Solidification of Non-halogen Fire-retardant Liquid by Encapsulation within Porous Hollow Silica Microspheres of Narrow Size Distribution for Flame-retardant Applications

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Abstract: Hollow silica microspheres of narrow size distribution were prepared by coating polystyrene (PS) template microspheres with SiO_2 nanoparticles, followed by removal of the PS core by combustion at 500 °C to yield porous hollow SiO_2 microspheres. New solid non-halogenated fire-retardant-containing microspheres were prepared by encapsulation of resorcinol bis(diphenyl phosphate) (RDP) within the hollow SiO_2 microspheres. The encapsulation was performed by vacuum application and the RDP was encapsulated up to 90% of the total microspheres weight. PS/RDP-filled SiO_2 microsphere blends were prepared by mixing PS standard with the RDP-filled SiO_2 microspheres. Thermogravimetric analysis illustrated that the thermal stability of the PS standard increases as the content of the RDP-filled SiO_2 microspheres increased (10-50% of total weight). An additional test for the performance of the RDP-filled SiO_2 microspheres as flame-retardant additives was performed by coating PET films with the RDP-filled SiO_2 microspheres, decreasing their flammability, as was shown by a vertical burn test. The high thermal stability and low flammability of both the RDP-filled SiO_2 microspheres and the RDP-filled SiO_2 microspheres/polymer blends indicate the potential of these microspheres as flame-retardant additives. In addition, in light of these findings, we offer the encapsulation process for fire-retardents described herein as a model for encapsulation ot other suitable chemicals for other uses such as industrial, pharmateutical and cosmetic applications.

Keywords: Non-halogen fire retardant; Resorcinol bis(diphenyl phosphate); RDP; polystyrene; porous hollow SiO_2 microspheres; oil encapsulation.

I. INTRODUCTION

Flame-retardants (FR) are commonly added to polymeric blends that compose everyday household goods, structures, clothing and more. Polymers such as polystyrene, polypropylene, polycarbonate and others, containing FR additives of a certain percentage are known to exhibit flame-retardant properties [1–4]. In the past, halogen-based FR were mostly used, although nowadays halogen-free FR are sought after, due to increased environmental awareness [5]. Halogen-based FR pollute the environment as a result of the evolution of toxic gases and corrosive smoke during combustion [6,7]. The search for halogen-free FR has led to the development of different alternatives, such as phosphorus based FR. Phosphorus based FR have three mechanisms of action when exposed to heat/fire: they create an insulating layer between the polymer and both oxygen and the heat, their polymerization releases water molecules that dilute the oxidizing gas and phosphorus radicals (PO_2, PO, and HPO) similarly to bromine, can act as scavengers of OH and H radicals [8–10]. Resorcinol bis(diphenyl phosphate) (RDP; Fig. 1) is an example for phosphorous-based FR widely used in high-performance polymer blends [11–13]. RDP is an organic liquid of low volatility and high thermal stability, which is usually

incorporated in polymers by an extrusion process. The extrusion process of RDP along with different polymers is relatively difficult to achieve and requires special equipment. The difficulties in combining RDP and a host polymer into a blend, is derived from the large difference in the polarities between the FR and the host polymer and frequent splashing and lubricating effect of the liquid FR. Hence, preparation of the master batch (concentrated mixture of the additive) is almost impossible [9,11].

Silica (SiO2) has been widely studied in different fields of research and found to have many applications such as semi-conductors, photovoltaic cells, super-hydrophilic and super-hydrophobic coatings, additives for pharmaceuticals, etc. [14–17]. Amongst them, SiO2 has shown some FR abilities as well [18,19]. Moreover, there are non-halogen FR based on silicon and SiO2 nanoparticles [20,21].

