Xu et al. 2017; Wagner et al. 2016) containing compounds, due to their synergistic effect in reducing the formation of combustible volatiles and catalyzing the char formation as well. On the other hand, it was revealed that the fire protection and barrier efficiency of flame-retardant coatings can be strongly influenced by the anti-oxidation property and mechanical strength of the char layer (Alongi et al. 2015). Based on this, the phosphorus-based flame retardants were improved by introducing various types of organic oligomers such as epoxy resin (Shi and Wang 2016; Toldy et al. 2017) and phenol formaldehyde (Guo et al. 2016).

Resorcinol bis(diphenyl phosphate) (RDP) is an organophosphorus flame retardant widely used in a variety of polymers, plastics and electronic consumer products (Toldy et al. 2017; Liu and Yao 2018; Wang et al. 2016; Guo et al. 2017; Ju et al. 2016). The high-low aquatic toxicity of RDP has been reported to be probably caused by its toxic impurities of triphenyl phosphate (TPhP; 1−5%) in the RDP commercial products (Ballesteros-Gómez et al. 2015; Liang et al. 2018). But they have been proven to pose a significantly low risk to environment and human health (Guo et al. 2017). RDP is known to be liquid at room temperature, act as a plasticizer when mingled with a polymer melt, and give luster to the surface of material. Guo et al. (2017) found that RDP can be strongly adsorbed onto cellulose with hydroxyl groups on the surface and achieve a flame retardant poly latic acid composite. However, we regard that it is necessary to find a suitable cross-linking agent which combines strongly RDP with cellulose. In this work, we show that RDP can be strongly bonded to cellulose by a cross-linking agent of urea formalin resin (UFR), which maintains its good flame retardant property and other properties of cotton fabric.

Materials and methods

Materials

Resorcinol ($C_6H_4(OH)_2$, 99%) and phenol (C_6H_5OH, 99%) were purchased from Shanghai Nanxiang Organic Plant (Shanghai, China). Phosphorus oxychloride ($POCl_3$, 99%) was obtained from Shanghai Guoyao Chemical Group (Shanghai, China). Toluene ($C_6H_5CH_3$, 98%), magnesium chloride ($MgCl_2$, 99.5%), oxalic acid ($(COOH)_2$, 98%), sodium hydroxide (NaOH, 98%), urea ($CO(NH2)_2$, 98.5%), and formaldehyde (HCHO, 37-40%) were provided by Chengdu Kelong Chemical Reagent Co., Ltd (Chengdu, China). The cotton fabrics (100% woven cotton fabrics, 0.23 g/cm^2) was purchased from the local market, and washed thoroughly with distilled water and ethanol. All chemicals were of analytical grade, and they were used without further purification.

Synthesis of flame-retardant agent, RDP

In the first step, resorcinol (88.05 g, 0.785 mol), phosphorus oxychloride (550.82 g, 3.592 mol) and anhydrous magnesium chloride (1.50 g, 0.016 mol) were added to a round-bottomed flask with 4 necks (1000 mL), which was equipped with thermometer, magnetic stirrer and reflux condenser. Note that $MgCl_2$ was used as a catalyst. The mixture was heated to 90 °C and reacted for 5 h with continuous stirring. After reaction, distillation was performed to remove unreacted $POCl_3$, and subsequently reduced pressure distillation (vacuum degree of 5 KPa) was carried out at 150 °C to obtain a liquid product (238.60 g) in light yellow color, being a resorcinol diphosphoryl tetrachloride (RDT, $C_6H_6(OPOCl_2)_2$). The synthesis yield in this step was estimated to be 86.7%.

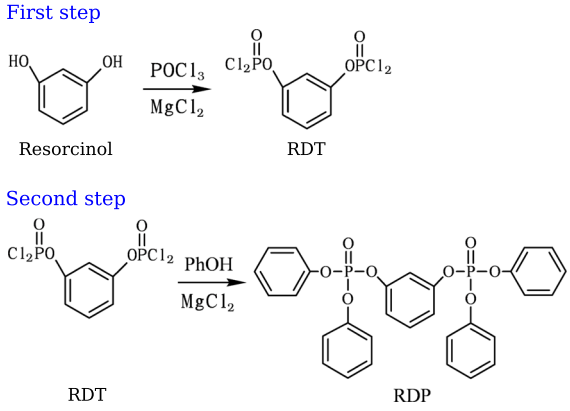
In the second step of reaction, the obtained RDT, molten phenol (596.50 g, 6.338 mol) and anhydrous magnesium chloride (4.50 g, 0.047 mol) were added to a flask with 4 necks (2000 mL), equipped with thermometer, magnetic stirrer and reflux condenser. The mixture was heated to 120 ∼ 125 °C and esterification reaction was performed for 7 h to obtain a crude product in light yellow color. The crude product was dissolved in toluene of twice volume, washed with 1% oxalic acid, and separated to produce the organic phase. Then, the organic phase was washed twice with

2% NaOH solution of the same volume and subsequently with distilled water to become neutral solution. Finally, the solution was distilled to remove the remaining toluene and the reduced pressure distillation (5 KPa) was performed at 160 ~ 165 °C to remove the unreacted intermediate products and obtain the final liquid product in pale yellow color, resorcinol bis(diphenyl phosphate) (RDP, 363.10 g) with a yield of 91.2%. Scheme 1 shows the reaction route.

Vertical flammability test and characterization

The immersion solution was prepared by dissolving the synthesized flame-retardant agent of RDP (with a mass concentration of 15%, 20%, 25%, 30%, and 35%) in alcohol. The cross-linking solution was prepared by mixing urea and formalin in 1:2 molar ratio, resulting in urea-formalin resin (UFR with a mass concentration of 5%, 10%, 15%, 20%, and 25%). The treating procedure of cotton fabric was as dip pressing, cross-linking treating, heat treating, alkali washing (sodium carbonate), water washing and drying. Firstly, the cotton fabric was dipped in the RDP immersion solution in air-tight condition and then compressed. After that, the RDP-coated cotton fabric was dipped in UFR solution and then heated at different temperatures of 140 °C, 160 °C, and 180 °C for different durations of 2 min and 4 min. The heat-treated cotton fabric was washed with alkali solution of sodium carbonate and then distilled water. The treated fabrics were dried in open air.

