

Thermal Stability and Flame Retardancy of Polyester, Cotton, and Relative Blend Textile Fabrics Subjected to Sol–Gel Treatments

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Received 14 April 2010; accepted 15 June 2010

DOI 10.1002/app.32954

Published online 23 August 2010 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: Polyester (PET), cotton (COT), and two relative blend textile fabrics were treated by sol–gel processes. Tetraethoxysilane (TEOS) was used as inorganic precursor of silica phases; furthermore, different TEOS/H₂O ratios were examined to explore the effect of the presence of SiO₂ on the thermal and fire stability of the textile fabrics investigated. The distribution and dispersion of SiO₂ were observed by means of scanning electronic microscopy (SEM). SEM magnifications showed the formation of a continuous silica film located in the neighboring fibers; furthermore, in the case of PET, such a film incorporated silica particles with an average diameter ranging between 0.2 and 6 μm. The thermal and thermooxidative stabilities of the treated samples were investigated by thermogravimetric analysis: after the sol–gel treatment, the degradation mechanism was modified both in nitrogen and in air, and the improvement in the thermal stability

was attributed to the presence of silica, which played a protective role in the degradation of the textile fabrics. Finally, we investigated the combustion behavior of the textile fabrics by cone calorimetry, measuring the time to ignition, the heat release rate, and the relative peak. The former was found to depend on the type of fabric; the latter generally evidenced a remarkable decrease for all of the treated samples, up to 35% compared to the neat counterparts. This indicated that the sol–gel treatments improved the flame retardancy of the PET/COT fabrics. This conclusion was also confirmed by limiting oxygen index tests, which evidenced burning kinetics changes in the presence of the silica coating. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 1961–1969, 2011

Key words: fibers; flame retardance; polyesters; silicas; thermogravimetric analysis (TGA)

INTRODUCTION

Flame retardant textiles represent an important class of materials to be used in different fields, such as in military, automotive, and aerospace applications and in safety and protective garments.¹ Since the 1990s, the exigency to reduce the amount of and/or replace halogen additives as flame retardants has obliged the academic and industrial research communities to develop new and innovative products in all of these fields; this has comprised textile applications.^{2–4} Nowadays, the attention of the world is focused on the possibility of formulating novel, efficient systems to improve the fire retardancy of polymeric materials and, at the same time, retaining a low environment impact. Different approaches have been carried out in the textile field, where the nature of the fiber represents a key factor in reducing the flammability. Indeed, at this point, it is not possible to use the same technological approach (i.e., the same additives or processing) to increase the fire retardancy of natural

[i.e., cotton (COT)] and synthetic [i.e., polyester (PET)] fibers. This latter aspect is very important and restrictive because, at present, one of the main goals is to use COT/PET blends to exploit the advantages of both of the fibers, including the comfort, softness, and transpiring of COT and the low cost of PET.

In the textile field, different methodologies are optimized to give flame retardancy to COT and PET fibers; indeed, in the case of synthetic fibers, it is possible to introduce flame-retardant additives directly into the bulk within the polymer matrix during the spinning (melt mixing, solution mixing, or *in situ* polymerization) or, alternatively, during the finishing step.

However, only few studies on the fire retardancy of COT and PET have been done up to this point; in particular, different additives, such as phosphorus species,^{5–11} polyhedral oligomeric silsesquioxanes,^{12–14} silica particles,¹⁵ and halogen compounds,¹⁶ have been investigated to reach this goal in the finishing step of textile fabrics.

Two trademarked products, Proban and Pyrovatex, are currently used for the modification of COT, PET, and their relative blends.¹⁷ Proban (from Rhodia, Inc. Paris-France) uses tetrakis (hydroxymethyl) phosphonium sulfate, whereas Pyrovatex (from Portwest, Inc. Westport-Ireland) is based on *N*-methylol dialkyl

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phosphonopropionamide. Obviously, the natures of these flame retardants lead to different efficiencies in fire retardancy.

In this scenario, nanotechnology shows real and great potential in the textile industry, especially when one considers that the conventional methods used to impart different properties to fabric textiles do not often lead to permanent effects against wearing or laundering. As a matter of fact, the application of nanotechnology has been proven to give high durability to fabrics and improve their overall performance, thanks to the nanomorphology of the fillers used.¹⁸

The sol-gel process^{5, 15, 19-26} is a relatively novel process in the textile field when applied to impart such properties as flame retardancy, thermal stability, hydrophobicity, and antistaticity. By this technique, it is possible to induce the formation of a homogeneous coating of (nano)particles directly on the textile fabrics. In recent years, the sol-gel technique has remarkably proven its exceptional potential with regard to the synthesis of new materials with a high degree of homogeneity at molecular level and with extraordinary physical and chemical properties. It is based on two steps involving hydrolysis and condensation reactions starting from metal alkoxides, such as tetraethoxysilane (TEOS), tetramethoxysilane, and titanium tetraisopropoxide.

Current efforts in academic research have shown that the addition of a relatively small amount of Si compounds to various polymer materials can significantly improve their flame retardancy. In addition, these compounds are considered environmentally friendly additives because their use leads to a reduction in harmful effects on the environment compared to those of existing flame retardants.