In this study, we encapsulated and solidified liquid RDP within porous hollow uniform SiO_2 microspheres (MS) in order to achieve better compatibility with host polymers and an easier extrusion process to form polymeric blends. The SiO_2 hollow MS, composed of sintered SiO_2 nanoparticles, were made by a simple process of surface-coating template polystyrene (PS) MS of narrow size distribution with three successive layers of SiO_2 nanoparticles. Hollow SiO_2 MS were made by removal of the template core PS by combustion at 500 °C, followed by the encapsulation of RDP within the SiO_2 MS by vacuum application [22–24]. RDP was encapsulated up to 90% of the total MS weight (9:1 relative to the SiO2) and the RDP-filled SiO_2 MS were characterized. Blends of the RDP-filled SiO_2 MS with PS standard were used to demonstrate and characterize the FR ability of these MS. Thermogravimetric analysis (TGA) of PS/RDP-filled SiO_2 MS blends show that the thermal stability of the PS increased as the concentration of the RDP-filled SiO_2 MS increased. Furthermore, polyethylene terephthalate (PET) films were coated by RDP-filled SiO_2 MS, exhibited decreased flammability compared to non-coated films as was demonstrated by the vertical-burn test.

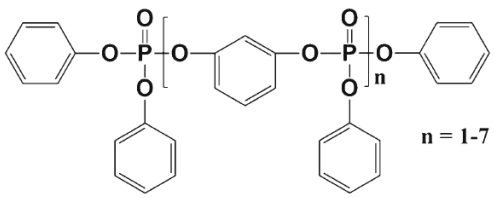

Fig. 1 Chemical structure of resorcinol bis(diphenyl phosphate) (RDP).

II. MATERIALS AND METHODS

A. Materials

The following analytical-grade chemicals were purchased from Sigma Aldrich and used without further purification: benzoyl peroxide (98%), poly(vinylpyrrolidone) (PVP, mw 360,000 Da), ethanol (HPLC), 2-methoxy ethanol (HPLC), ammonium hydroxide (NH4OH, 28%), tetraethyl orthosilicate (TEOS, 99%), styrene (99%) and PS standard (25 kDa). Double distilled water was obtained from a TREION™ purification system. Resorcinol bis(diphenyl phosphate) (RDP) was obtained from ICLIP, Germany. A-131-X film former (composed of modified polyethylenimine dissolved in an aqueous solution) was from MICA Corporation (Shelton, CT). PET films were provided kindly from Hanita Coatings Ltd (Hanita, Israel).

B. Methods

1) Synthesis

a) Synthesis of polystyrene template microspheres of narrow size distribution

Monodispersed uniform PS MS were prepared by dispersion polymerization mechanism according to a procedure previously described by our group [22]. Briefly, PS MS were synthesized in a three-neck round-bottom flask equipped with a condenser and immersed in a silicone oil bath at a preset constant temperature of 73 °C. PS MS of 2.5±0.2 µm were formed by adding into the reaction flask a solution containing PVP, mw 360,000 Da (3.75 g, 1.5% w/v) dissolved in a mixture of ethanol (150 ml) and 2-methoxyethanol (62.5 ml). The reaction was stirred while N2 was bubbled through the solution to exclude air. After 15 min, a solution containing the initiator benzoyl peroxide (1.5 g, 0.6% w/v) and styrene (37.5 ml, 15% w/v) was added to the reaction flask and the reaction was left to stir for 24 h. The polymerization reaction was stopped by cooling the flask to room temperature. The formed PS MS were washed by extensive centrifugation cycles with ethanol followed by water. The particles were then freeze-dried to obtain a powder.

b) Synthesis of porous hollow SiO_2 microspheres of narrow size distribution

SiO_2 coating of the template core PS MS was carried out similarly to a procedure previously described by our group [23]. Briefly, 3 g of PS template MS (2.5±0.2 µm) were placed in a flask containing ethanol (235 ml) and dispersed by sonication for 20 min. The first nanoparticle SiO_2 coating layer was achieved by adding water (4.5 ml), NH4OH (3.5 ml) and TEOS (8 ml) to the PS MS suspension, the suspension was then left to stir for 18 h at room temperature. Second and third layers of silica coating, were each achieved by addition of 8 ml TEOS to the suspension followed by 18 h stirring at room temperature. After completion of 3 coating cycles, the silica-coated PS MS, or PS/SiO_2 core-shell MS, were washed by extensive centrifugation cycles with ethanol followed by water to remove the excess non-grafted SiO_2 nanoparticles. After centrifugation, the PS/SiO_2 MS were freeze-dried. In order to obtain porous hollow SiO_2 MS of narrow size distribution, the dry PS/SiO_2 MS were placed in an oven, at 500 °C, under air over-night. The PS core was burned to obtain uniform hollow porous SiO_2 MS.