The limiting oxygen index (LOI) was measured using JB-2 oxygen index tester (Shaghai Jiubin Instrument Co., Ltd., China) based on ASTM D2863-2000 standard. Content of free formaldehyde in the treated cotton fabrics was confirmed to be negligible, not detectable in measurement.



Scheme 1 Synthesis route of RDP

The flame-retardancy test was performed according to the vertical flame test standard, GB/T5455-1997, as applied to cotton fabrics (Chen et al. 2015; Xu et al. 2017). In this method, the fire from a butane gas burner was applied to the cotton fabrics with a size of 30 cm × 8 cm for 12 s and then removed, measuring the fire duration and damage length.

The surface morphology of uncoated sample, coated sample, and the char residues of coated samples were obtained by using a JSM-6610A (Jeol, Japan) scanning electron microscope (SEM). The SEM images were second-electron ones taken under an accelerating voltage of 5 kV and working distance of 10 mm. For a conductance treatment of surface, the samples with a size of 5 mm × 5 mm were fixed on a stand, attached with conductive carbon duplex adhesive tape, and then coated with gold thin film of 6 ~ 7 nm thickness by using gold as an anode at evaporation current of 40 mA for 150 s with an automatic evaporator (Jec-3000FC). Energy dispersive X-ray (EDX) analysis was carried out to identify elements on the surface of samples.

The Fourier-transform infrared (FT-IR) spectra of RDP and coated samples were obtained by using a Nicolet 6700 (Thermo Fisher Scientific, USA) FT-IR spectrophotometer with diamond in the range of 4000−400 cm^{-1} with a resolution of 4 cm^{-1}.

The thermogravimetric (TG) analysis of uncoated and coated cotton fabric samples was performed by using a Shimadzu TGA-50H (Shimadzu, Japan) instrument at a heating rate of 20 °C/min from 30 to 700 °C.

Computational method

The structural property and Raman spectrum of RDP were theoretically investigated by performing first-principles calculations within density functional theory (DFT) framework. We utilized the pseudopotential and pseudo atomic orbital basis set method as implemented in SIESTA program package (version 4.1) Soler et al. (2002). The double-ζ plus polarization (DZP) basis set was used for all the atoms with an energy shift of 300 meV for orbital-confining cutoff radii and a split norm of 0.25 for split-valence of basis. The norm-conserving pseudopotentials were

generated by executing the ATOM code, with valence electron configurations of H:$1s^1$, C:$2s^2 2p^2$, N:$2s^2 2p^3$ O:$2s^2 2p^4$, and P:$3s^2 3p^3$. The BLYP functional (Becke 1988; Lee et al. 1988) was used for the exchange-correlation interaction, and van der Waals (vdW) dispersion was considered by using the Grimme's approach (Grimme 2006). The plane-wave cutoff energy for the grid was set to 300 Ry, and only Γ-point was used. The cubic supercell with a lattice constant of 40 Å was constructed to simulate the isolated molecule. All the atoms were allowed to relax until the forces converged to 0.02 eV/Å.

Results and discussion

Vertical flammability tests

Flame-retardant coating solutions were prepared with the flame-retardant agent of RDP in different mass concentrations of 15%, 20%, 25%, 30% and 35%, and the cross-linking agent of UFR in different concentrations of 5%, 10%, 15%, 20% and 25%. To make coating, the cotton fabric samples were immersed in the RDP/UFR solutions, dried in air-tight condition, and heat-treated at different temperatures of 140 °C, 160 °C and 180 °C for different durations of 2 min and 4 min. We measured the flame duration and damage length for the coated cotton fabrics as quantitative check for flame-retardancy with vertical flame test. In addition, mass increment and qualitative change such as color change, resistance to washing and hand feeling by RDP coating were characterized. Table 1 summarizes the results for the coated cotton fabric samples treated with the different concentrations of agents and different heating conditions.

Vertical flame tests were carried out on the uncoated sample and the samples treated with RDP in concentrations of 15%, 25%, and 35% and UFR in concentration of 10% under the heat-treating condition of 140 °C and 2 min. The uncoated sample served as a control. The fabric samples were exposed to a direct flame for 12 s before removing the flame. Figure 1 shows the testing images. Directly after exposure to flame, the uncoated cotton fabric was completely burned with vigorous flame, which quickly spread out, and thick smoke (see Fig. 1a). In contrast, for the RDP/UFR-treated fabric samples, the flame and smoke became weak and the flame propagation lost in speed, as increasing the concentration of RDP in the immersion solution (Fig. 1b–d). In fact, the flame on the coated sample was successfully suppressed at short time after ignition, leaving damage trace with a certain length. As increasing the concentration of RDP, the flame duration became shorter from 6 s at 15% to 3 s at 20% and to finally 0 s above 25%, while the damage length decreased as listed in Table 1.

Figure 2 presents the mass increment and damage length of the coated cotton fabric samples as a function of RDP and UFR concentrations under the heat-treating condition of 140 °C and 2 min. When fixing the UFR concentration in the immersion solution as 10%, the mass increment of cotton samples increases linearly whereas the damage length decreases as increasing the concentration of RDP, as shown in Fig. 2a. For these data, we did linear regression for the mass increment, resulting in $y = -5.210 + 0.878x$ (%), and cubic polynomial regression for the damage length, giving $y = -1.471 + 2.275x - 0.111x^2 + 1.467 \times 10^{-3}x^3$ (cm). Similarly to this, when fixing the RDP concentration in the immersion solution as 25%, the mass increment increases according to the linear function of UFR concentration, $y = 11.73 + 0.474x$ (%), while the damage length decreases according to the quadratic function, $y = 10.680 - 0.221x + 4.571 \times 10^{-3}x^2$, as shown in Fig. 2b.