In this context, our study on the correlation between the combustion behavior of textiles and the deposition of silica as a flame retardant becomes interesting. For this purpose, PET, COT, and relative blend textile fabrics [containing 15% COT (COT15) and 35% COT (COT35)] were sol-gel-treated with TEOS as a precursor at different TEOS/H₂O ratios [1:1 (TEOS1), 2:1 (TEOS2), and 3:1 (TEOS3)]. The distribution of SiO₂ on the different textile substrates was evaluated by scanning electron microscopy (SEM) analysis. Furthermore, the effect of the sol-gel process on the thermal stability of the textile fabrics was studied with thermogravimetric analysis (TGA) to verify an eventual protective effect of the formed silica phases. Finally, the combustion behavior of the textile fabrics was investigated by means of cone calorimetry and limiting oxygen index (LOI) testing.

EXPERIMENTAL

Materials

COT, PET, and two relative blends (COT15 and COT35) were kindly supplied as textile fabrics by

Klopman International Srl (Frosinone-Italy) and were used as received without any further treatment. TEOS, water, ethanol (EtOH), dibutyltindiacetate, and HCl (all reagent grade) were purchased from Sigma-Aldrich (Milan-Italy) and were used as received.

Sol-gel treatments of the textile fabrics

The silica phases were synthesized by the sol-gel method with TEOS as an alkoxide precursor. The pure silica sol was prepared via acidic hydrolysis: a mixture containing TEOS, EtOH (EtOH/TEOS molar ratio = 0.07), distilled water, and HCl (1 wt %) was stirred for 10 min at room temperature. Then, dibutyltindiacetate (0.9 wt %) was added to catalyze the formation of silica. Different TEOS/H₂O molar ratios were investigated (TEOS1, TEOS2, and TEOS3). The TEOS/H₂O ratios under study were chosen in contraposition with data found in the literature. In fact, Sequeira et al.²⁷ affirmed that the molar portion of water and TEOS is a crucial factor for the synthesis of siloxane prepolymers and that the water content influences the rate of TEOS hydrolysis. Thus, the best TEOS/H₂O molar ratio seems to be 1:2. Nevertheless, in our case, a higher precursor content was used because the textile had to be impregnated in the sol solution, squeezed, and then thermally treated. Therefore, only a small fraction of the sol solution could be exploited for the occurrence of the subsequent sol-gel process. Consequently, all of the fabrics were immersed at room temperature in the silica sol to impregnate them, and then, the sol-gel treatment was completed at 70°C for 24 h in an oven.

The treated textiles were coded with the name of the textile plus TEOSX, where X indicates the TEOS/H₂O molar ratio. For example, COT-TEOS1 means COT treated with TEOS/H₂O at a 1:1 molar ratio.

Characterization techniques

To study the SiO₂ distribution in the textile fabrics, digital images were obtained of the textile surfaces with a LEO-1450VP scanning electron apparatus (High Wycombe-UK) equipped with an INCA Energy Oxford X diffractometer (Cu K α X-ray source, lambda as wave length = 1.540562 Å); this was useful for performing elemental analysis through energy dispersive spectroscopy (EDS). For SEM examinations, small pieces of the textiles were cut and fixed to conductive adhesive tapes; then, the samples were gold-coated to increase their surface conductivity. To investigate the average diameter of the SiO₂ particles incorporated into the silica coating, a statistical investigation of the SEM images was performed on 200 particles with ImageJ software (Bethesda-USA).