c) Preparation of RDP-filled SiO_2 MS by vacuum application

Hollow SiO_2 MS (100 mg) were added to a two neck 100 ml round bottom flask equipped with a septum. The flask was then deflated and vacuumed using a water vacuum system for 20 min at room temperature. Then, the vacuum system was stopped and liquid RDP (400, 900 and 1400 mg) was added slowly to the reaction flask. Vacuum was applied again (20 min) until the RDP-filled SiO_2 MS were completely dry [24].

d) Preparation of PS/RDP-filled SiO_2 MS blends

PS/RDP-filled SiO_2 MS blends containing different concentrations (10, 20, 25 and 50 weight%) of the RDP-filled SiO_2 MS were prepared by mixing different concentrations of the RDP-filled SiO_2 MS with fix amounts of PS standard (25 kDa).

e) Praparation of PET films coated with RDP-filled SiO_2 MS

RDP and RDP-filled SiO_2 MS were mixed with the film former A-131-X in different concentrations (5, 10 and 20% w/v) and spread on the 50 µm PET film with a Mayer rod, followed by drying the coating on the PET film for 10 min at 80 °C [25].

2) Characterization

a) High resolution scanning electron microscopy

Surface morphology, size and size distribution of the PS, PS/SiO_2 and hollow SiO_2 MS were determined with a JEOL high resolution scanning electron microscope (HR SEM) model JSM-840, Japan. For this purpose, a drop of diluted MS dispersion in ethanol was spread on a glass surface and dried at room temperature. The dried sample was coated with iridium in vacuum before viewing under SEM. The average particle size and size distribution were determined by the measurement of the diameter of more than 200 particles with image analysis software (Analysis Auto, Soft Imaging System GmbH, Germany).

b) Fourier-transform infrared spectroscopy

FTIR measurements of PS, PS/SiO_2, hollow SiO_2 MS, RDP and RDP-filled SiO_2 MS were performed by the attenuated total reflectance (ATR) technique, using Bruker ALPHA-FTIR QuickSnapTM sampling module equipped with platinum ATR diamond module.

c) Thermal analysis

The thermal behavior of PS, RDP, RDP-filled SiO_2 MS, PS/20% RDP blend and PS/20% RDP-filled SiO_2 MS blend (as well as 10, 25 and 50% blends) were determined by TGA with a TGA/DSC 1 STARe system (Mettler Toledo, Switzerland). The samples were heated between 25 to 700 °C at a rate of 10 °C/min under air atmosphere.

d) Vertical burn test

The UL 94 VTM vertical burn test for the RDP-filled SiO_2 MS coated PET films was performed to evalute the films flammability [25]. The material is rated VTM-0 if the flame extinguished within 10 s after removal of the burner. The VTM-1 and VTM-2 rating requires that the flame extinguished within 30 s after removal the burner. In a typical experiment, a specimen e.g., RDP-filled SiO_2 MS 5, 10 and 20% coated PET films of 20 cm long and 5 cm wide, was exposed vertically to a Bunsen burner blue flame. The specimen was supported in a vertical position, and the flame of the burner was applied to the bottom of the specimen for 5 s and then removed. This process was then repeated twice. If the specimen caught fire in the first 5 s, it was left to extinguish, and the Bunsen flame was similarly reapplied for the next 5 s. Two sets of five specimens were tested. The specimen was rated according to the criteria listed in the literature as VTM-0, VTN-1, or VTM-2 [8,24,25].

III. RESULTS AND DISCUSSION

The stages of RDP-filled SiO_2 MS synthesis are illustrated in Fig. 2. The hollow SiO_2 MS were made by coating PS micrometer-sized uniform template particles by three successive layers of SiO_2 nanoparticles, followed by combustion of the PS at 500 °C. The combustion of the particles was used to remove the core PS and to generate pores in between the produced sintered hollow SiO_2 nanoparticles. The liquid FR, RDP, was then encapsulated within the hollow SiO_2 MS by applying vacuum as described in the methods section.