Although higher concentration of RDP gives a cotton fabric better flame-retardancy (shorter damage length and larger LOI value), the rate of mass increment in fabric became higher with appearance of color change, being negative effect on cotton fabric. Considering the flame-retardancy, mass increment and color change together, suitable concentration of flame-retardant agent of RDP can be said to be 25%, at which damage length, LOI value and flame duration were measured to be 8.5 cm, 29.9%, and 0 s, respectively. Also, the optimal concentration of cross-linking agent of UFR was determined to be 15%, at which the mass increment and damage length were moderate while the LOI value was relatively large (32.4%) and the resistance to washing and hand feeling were good (Table 1). In fact, at lower concentration of UFR, the bridged bond between fiber molecule and RDP might be weak, leading to a release of RDP into solution by

Table 1 Vertical flammability and material properties of cotton samples treated with flame-retardant agent of RDP and cross-linking agent of UFR with different mass concentrations

RDP concentration (%)	Mass increment	Damage length (cm)		LOI	Flame	Color	Hand
(with 10% UFR, 140 °C, 2min)	(%)	before washing	after 10 washing	(%)	duration (s)	change	feeling
15	8.4	12.5	–	23.6	6	No	Good
20	12.1	11.3	–	27.8	3	No	Good
25	16.5	8.5	–	29.9	0	Slight	Good
30	20.6	6.2	–	31.7	0	Great	Bad
35	26.1	4.5	–	33.1	0	Great	Bad
UFR concentration (%) (with 25% RDP, 140 °C, 2min)							
5	14.1	9.7	14.9	28.6	1	No	Good
10	16.5	8.9	12.5	31.8	0	Slight	Good
15	18.8	8.4	9.5	32.4	0	Slight	Good
20	21.2	8.1	8.9	32.6	0	Slight	Bad
25	23.6	8.0	8.4	32.9	0	Slight	Bad
Heat treating condition (with 25% RDP and 15% UFR)							
Temperature (°C) / Duration (min)							
140 / 2	18.8	8.3	10.3	32.3	0	No	Good
140 / 4	19.1	8.4	10.1	32.7	0	No	Good
160 / 2	19.5	7.5	8.8	33.9	0	No	Good
160 / 4	19.7	7.7	8.4	34.3	0	No	Good
180 / 2	19.7	7.6	8.5	34.4	0	Slight	Bad
180 / 4	20.1	7.9	8.2	34.7	0	Great	Bad

Tests in the upper part were carried out with 10% UFR and heat-treating condition of 140 °C and 2 min, tests in the middle part with 25% RDP and the same heat treatment condition, and tests in the lower part with 25% RDP and 15% UFR. LOI stands for limiting oxygen index

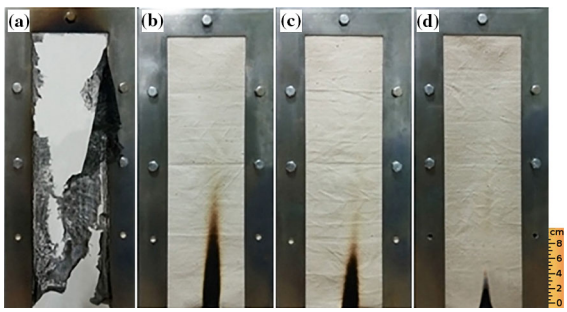


Fig. 1 Vertical flame testing images of (**a**) uncoated and RDP-coated cotton fabric samples with RDP concentrations of (**b**) 15%, **c** 25% and **d** 35%

alkali (sodium carbonate) washing and thus lower flame-retardancy. On the other hand, UFR in high concentration over 15% supports sufficient flame-retardancy but hand feeling is like being stiff, which is negative effect together with a high rate of mass increment of fabric.

Figure 3 shows the damage length of cotton fabric treated with RDP/UFR in their determined optimal concentrations of 25%/15% as changing heat treating temperature and duration. It was found that the heat treating condition of 160 °C and 2 min allows the lowest damage length, together with a good resistance to washing and no color change (Table 1). With respect to the LOI value, the condition of 160 °C and 4 min was found to give sufficiently large value of 34.3%, being larger than that of pristine cotton (18.2%) and flame retardant standard (26.0−28.0%).

Surface morphology of cotton fabric

To observe the surface morphology of the cotton fabric, SEM test was performed. Figure 4 shows the

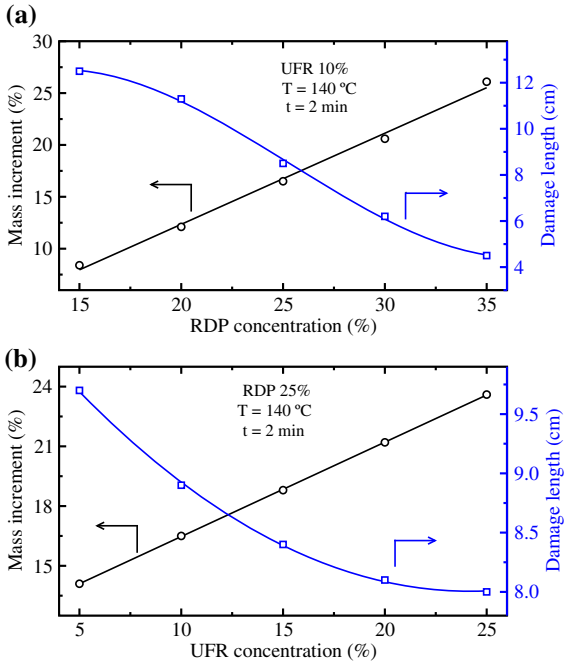


Fig. 2 Mass increment and damage length of coated cotton fabric samples as increasing the concentration of (**a**) RDP with fixed UFR concentration of 10% and **b** UFR with fixed RDP concentration of 25%. Solid lines indicate linear, quadratic and cubic regression result

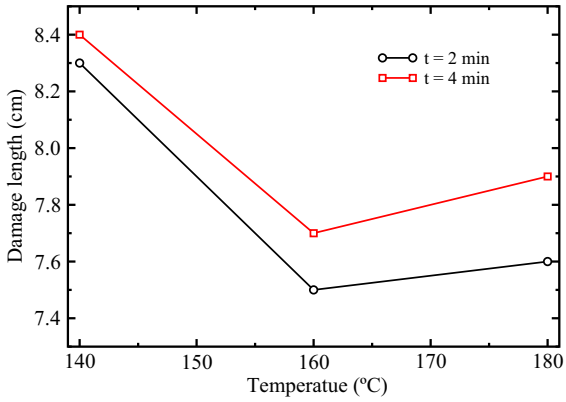


Fig. 3 Damage length of coated cotton fabric samples with fixed RDP concentration of 25% and UFR concentration of 15% as increasing temperature for heat treatment

SEM images of the pristine cotton and RDP- and RDP/UFR-treated cotton fabrics. The surface of the pristine fabric is seen to be smooth and clean with a flat and ribbon weave structure composed of winding and thin cotton fibers (Fig. 4a). The coated cotton fabric treated with only 25% RDP presents similar surface morphology, well covered with RDP layer, but chemical bonding between the fibers is not observed due to absence of cross-linking agent (Fig. 4b). After treated with RDP/UFR, the fibers appear coated and rough by a thin coating, and the adjacent fibers are clearly seen to be joined, indicating that the cellulose molecules are chemically bonded with the flame-retardant agent of RDP. The particles attached to cotton fibers, which seems to be UFR, have an average size of $\sim$ 3 μm. In addition, the further increase in mass concentration of RDP in the immersion solution results in more reacted flame retardant and cross-linking agent due to smaller size of particles and smoother surface.