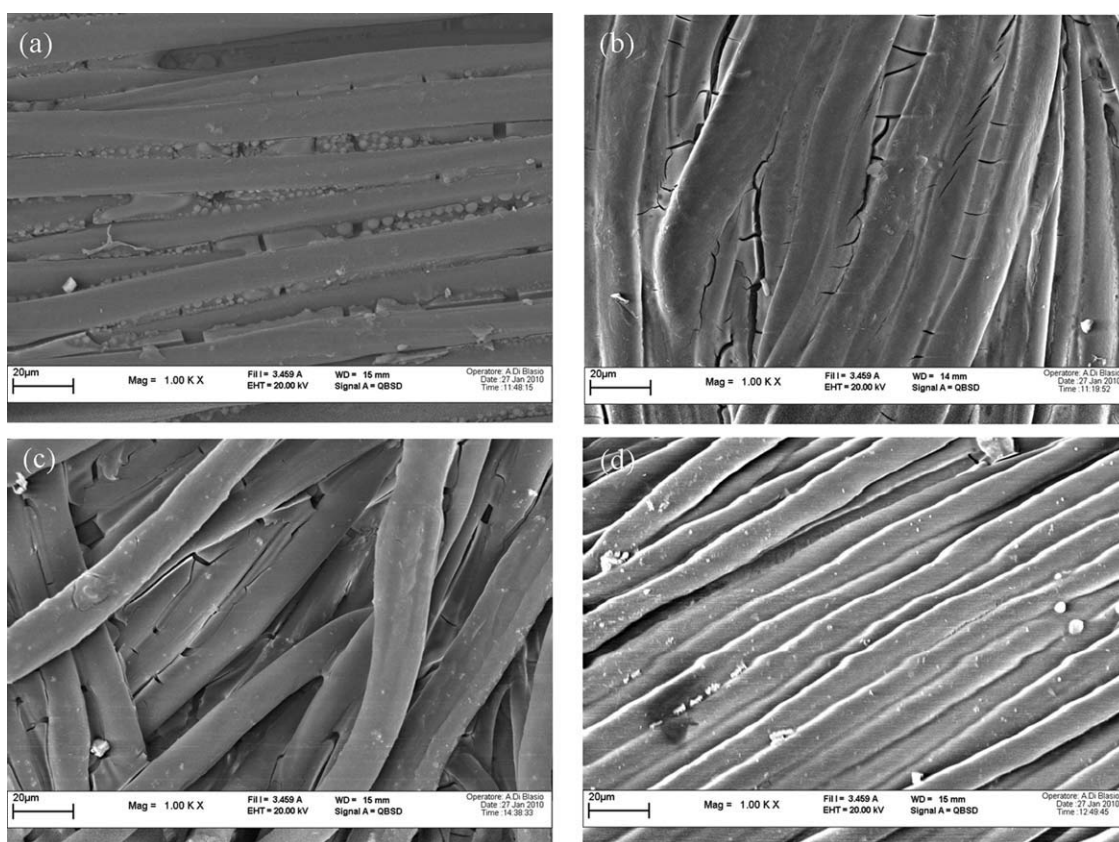


Figure 1 Magnified SEM images of (a) PET, (b) COT, (c) COT15, and (d) COT35 with TEOS1.

The thermal stability of the textiles was evaluated by TGA from 50 to 700°C with a heating rate of 10°C/min under an air or nitrogen atmosphere with a Pyris 1 TgAQ500 analyzer (Milan, Italy). The textile fabrics were placed in open alumina pans.

The flame retardancy of the textiles was determined by cone calorimetry and LOI tests with a FIRE oxygen index apparatus according to the standard ISO 4589-2.

We performed the cone calorimeter tests (fire-testing technology) according to ISO 5660, following the procedure described elsewhere.²⁸ Square specimens (100 × 100 × 0.5 mm³) were irradiated at a heat flux of 35 kW/m² in a horizontal configuration. The fabrics were placed on a sample holder and maintained in the correct position with a metallic grid. The measured parameters were time to ignition (TTI; s), total heat release (THR; kW/m²), heat release rate (HRR; kW m⁻² g⁻¹), and peak heat release rate (pkHRR; kW m⁻² g⁻¹). For each formulation, the test was repeated three times.

RESULTS AND DISCUSSION

Morphology of the silica phases

To investigate in detail the distribution and the dispersion of silica, SEM analysis was performed.

Indeed, SEM magnifications showed the formation of a continuous silica film located in the neighboring fibers and partially covering their walls [Figs. 1(b–d)]; furthermore, only in the case of PET did the film incorporate silica particles, with their average diameter ranging between 0.2 and 6 μm [Fig. 1(a)],

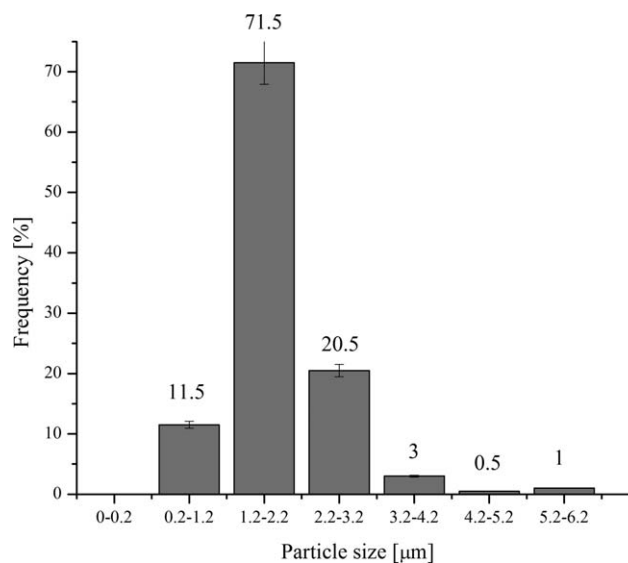


Figure 2 Statistical distribution of the silica particles in PET-TEOS1.