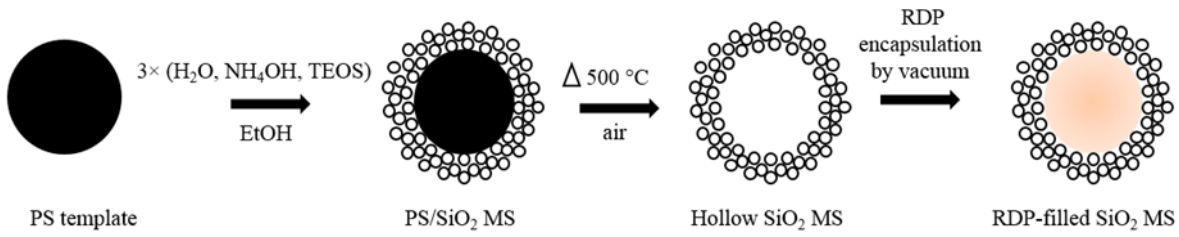

Fig. 2 Synthesis of hollow SiO_2 MS and RDP-filled SiO_2 MS.

A. Microspheres characterization

After each step of the MS synthesis, the particles were characterized by HR-SEM to determine their size and size distribution in terms of diameter (Fig. 3). Monodispersed uniform PS template MS size in diameter was 2.5±0.2 µm, as measured by HR-SEM (Fig. 3A), after coating of the PS MS by three layers of SiO_2 nanoparticle (31±4 nm) the MS size increased to 2.6±0.4 µm (Fig. 3B), leading thereby to a SiO_2 shell thickness of 1.0±0.2 µm. After PS combustion, the hollow SiO_2 MS size in diameter measured was 2.4±0.3 µm (Fig. 3C). The hollow MS diameter decreased, probably due to the combustion process that cause the SiO_2 nanoparticle to sinter [26]. Furthermore, a morphology difference between the MS during the synthesis stages can be noticed, PS MS have a smooth surface, whereas PS/SiO_2 MS have a rough surface due to the grafted nanoparticles (Fig. 3A and 3B, respectively). The hollow SiO_2 MS however, quite surprisingly, seem to have a smooth surface (Fig. 3C). It can be anticipated that after PS combustion the particles surface is smoothened, in addition, the SEM image under the described experimental conditions could not visualize the fine structure of the SiO_2 nanoparticles that compose the hollow MS.

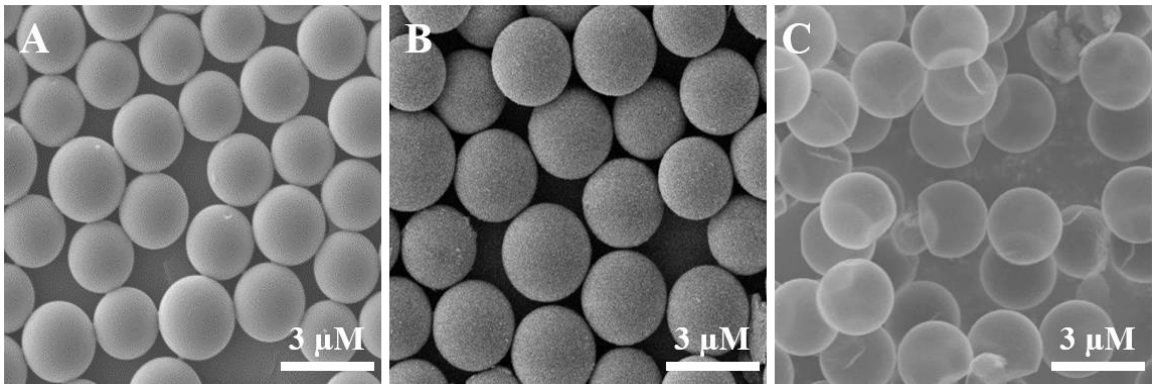

Fig. 3 SEM images of PS (A), PS/SiO_2 (B) and hollow SiO2 MS (C).