In the vertical flame test, only $\sim$ 10 cm of the cotton fabric treated with RDP/UFR became charred and turned black, remaining most of the fabric intact. This indicates that RDP/UFR coating gives the cotton fabric the flame-retardant function by forming a protective char barrier. The charred fabric was observed by SEM, as shown in Fig. 5. It was found from the SEM images that the coated fabric after burning maintained the original weave structure and integrity well. The surface of burned fibers keeps smooth but contains ultrafine bubbles with a size of several tens of nanometer, being formed by evaporation of volatile constituents originated from charred fiber. As a probable mechanism for flame-retardant effect, it can be suggested that RDP bonded with fiber molecules makes a formation of char layer on the surface of fiber, which inhibits oxygen, heat and volatile gas, resulting in effective suppress of combustion.

The chemical composition on the fiber surface was characterized by EDX test, as shown in Fig. 6. For the pristine cotton fabric, only C and O signals were obtained with element mass contents of 47.28% and 52.72% respectively (Fig. 6a). The obvious P signal was identified in mass percent of 0.29% for the cotton fabric coated with only 25% RDP in Fig. 6b. After further treatment with the cross-linking agent of UFR in 15% mass concentration, the nitrogen element was found additionally with 20.72% mass percent, while increased mass content of phosphorus element was observed to be 2.59% (Fig. 6c). For the burned cotton fabric, it was found that the mass content of C element increased from 37.82% to 54.37% whereas the mass content of O element decreased from 38.87 to 24.32%, indicating a formation of char layer.

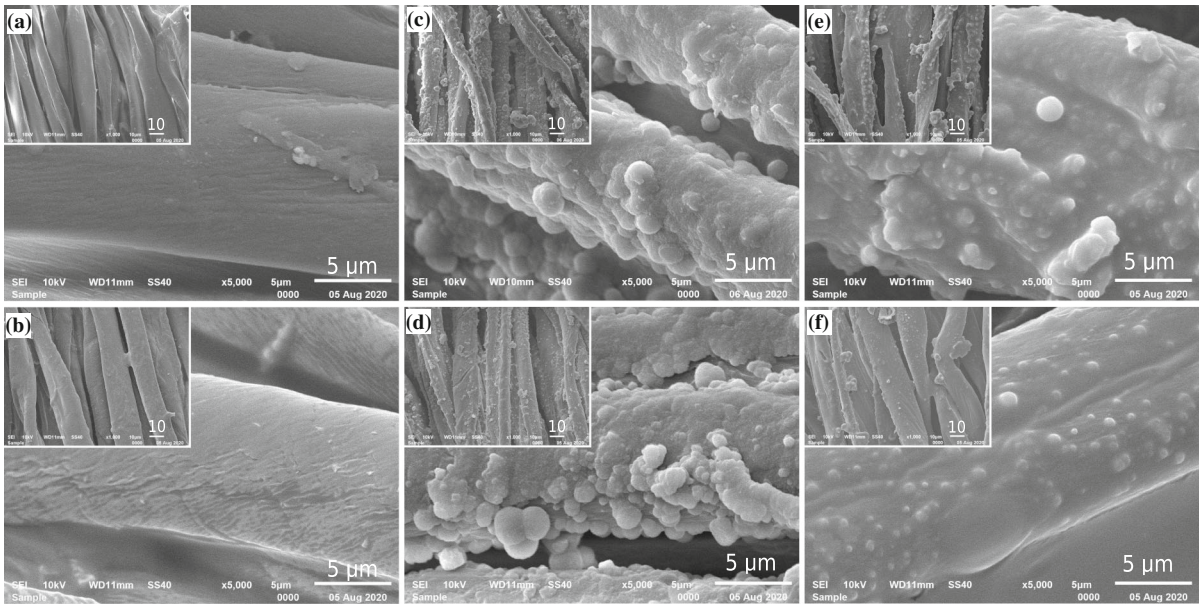


Fig. 4 SEM images of (**a**) pristine cotton fiber, **b** cotton fiber samples treated with only 25% RDP, **c**–**f** samples treated with 15%, 20%, 25%, 30% RDP together with 15% UFR

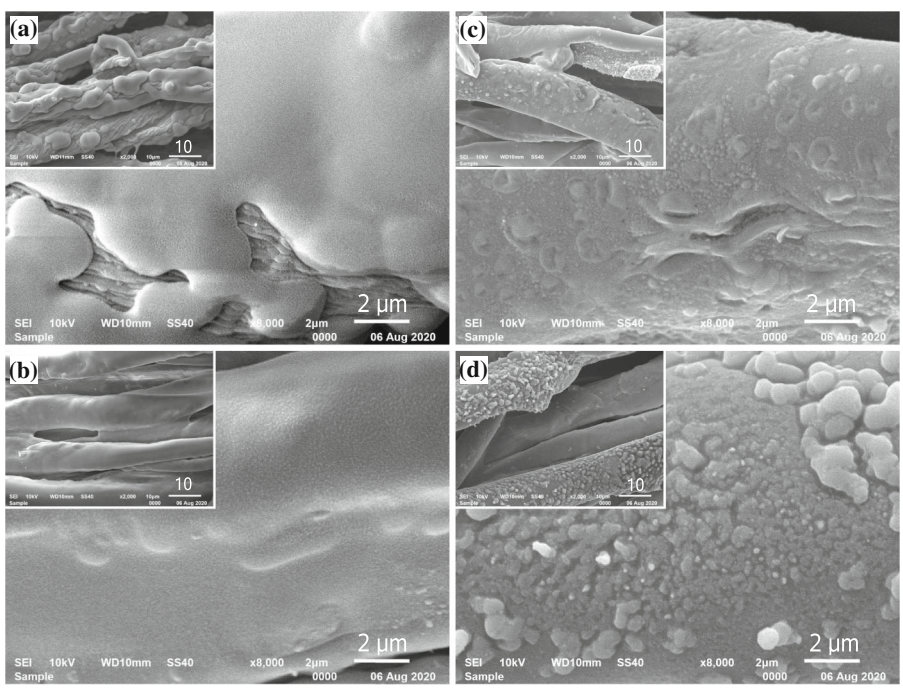


Fig. 5 SEM images of burned RDP/UFR-treated cotton fibers. **a**–**d** 15%, 20%, 25%, 30% RDP together with 15% UFR