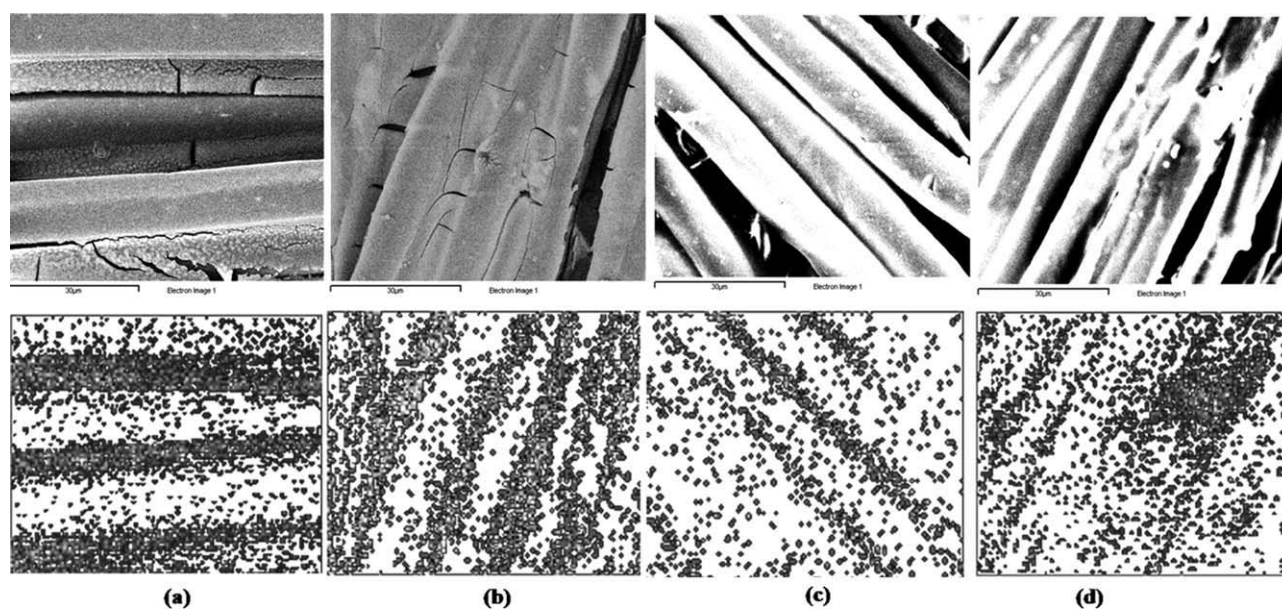


Figure 3 EDS mapping of (a) PET, (b) COT, (c) COT15, and (d) COT35 with TEOS3.

as confirmed through a statistical investigation by the ImageJ software. The formation of the continuous silica film was ascribed first to the quite high TEOS/H₂O molar ratio; second, the COT hydroxyl functionalities could have taken part in the sol-gel reactions and inhibited the formation of silica particles. Furthermore, the TEOS/H₂O ratio did not seem to influence the formation of the silica film; nevertheless, when the sol-gel treatment was performed with a high TEOS/H₂O ratio (i.e., TEOS3 solution), the textile fabrics became more rigid, and some visible cracks appeared on the surface of the fabric [Fig. 1(b)].

As far as PET was concerned, the size of the spherical particle embedded in the silica film was measured on the SEM micrograph, shown in Figure 1(a). In the case of PET-TEOS1, most of the silica particles (up to 70%) had diameters in the range 1.2–2.2 µm (Fig. 2).

Finally, elemental analysis was performed on all of the treated substrates with an EDS probe. As a typical example, Figure 3 shows the Si mapping for all of the fabrics treated with TEOS3. The distribution and the dispersion level of Si on the textile fabrics and within the fibers was very homogeneous.

Thermal stability

The thermal and thermooxidative stability of the samples was investigated by means of TGA. The obtained data are collected in Tables I and II for nitrogen and air, respectively.

With regard to PET, the degradation mechanism was not modified in nitrogen [Fig. 4(a) and Table I], although it changed slightly in air for all of the sol-

gel formulations. This resulted in an enhanced thermooxidative stability of the treated fabrics [Fig. 5(a) and Table II]. Usually, PET shows a two-step degradation in air: the former involves the decomposition of the main chain [at 434°C, Fig. 5(a)], and the latter involves the carbonization reactions (at 554°C). When PET was sol-gel-treated, the second peak widened and flattened because the silica coating acted as physical barrier to air, playing a protective role with respect to the thermooxidation process. In any case, a general increase in the final residue at 700°C was registered.

TABLE I
TGA Data in Nitrogen

Formulation	T_1^* (°C)	T_2^* (°C)	Residue at 700°C (%)
PET	—	440	14
PET-TEOS1	—	437	25
PET-TEOS2	—	437	24
PET-TEOS3	—	437	24
COT	365	—	17
COT-TEOS1	361	—	37
COT-TEOS2	361	—	32
COT-TEOS3	361	—	32
COT15	364	434	10
COT15-TEOS1	361	434	25
COT15-TEOS2	361	433	33
COT15-TEOS3	361	433	31
COT35	363	433	13
COT35-TEOS1	357	426	34
COT35-TEOS2	357	426	30
COT35-TEOS3	357	426	32

T_1^* and T_2^* are the temperatures of maximum weight loss calculated from the differential TG curves.

TABLE II
TGA Data in Air

Formulation	T_1^* (°C)	T_2^* (°C)	T_3^* (°C)	Residue at 700°C (%)
PET	—	434	554	1
PET-TEOS1	—	434	561	14
PET-TEOS2	—	447	561	18
PET-TEOS3	—	447	561	23
COT	344	—	501	1
COT-TEOS1	338	—	507	24
COT-TEOS2	338	—	507	24
COT-TEOS3	338	—	507	18
COT15	364	433	545	1
COT15-TEOS1	363	442	535	19
COT15-TEOS2	364	442	558	24
COT15-TEOS3	364	442	558	15
COT35	353	429	520	1
COT35-TEOS1	348	431	528	16
COT35-TEOS2	348	431	528	16
COT35-TEOS3	348	431	528	18

T_1^* , T_2^* , and T_3^* are the temperatures of maximum weight loss calculated from the differential TG curves.