For the next step, PS MS, PS/SiO_2 MS, hollow SiO_2 MS, RDP and RDP-filled SiO_2 MS were characterized by FTIR (Fig. 4). PS template MS show characteristic peaks at 700 and 760 cm^{-1}

indicating the benzyl ring of the styrene, and peaks at 1452 and 1495 cm^{-1}, attributed to alkyl groups of the styrene. For PS/SiO_2 MS, after the SiO_2 coating, characteristic SiO_2 peak at 450 and 1061 cm^{-1} appeared, belonging to Si-O-Si bond [27]. Hollow SiO_2 MS, after removal of PS, display characteristic SiO_2 peaks at 450 and between 1000-1270 cm^{-1} only, therefore indicating that the PS core was completely removed by the combustion of the particles. The FTIR spectrum of the RDP demonstrates absorption peaks at 505 and 575 cm^{-1} corresponding to the O-P-O bands, at 685 and 760 cm^{-1} belonging to the C-C vibration band, at 945, 1072, and 1187 cm^{-1} corresponding to the P-O-C bands, at 1150-1250 and 1250-1350 cm^{-1} corresponding to the P=O bands, at 1483 cm^{-1} corresponding to the aromatic CH stretching bands and at 1595 cm^{-1} belonging to the aromatic C=C bands [24]. RDP-filled SiO_2 MS were preaperd by encapsulating RDP within the hollow SiO_2 MS by vacuum process, as described in the methods section. RDP-filled SiO_2 MS FTIR spectrum show a combination of the typical peaks of both the SiO_2 and RDP, as expected. The SiO_2 peaks at 450 and 1061 cm^{-1} are presented by the arrows, Fig. 4. The intensity of the SiO_2 peaks is much lower than the RDP peaks, indicating the high amount of RDP encapsulated compared to the SiO_2 shell.

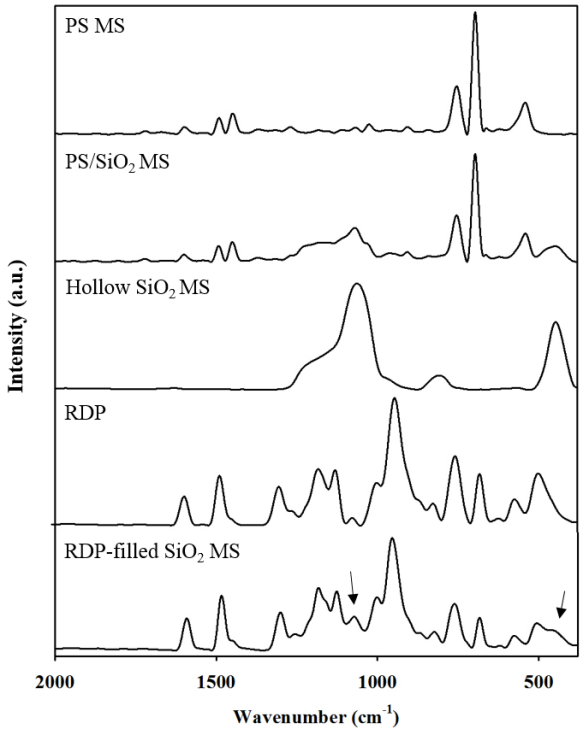

Fig. 4 FTIR spectra of PS MS, PS/SiO2 MS, hollow SiO2 MS, RDP and RDP-filled SiO2 MS.

Hollow SiO_2 MS are a dry white powder, whereas RDP is a clear-yellow liquid. The encapsulation process, using vacuum, successfully resulted in encapsulated RDP that remains as dry white powder after encapsulation of the liquid FR agent through the pores of the SiO_2 MS (Fig. 5). Liquid RDP was encapsulated in three weight cocentrations 1:5, 1:10 and 1:15 (SiO_2: RDP-filled SiO_2 MS). The maximum loading capacity of the liquid RDP within the hollow microspheres was determined for 1:10 (100 mg SiO_2 particles and 900 mg RDP, as described in the method section). Beyond the maximum loading capacity, for example 1:15 (SiO_2: RDP-filled SiO_2 MS), the particles become noticeably wet, due to surface adsorption of the excess RDP that was not encapsulated. It should be noted that since the highest encapsulation yield was obtained for the weight ratio between SiO_2 to RDP-filled SiO_2 MS of 1:10, these particles were chosen for further study.