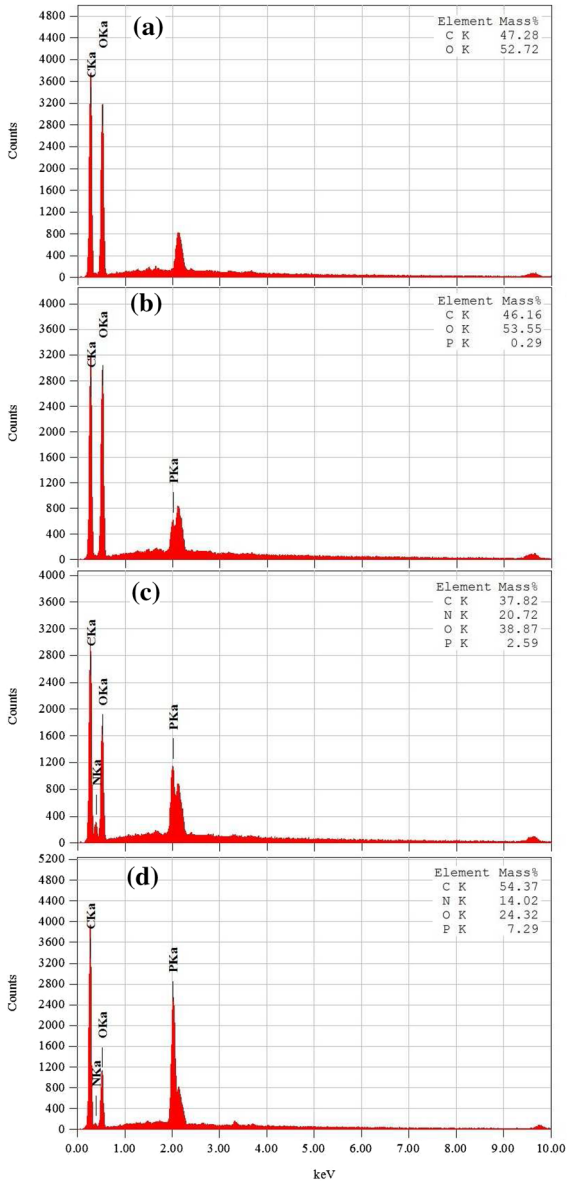


Fig. 6 EDX images of (**a**) pristine cotton fabric, and cotton fabric samples coated with (**b**) only 25% RDP and **c** 25% RDP and 15% UFR, and **d** burned cotton fabric sample coated with 25% RDP and 15% UFR

FT-IR analysis

To investigate the reaction between RDP and the cotton fiber, FT-IR spectra of RDP, pristine cotton and the flame retardant cotton fabrics treated with only 25% RDP and with RDP (25%)/UFR (15%) were analyzed. As shown in Fig. 7a for RDP, the peak at 3066 cm^{-1} is attributed to the C−H stretching

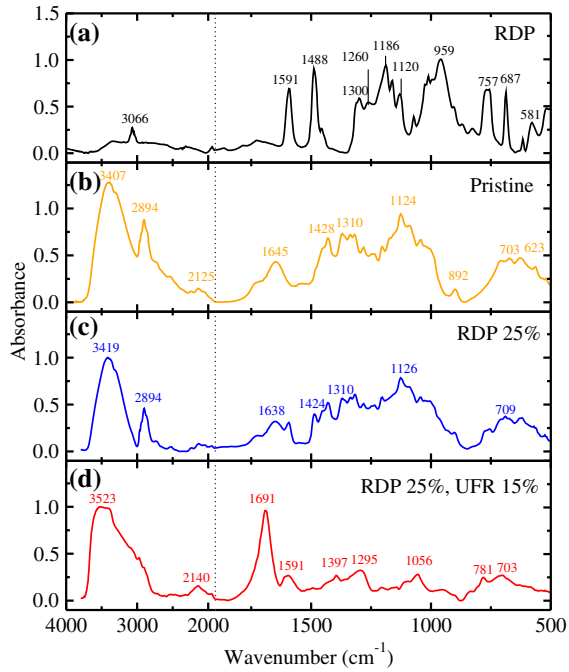
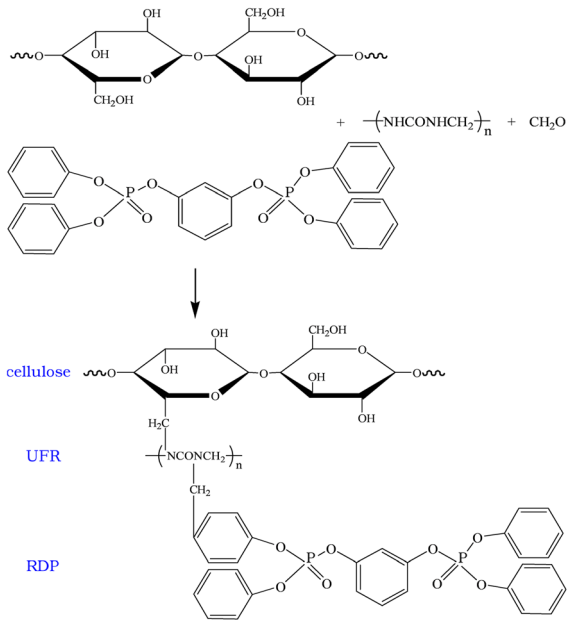