In the case of COT, the thermal degradation was found to change in both the atmospheres; the thermogravimetry (TG) curves in nitrogen and air are plotted in Figures 4(b) and 5(b), respectively. Usually, COT pyrolyzes in nitrogen according to two alternative pathways, which involve the decomposition of the glycosyl units to char at lower temperatures and the depolymerization of such units to volatile products containing levoglucosan at higher temperatures. Such behavior has been reported in the literature.²⁹ Figure 4(b) shows that the COT under study thermally degraded by only one step because of the decomposition of the glycosyl units to char (365°C, Table I). On the other hand, the sol-gel treatment turned out to be efficient because the presence of the silica film favored the formation of char. Indeed, a general increase in the final residue at 700°C was registered, as reported in Table I, even when the same coating was also responsible for a slight anticipation in the process. In air, cellulose decomposes in three steps, which were described well by Price et al.³⁰ The

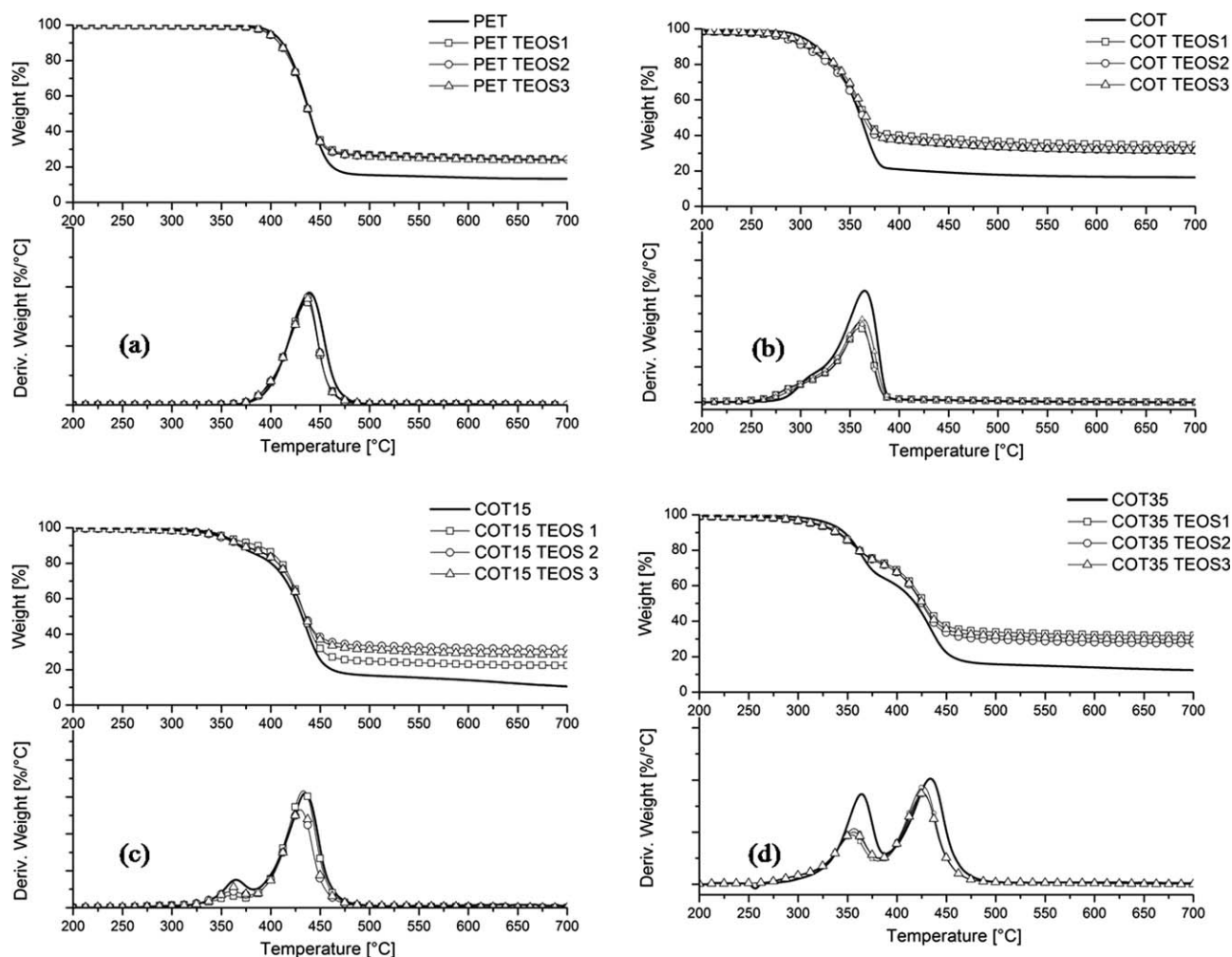


Figure 4 TGA thermograms in nitrogen of (a) PET, (b) COT, (c) COT15, and (d) COT35.