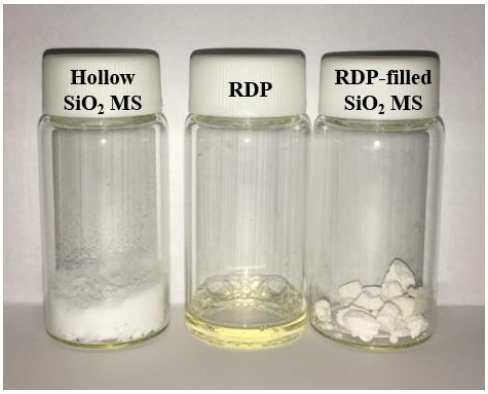

Fig. 5 Appearance of initial and final FR materials. From left to right: hollow SiO2 MS, RDP, and RDP-filled SiO2 MS prepared by the vacuum encapsulation process, as described in the methods section.

B. Thermal stability of PS standard and PS/RDP-filled SiO_2 MS blends

The thermal stability of PS standard, RDP, RDP-filled SiO_2 MS, PS/RDP and PS/RDP-filled SiO_2 MS blends were evaluated by TGA in air. The TGA results are shown in Fig. 6 and in Table 1. All materials tested by TGA show one decomposition slope. The temperature of 50% weight loss by decomposition was at 376 °C for PS standart (solid line, Fig. 6). The TGA thermogram of RDP shows decomposition with 50% weight loss at 378.5 °C (dotted line, Fig. 6). Encapsulated RDP within SiO_2 MS increased the decomposition temperature, where 50% weight loss is observed at 388.8 °C, probably due to the encapsulation, which provides protection to the FR (medium deshed line, Fig. 6). It should be noted, that after the RDP decomposed completely (at 500 °C) 10% of the initial weight was left, belonging to the SiO_2 shell. The SiO_2 is not affected by the high temperature, and the amount of SiO_2 left attests to the 90% RDP encapsulated. The PS/20% RDP blend has increased the decomposition temperature of PS to 402 °C (50% weight loss, short dashed line, Fig. 6), while the PS/20% RDP-filled SiO_2 MS blend has increased the 50% weight loss temperature of the PS standard to 416.8 °C (long dashed line, Fig. 6). Table 1 shows that the decomposition temperature increases as the content of the RDP-filled SiO_2 MS in the blends increases, the decomposition temperature of 50% weight loss of the PS and the PS/RDP-filled SiO_2 MS blends with 10, 25, and 50% are 405, 413 and 422 °C, respectively. These TGA results indicate the effectiveness of the composite FR microspheres in combustion conditions.

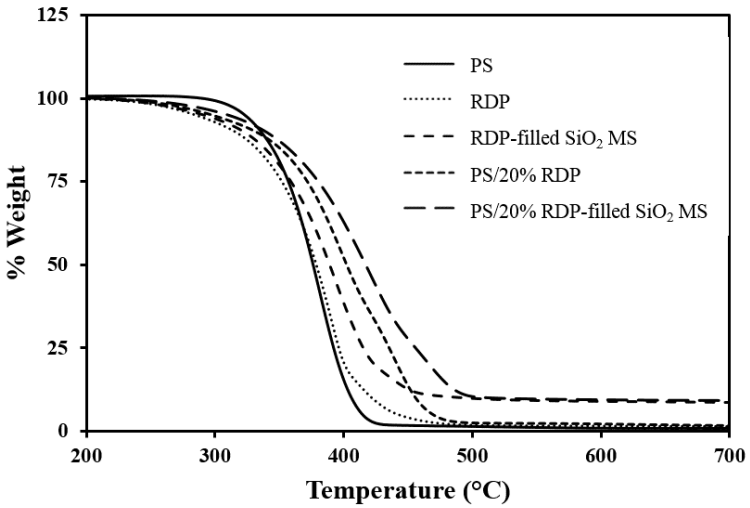

Fig. 6 TGA of PS, RDP, RDP-filled SiO_2 MS, PS/20% RDP and PS/20% RDP-filled SiO_2 MS blends. The RDP- filled SiO_2 MS were prepared by vacuum encapsulation of 900 mg RDP within 100 mg hollow SiO_2 MS, according to the description in the methods section.