Fig. 7 FT-IR spectra of (**a**) RDP, **b** pristine cotton, and flame retardant cotton fabrics treated with (**c**) 25% RDP and with (**d**) 25% RDP and 15% UFR

vibration of benzene ring, and the peaks at 1591 cm^{-1} and 1488 cm^{-1} correspond to the C=C stretching vibrations of aromatic ring. The absorptions at 1260 cm^{-1}, 1186 cm^{-1}, and 1120 cm^{-1} are due to the aromatic C−O vibrations. The peaks at 1300 cm^{-1} and 581 cm^{-1} are associated with the absorptions of double bonded P=O, and the peak at 959 cm^{-1} is for P−O vibration. The characteristic C−H vibration of mono-substitution product of benzene ring appears at 687 cm^{-1}. The peak positions are well agreed with the previous work (Liu and Yao 2018). In Fig. 7b, the FT-IR spectra of the pristine cotton fiber shows the absorption peaks; 3407 cm^{-1} due to O−H bending, 2894 cm^{-1} related to C−H stretching, 1428 cm^{-1} and 1310 cm^{-1} contributed from C−H bending, 1645 cm^{-1} due to C=O stretching, and 1124 cm^{-1} due to C−O bending (Taherkhani and Hasanzadeh 2018).

The FT-IR spectra of cotton fabric samples treated with 25% RDP and with RDP (25%)/UFR (15%) are shown in Fig. 7c and d, respectively. The different features between the samples are clearly shown. The absorption peak at 2894 cm^{-1}, corresponding to C−H stretching vibration of the tertiary carbon atom combined with the primary hydroxyl group of

cellulose, was still observed in the sample treated with only 25% RDP, but not in the sample treated with RDP/UFR. This indicates that in the latter sample the primary hydroxyl group joined in the chemical reaction with the cross-linking agent, resulting in reduction of the vibration of the combined tertiary carbon atom. Moreover, the absorption peak at 1691 cm^{-1} originated from the C=O stretching vibration of UFR adduct that acts as a bridging agent between the phenyl groups of RDP. Before bridging action, the strong peaks appeared within the region of 1400−800 cm^{-1}, but they became weak by cross-linking. For the sample treated with RDP/UFR, the absorption peaks appeared at 1397 cm^{-1}, 1295 cm^{-1}, and 1056 cm^{-1} within this region, which are related to the bridged bond of CH_2OH, i.e., O−H bending and C−O stretching vibration. The 703 cm^{-1} and 781 cm^{-1} correspond to the C−H bending of p-substituent of benzene ring, indicating that the primary hydroxyl group of cellulose bridged with the methylene group at the p-position of phenyl of RDP. The flame-retardant agent of RDP bridged with the cellulose by the action of the cross-linking agent of UFR, as shown in Scheme 2. Such bridging reaction of cellulose−UFR−RDP allows the flame-retardant agent of RDP to be strongly combined with cellulose and act for a long time. It should be noted that nitrogen element contained in UFR has a certain flame-retardant ability, giving the synergistic effect on enhancing the flame-retardancy of the treated cotton fabrics (Jia et al. 2017; Grancaric et al. 2015; Su et al. 2014; Wang et al. 2013).



Scheme 2 Reaction equation of RDP and cellulose bridged by urea formalin resin

Thermal decomposition analysis

The thermal stability and degradation of flame-retardant agent of RDP, uncoated and coated cotton fabrics were assessed in air, by measuring the weight loss as a function of temperature. Figure 8 depicts the TG curves of RDP, pristine cotton fabric, and the samples coated with only 25% RDP and with RDP (25%)/UFR (15%). For all the fabrics and RDP, the initial low weight loss was observed below 100 °C, being caused by the evaporation of the physically bound water. The thermal degradation of the pristine cotton fabric in air was found to proceed by four stages including water evaporation. The initial decomposition temperature was 250 °C. The prominent thermal decomposition of the pristine cotton fabric occurred in the range of 370−450 °C with a weight loss of 83% at 450 °C, producing volatiles and aliphatic char by depolymerisation and dehydration of cellulose (Li et al. 2019; Price et al. 1997). Then, the third decomposition happened at 504 °C with a remaining weight of 2%. In this stage, alphatic char transformed to aromatic form with the successive release of CO and CO_2 by further carbonization and oxidization (Li et al. 2019; Xu et al. 2017). In the final stage, the aromatic carbon

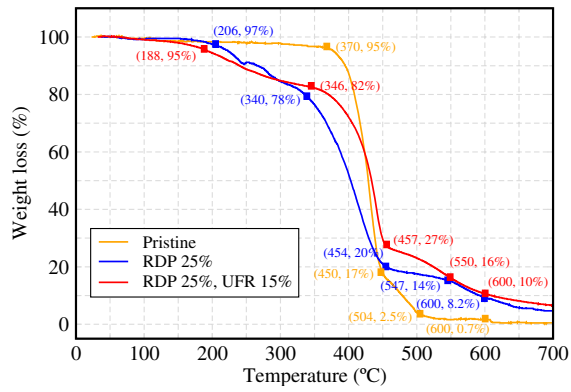


Fig. 8 TG curves of pristine cotton, and cotton samples treated with 25% RDP solution and with 25% RDP and 15% UFR solution

decomposed into ethylene with a residue of 0.25% at 700 °C (Alongi and Malucelli 2015).

As for the treated cotton samples, the thermal decomposition could be divided into four stages as well. The first decomposition was at 206 °C and 188 °C with weight losses of 3% and 5% for samples treated with only 25% RDP and with 25% RDP and 15% UFR, respectively. In the ranges of 206−340 °C and 188−346 °C, relatively much higher weight losses were observed as 22% and 18% respectively, when compared with that of the control sample. In this stage, the flame-retardant agent of RDP can be decomposed, generating the phosphoric acid or poly (phosphate) acid, which would promote the formation of char barrier. The main thermal decomposition occurred in the ranges of 340−454 °C and 346−457 °C, and at 550 °C, the residues were 14% and 16%, which were much higher than that (<0.5%) of control sample. This indicates that RDP changed the decomposition route of cellulose, and increased the quantity of char instead of volatile gases.