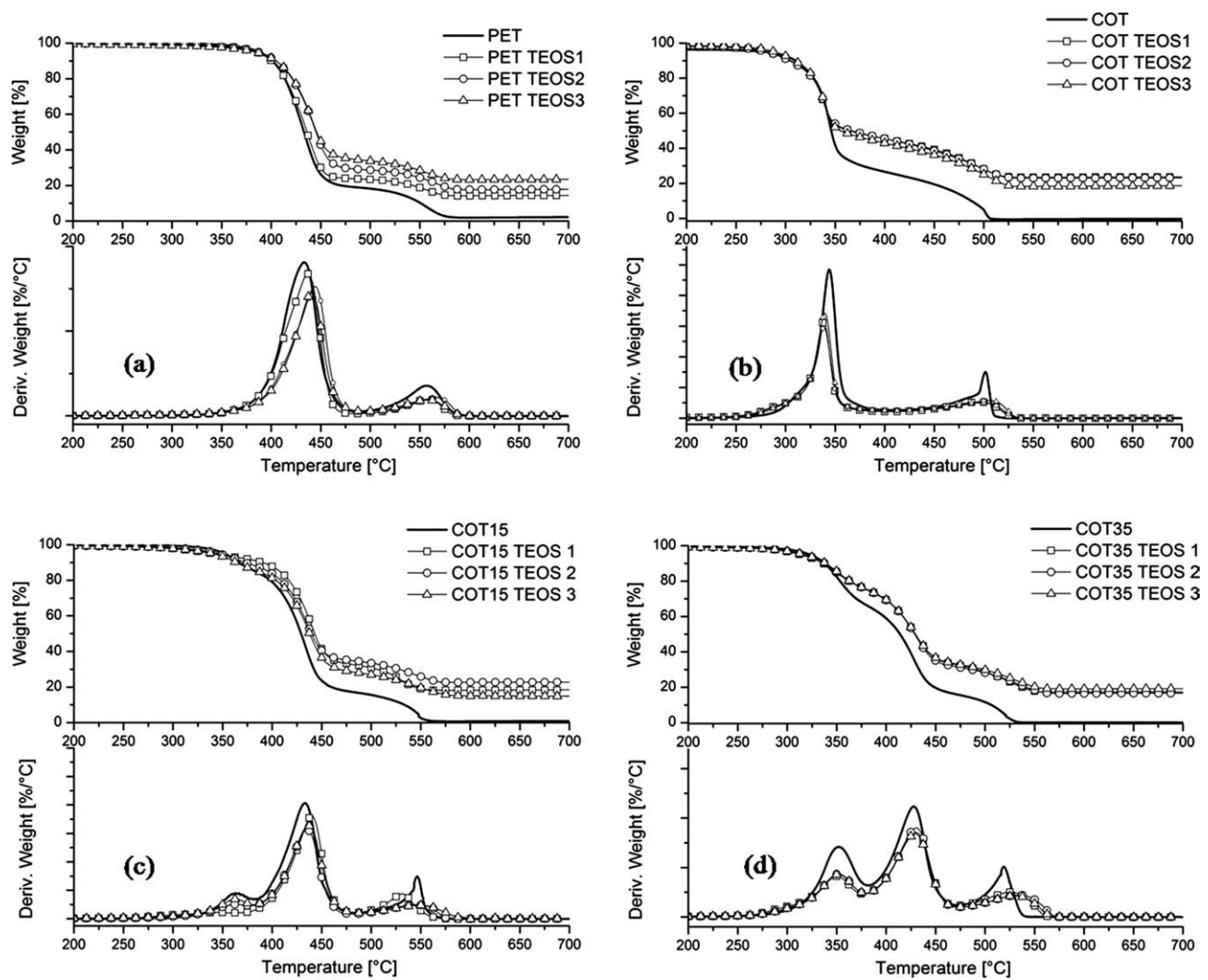


Figure 5 TGA thermograms in air of (a) PET, (b) COT, (c) COT15, and (d) COT35.

TABLE III
Combustion Data from Cone Calorimetry and LOI Tests

Formulation	TTI (s)	δ TTI (%)	THR (MJ/m ²)	pkHRR (kW/m ² g)	δ (%)	LOI (%)
PET	164	—	3	52	—	21
PET-TEOS1	78	-52	2	48	-8	22
PET-TEOS2	72	-57	3	50	-4	22
PET-TEOS3	62	-62	3	45	-13	22
COT	14	—	3	57	—	20
COT-TEOS1	16	+7	2	39	-32	22
COT-TEOS2	9	-40	3	38	-33	22
COT-TEOS3	18	+20	3	37	-35	22
COT15	59	—	4	53	—	22
COT15-TEOS1	47	-20	4	46	-13	23
COT15-TEOS2	46	-22	4	43	-19	23
COT15-TEOS3	67	+14	4	52	-2	23
COT35	14	—	3	56	—	21
COT35-TEOS1	26	+86	3	44	-21	22
COT35-TEOS2	27	+93	3	43	-23	22
COT35-TEOS3	24	+71	3	37	-34	22