Table 1 Thermal stability of the PS/RDP-filled SiO_2 MS blends with altering RDP-filled SiO_2 MS content

	RDP-filled SiO2 MS content in PS/RDP-filled SiO2 MS blend (weight %)			
	PS standard	**10**	**25**	**50**
Temperature at 50% weight loss (°C)	376.0	405.0	413.4	422.7

Temperatures at 50% weight loss were detemined by TGA, as described in the experimental section.

C. Vertical burn test of PET films coated with RDP-filled SiO_2 MS

To provide an assessment of the FR performance of RDP-filled SiO_2 MS in a different application as a coating material, PET films were coated with different concentrations of RDP-filled SiO_2 MS in the film former (5, 10 and 20%) and characterized by the UL 94 VTM vertical burn test. RDP and RDP-filled SiO_2 MS were mixed with a water-based film former (A-131-X) and spread on to the PET films. Although RDP is an organic liquid, the A-131-X-RDP mixture (20% RDP) was able to mix sufficiently, however, when the coating was applied and dried, RDP droplets appeared on the PET film, meaning RDP itself cannot serve as a film coating under these conditions, therefore it was not tested. For a control film, PET film coated with A-131-X only was used. Coating with RDP-filled SiO_2 MS mixed with the film former yielded a dry and homogeneous surface, compatible with the PET film. The UL 94 VTM vertical burn test, is a simple test of vertical combustion that classifies materials as VTM-0, VTM-1, or VTM-2. In our study, the RDP-filled SiO_2 MS/PET films were classified as VTM-0 (Table 2). The films were also measured after the test for length loss, the length loss measured was 13, 12, 9 and 5 cm for control, 5, 10 and 20% RDP-filled SiO_2 MS coated PET films, respectively (Fig. 7).

Fig. 7 Images of PET films coated with A-131-X film former(control) and with RDP-filled SiO_2 MS-film former mixtures (5, 10 and 20% w/v) following the vertical flame testing.

Table 2 Flammability of PET films coated with A-131-X polymer former (control) and with RDP-filled SiO2 MS-polymer former mixtures (5, 10 and 20% w/v) tested by the UL 94 VTM vertical burn test.

Film type	Burning time (sec)	Length loss (cm)	Combustion up to holding clamp
Control	≤10	13	no
5% RDP-filled SiO_2 MS	≤10	12	no
10% RDP-filled SiO_2 MS	≤10	9	no
20% RDP-filled SiO_2 MS	≤10	5	no

IV. CONCLUSIONS

The present article describes a method of encapsulation and solidification of liquid FR, RDP, within hollow porous SiO_2 MS of narrow size distribution. The MS were synthesized and characterized by SEM and FTIR. SEM images showed the different stages of achieving the hollow SiO_2 MS and their uniform size and size distribution. RDP was encapsulated within the SiO_2 MS by vacuum application, up to 90% of the total MS weight. The RDP-filled SiO_2 MS particles were blended with PS standard and the improved thermal stability of the blends containing different percentage of RDP-filled SiO_2 MS was demonstrated by TGA. Furthermore, the encapsulation of the RDP within the SiO_2 MS increase the RDP decomposition temperature. The decomposition temperature of PS blend containing the RDP-filled MS was raised by 29-47 °C. This property of the RDP-filled SiO_2 MS shows their potential as flame-retardant additives. The decreased flammability of PET films coated with RDP-filled SiO_2 MS was demonstrated as well. Vertical burn test of PET films coated with RDP-filled SiO_2 MS was classified as VTM-0 and the films length increased as the concentration of the RDP-filled SiO_2 MS increased. In future study, we plan to try to compound the RDP-filled SiO_2 MS with different host polymers and test their FR properties, moreover we plan to try and encapsulate different FR within the hollow SiO_2 MS and characterize their thermal stability. It should also be mentioned that the present encapsulation process for fire-retardents within the hollow porous SiO_2 MS may be broadened andused for encapsulation of other suitable chemicals for other uses such as industrial, pharmateutical and cosmetic applications.

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