Molecular structure and Raman spectrum of RDP

Finally we present the results of DFT calculation for RDP. Figure 9 shows the optimized molecular structure and Raman spectrum of RDP. The calculated bond lengths and bond angles of RDP are listed in Table 2. In order to find out the conformer with the lowest energy, a systematic grid scan method was applied to RDP, allowing all the torsion angles to systematically vary over a grid of equally spaced values. The average C−C and C−H bond lengths of the outer benzene rings (No. 1, 4) were found to be slightly larger than those of the inner benzene rings (No. 2, 3), and the central benzene (No. 5) had the largest bond lengths. Similar tendency was observed in the bond length between the carbon atom of benzene and the oxygen atom of phosphate group (PO_4). The bond length of double bond P=O was calculated to be 1.489 Å, being smaller than those of P−O bond lengths. On the other hand, the P−O−C bond angles (average 126.71°) were larger than the O−P−O bond angle (∼ 109.10°). In overall, the optimized molecular structure of RDP has the well-symmetrized structure along the P−O−3C−O−P backbone. Using the optimized geometry, the Raman spectrum of RDP was calculated to study its vibrational modes. As shown in Fig. 9b, the main absorption peaks were observed in the region of 1000–1300 cm^{-1} and some weak peaks in the region of 3000−3500 cm^{-1}, being similar to the experimentally obtained spectrum in Fig. 7a.

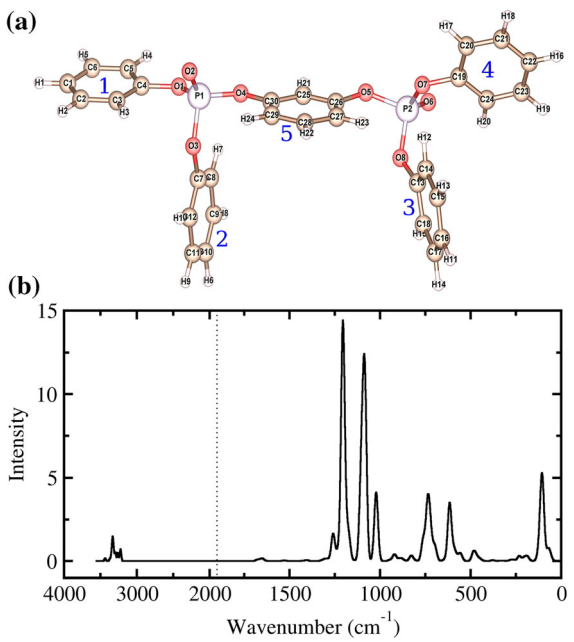


Fig. 9 DFT calculation results for (**a**) molecular structure and **b** Raman spectrum of RDP

Conclusions

In this work, we have presented a method to synthesize a halogen-free phosphorus-containing flame retardant compound of RDP with resorcinol, phenol and phosphorus oxychloride under a catalytic action of $MgCl_2$. The synthesized RDP, together with a cross-linking agent of UFR, was applied to cotton fabrics to endow them with good flame retardancy. The vertical flammability tests have been performed on the cotton fabric samples treated with different concentrations of RDP and UFR, revealing that the 25% RDP together with 15% UFR gives the most reasonable flame retardancy without much detriment to other properties of cotton fabrics such as mass increment, color change, resistance to washing and hand feeling. We also tested different heat-treating temperatures and durations, finding the optimal condition of 160 °C and 2 min. The analysis of SEM images and EDX indicated that the cotton fabric treated with RDP/UFR generated only small portion of charred and

Table 2 Bond length (in Å) and bond angle (in deg) of RDP, obtained by geometry optimization

Bond length	Benzene number				
	1	2	3	4	5
C−C (ave.)	1.389	1.384	1.384	1.386	1.393
C−H (ave.)	1.075	1.070	1.069	1.072	1.078
C−O	1.413	1.395	1.396	1.409	1.410
					1.400
Bond length					
P1−O1	1.664	P2−O5	1.648		
P1−O3	1.653	P2−O7	1.673		
P1−O4	1.664	P2−O8	1.658		
P1=O2	1.489	P2=O6	1.489		
Bond angle					
P1−O1−C4	122.90	O1−P1−O2	119.80	O5−P2−O6	114.37
P1−O3−C7	129.88	O1−P1−O3	104.91	O5−P2−O7	101.42
P1−O4−C30	127.33	O1−P1−O4	96.05	O5−P2−O8	99.95
P2−O5−C26	127.32	O2−P1−O3	110.73	O6−P2−O7	115.84
P2−O7−C19	122.95	O2−P1−O4	119.38	O6−P2−O8	116.61
P2−O8−C13	129.89	O3−P1−O4	103.70	O7−P2−O8	106.47
ave.	126.71	ave.	109.09	ave.	109.10

Benzene number is indicated in Fig. 9a. For C−C and C−H bond lengths of benzene ring, the average values are presented

black within 10 cm, remaining most of the fabric intact. Through the FT-IR spectroscopy, RDP was found to be strongly bonded to cotton fiber with a bridging action of UFR. Furthermore, the TG analysis has been carried out to show the lowering of decomposition temperature and increment of residue by treating with RDP and UFR. By using DFT calculations, we obtained the optimized molecular structure and Raman spectrum of RDP.

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References

Alongi J, Carletto RA, Blasio AD (2013) Dna: a novel, green, natural flame retardant and suppressant for cotton. J Mater Chem A 1:4779–4785

Alongi J, Han Z, Bourbigot S (2015) Intumescence: Tradition versus novelty. a comprehensive review. Prog Polym Sci 51:28–73

Alongi J, Malucelli G (2015) Cotton flame retardancy: state of the art and future perspectives. RSC Adv 5:24239–24263

Ballesteros-Gómez A, Van den Eede N, Covaci A (2015) In vitro human metabolism of the flame retardant resorcinol bis(diphenylphosphate) (rdp). Environ Sci Technol 49:3897–3904

Becke AD (1988) Density-functional exchange-energy approximation with correct asymptotic behavior. Phys Rev A 38:3098–3100

Carja ID, Serbezeanu D, Vlad-Bubulac T (2014) A straightforward, eco-friendly and cost-effective approach towards flame retardant epoxy resins. J Mater Chem A 2:16230–16241

Chang SC, Slopek RP, Condon B, Grunlan JC (2014) Surface coating for flame-retardant behavior of cotton fabric using a continuous layer-by-layer process. Ind Eng Chem Res 53:3805–3812

Chen S, Li X, Li Y, Sun J (2015) Intumescent flame-retardant and self-healing superhydrophobic coatings on cotton fabric. ACS Nano 9:4070–4076