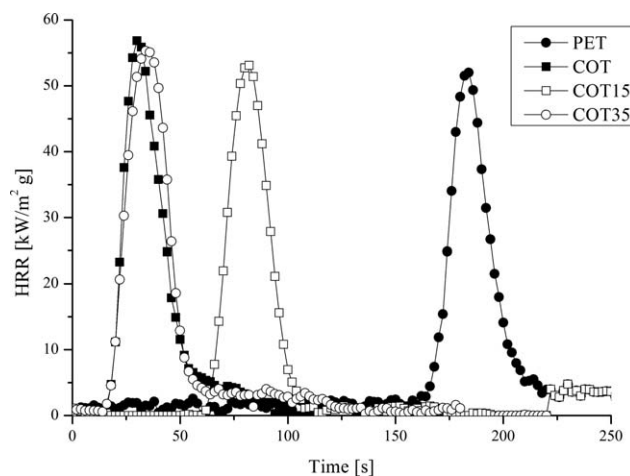
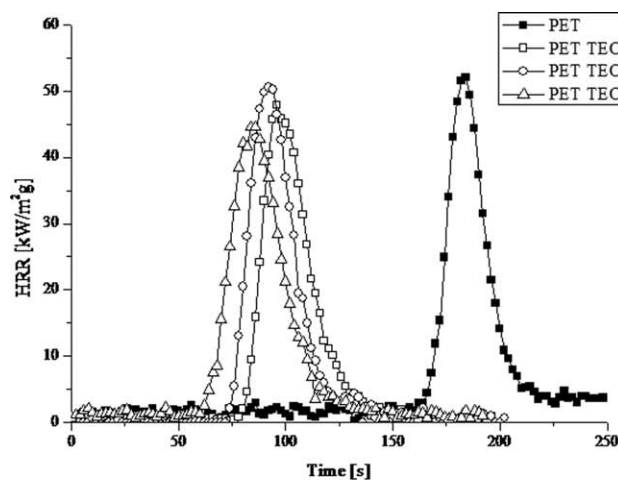


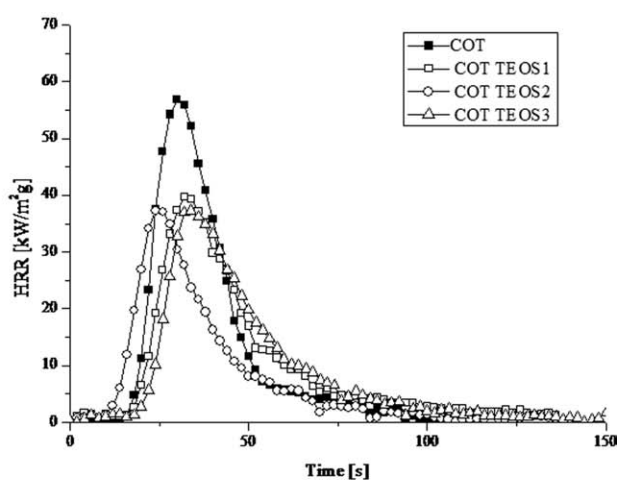
Figure 6 HRR curves of the neat textile fabrics.

first step (located in the range 300–400°C) involves two competitive pathways that yield aliphatic char and volatile products; in the second step (between 400 and 800°C), some aliphatic char converts to an aromatic form and yields CO and CO₂ as a consequence of simultaneous carbonization and char oxidation. During the last decomposition step at about 800°C, the char and any remaining hydrocarbon species are further oxidized, mainly to CO and CO₂. In this study, two decomposition peaks were observable between 340 and 520°C (Table II). In the presence of silica, regardless of the TEOS/H₂O molar ratio, the degradation mechanism changed [Fig. 5(b)]. Indeed, the first step was favored, and consequently, the formation of char occurred. In addition, the second peak widened because of the slowing of the degradation kinetics.

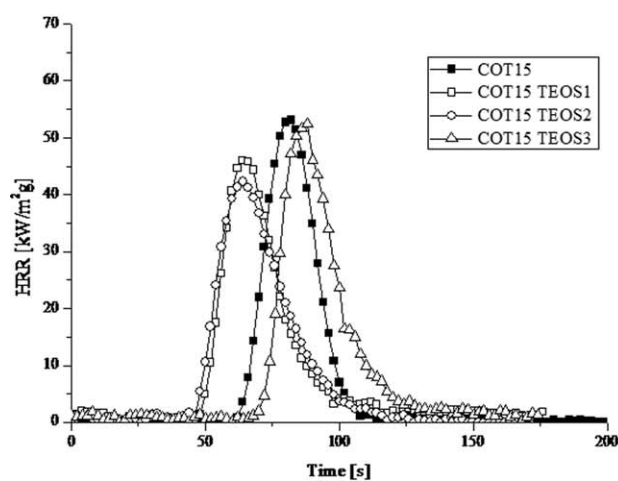
With regard to the two blends, their TG curves in nitrogen are plotted in Figure 4(c,d). Both systems



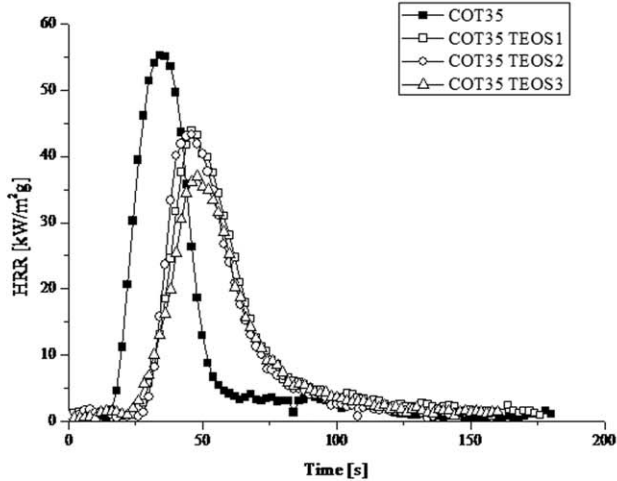
(a)



(b)



(c)



(d)

Figure 7 HRR curves of (a) PET, (b) COT, (c) COT15, and (d) COT35.

behaved similarly to a typical polymer blend; indeed, their thermal degradation consisted of two independent steps. The former was due to COT (364 and 363°C), and the latter was attributable to PET (434 and 433°C for COT15 and COT35, respectively). In the case of COT15, the first peak decreased with respect to COT35.

Figure 5(c,d) shows the TG curves in air of the blends. Three decomposition peaks are clearly visible (Table II). The first one was attributable to COT, the second to PET, and the third to the both of the fibers. In general, the sol-gel treatments, regardless of the TEOS/H₂O ratio, delayed the thermal degradation of the blends in nitrogen and their thermal oxidation in air and, at the same time, increased the final residue and suppressed the carbonization process of both fibers at about 500°C.

Combustion behavior

The combustion data for all of the textile fabrics investigated through cone calorimeter tests are listed in Table III. In addition, Figure 6 plots the typical HRR curves of the untreated fabrics. All of the fabrics burned very rapidly after ignition, and the combustion kinetics were described by a sharp HRR curve. PET and COT burned with different TTIs (164 and 14 s, respectively). For COT35 and COT15, TTIs equal to 14 and 59 s, respectively, were measured. This behavior seemed to depend on the COT content in the blend: for the highest amount (COT35), the blend burned, mimicking the neat COT. Thus, their TTIs were similar, and the two curves superimposed, as reported in Figure 6. On the other hand, when the COT content was lower (COT15), the TTI was between the values of those of the neat fabrics.

Figure 7 plots the combustion behavior of all of the fabrics subjected to the sol-gel treatment. As far as PET is concerned, all of the formulations anticipated the ignition of about 55%; at the same time, a slight decrease in pkHRR was registered (Table III) without any significant change in THR. Therefore, we concluded that the sol-gel treatments did not improve the fire retardancy of PET. This behavior was attributed to the incompleteness of the sol-gel process, which determined the presence of uncondensed hydroxyl groups together with the EtOH (byproduct) catalyzing PET hydrolysis³¹⁻³⁶ and, thus, anticipated the ignition. Otherwise, in the case of COT, TTI increased, with the exception of TEOS2. In addition, the COT15 blend showed improved combustion behavior only after it was treated with TEOS3. As far as the COT35 blend is concerned, the sol-gel treatments strongly improved its combustion behavior, regardless of the TEOS/H₂O molar ratio (Table III). Indeed, a significant increase in TTI (up to 98%) and a remarkable decrease in pkHRR (up to 34%) were observed. Finally, the flammability prop-

erties of the textiles were measured through LOI testing. Although the sol-gel treatment was not efficient enough to increase LOI in a remarkable way in comparison with the neat textiles (see the data collected in Table III), the burning kinetics changed in the presence of the silica coating. Indeed, the neat textiles burned very rapidly with a sparkling flame, whereas the treated textiles consumed themselves slowly in a incandescence front.

CONCLUSIONS

With the aim of improving their thermal stability and fire-retardant properties, PET, COT, and relative blend textile fabrics were treated by sol-gel processes with TEOS as inorganic precursor. SEM images revealed the formation of a continuous silica film located at the intersection of neighboring fibers. Furthermore, in the case of PET, such a film was found to incorporate silica particles with an average diameter ranging between 0.2 and 6 μm.

After the sol-gel treatment, the degradation mechanism was modified both in nitrogen and air, and the improvement in the thermal stability was attributed to the presence of silica, which played a protective role in the degradation of the textile fabrics. Finally, the combustion behavior of all of the treated textile fabrics was found to be strongly affected by the presence of the silica film. Indeed, the sol-gel treatments did not improve the fire retardancy of PET. On the other hand, the COT35 blend revealed a remarkable increase in TTI (up to 98%) and strong decreases in HRR and pkHRR (up to 34%). Therefore, the sol-gel process can be effectively used to improve the flame retardancy of COT-based textiles.

The authors thank Alberto Frache and Giovanni Camino for helpful discussion, Antonio Andretta for the fabrics, and Alessandro Di Blasio for technical support.

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