Gao WW, Zhang GX, Zhang FX (2015) Enhancement of flame retardancy of cotton fabrics by grafting a novel organic phosphorous-based flame retardant. Cellulose 22:2787–2796

Grancaric AM, Botteri L, Alongi J, Malucelli G (2015) Synergistic effects occurring between water glasses and urea/ammonium dihydrogen phosphate pair for enhancing the flame retardancy of cotton. Cellulose 22:2825–2835

Grimme S (2006) Semiempirical GGA-type density functional constructed with a long-range dispersion correction. J Comput Chem 27:1787–1799

Guo Y, He S, Zuo X, Xue Y, Chen Z, Chang CC, Weil E, Rafailovich M (2017) Incorporation of cellulose with adsorbed phosphates into poly (lactic acid) for enhanced mechanical and flame retardant properties. Polym Degrad Stabil 144:24–32

Guo Z, Wang C, Li J, Yao Q (2016) Micro-intumescent flame retardant polyamide 6 based on cyclic phosphate grafting phenol formaldehyde. Polym Adv Technol 27:955–963

Jia YL, Lu Y, Zhang GX, Liang YJ, Zhang FX (2017) Facile synthesis of an eco-friendly nitrogen-phosphorus ammonium salt to enhance the durability and flame retardancy of cotton. J Mater Chem A 5:9970–9981

Jing J, Zhang Y, Fang ZP, Wang DY (2018) Core-shell flame retardant/graphene oxide hybrid: a self-assembly strategy towards reducing fire hazard and improving toughness of polylactic acid. Compos Sci Technol 165:161–167

Ju Y, Liao F, Dai X, Cao Y, Li J, Wang X (2016) Flame-retarded biocomposites of poly(lactic acid), distiller's dried grains with solubles and resorcinol di(phenyl phosphate). Compos Part A Appl Sci Manuf 81:52–60

Laufer G, Carosio F, Martinez R, Camino G, Grunlan JC (2011) Growth and fire resistance of colloidal silica-polyelectrolyte thin film assemblies. J Colloid Interface Sci 356:69–77

Lee C, Yang W, Parr RG (1988) Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. Phys Rev B 37:786

Li S, Zhong L, Huang S, Wang D, Zhang F, Zhang G (2019) A reactive fluorine-free, efficient superhydrophobic and flame-retardant finishing agent for cotton fabrics. Cellulose 26:6333–6347

Liang K, Shi F, Liu J (2018) Occurrence and distribution of oligomeric organophosphorus flame retardants in different treatment stages of a sewage treatment plant. Environ Pollut 232:229–235

Liu C, Yao Q (2018) Mechanism of thermal degradation of aryl bisphosphates and the formation of polyphosphates. J Anal Appl Pyrolysis 133:216–224

Malucelli G, Barbalini M (2019) Uv-curable acrylic coatings containing biomacromolecules: a new fire retardant strategy for ethylene-vinyl acetate copolymers. Prog Org Coat 127:330–337

Pan HF, Wang W, Pan Y, Zeng WR, Zhan J, Song L, Hu Y, Liew KM (2015) Construction of layer-by-layer assembled chitosan/titanate nanotubes based nanocoating on cotton fabrics: flame retardant performance and combustion behavior. Cellulose 22:911–923

Price D, Horrocks AR, Akalin M, Faroq AA (1997) Influence of flame retardants on the mechanism of pyrolysis of cotton (cellulose) fabrics in air. J Anal Appl Pyro 40:511–524

Salmeia KA, Gaan S, Malucelli G (2016) Recent advances for flame retardancy of textiles based on phosphorus chemistry. Polymers 8:1–36

Shi Y, Wang G (2016) The novel epoxy/pepa phosphate flame retardants: Synthesis, characterization and application in transparent intumescent fire resistant coatings. Prog Org Coat 97:1–9

Soler JM, Artacho E, Gale JD, García A, Junquera J, Ordejón P, Sánchez-Portal D (2002) The siesta method for ab initio order-n materials simulation. J Phys Condens Matter 14:2745

Stieger G, Scheringer M, Ng CA, Hungerbühler K (2014) Assessing the persistence: Bioaccumulation potential and toxicity of brominated flame retardants: data availability and quality for 36 alternative brominated flame retardants. Chemosphere 116:118–123

Su X, Yi Y, Tao J, Qi H, Li D (2014) Synergistic effect between a novel triazine charring agent and ammonium polyphosphate on flame retardancy and thermal behavior of polypropylene. Polym Degrad Stabil 105:12–20

Suryaprabha T, Sethuraman MG (2018) Fabrication of superhydrophobic and enhanced flame-retardant coatings over cotton fabric. Cellulose 25:3151–3161

Taherkhani A, Hasanzadeh M (2018) Durable flame retardant finishing of cotton fabrics with poly(amidoamine) dendrimer using citric acid. Mater Chem Phys 219:425–432

Toldy A, Niedermann P, Rapi Z, Szolnoki B (2017) Flame retardancy of glucofuranoside based bioepoxy and carbon fibre reinforced composites made thereof. Polym Degrad Stabil 142:62–68

Wagner J, Deglmann P, Fuchs S, Adn CA, Fleckenstein MC, Döring M (2016) A flame retardant synergism of organic disulfides and phosphorous compounds. Polym Degrad Stabil 129:63–76

Wang S, Bian C, Jia B, Wang Y, Jing X (2016) Structure and thermal pyrolysis mechanism of poly (resorcinol borate) with high char yield. Polym Degrad Stabil 130:328–337

Wang G, Huang Y, Hu X (2013) Synthesis of a novel phosphorus-containing polymer and its application in amino intumescent fire resistant coating. Prog Org Coat 76:188–193

Xu L, Wang W, Yu D (2017) Durable flame retardant finishing of cotton fabrics with halogen-free organophosphonate by uv photoinitiated thiol-ene click chemistry. Carbohydr Polym 172:275–283

Yan L, Xua Z, Wang X (2018) Synergistic effects of organically modified montmorillonite on the flameretardant and smoke suppression properties of transparent intumescent fireretardant coatings. Prog Org Coat 122:107–118

Zheng DD, Zhou JF, Zhong L, Zhang FX, Zhang GX (2016) A novel durable and high-phosphorous-containing flame retardant for cotton fabrics. Cellulose 23:2211–2220