

Flame retarded polyurea with microencapsulated ammonium phosphate for textile coating

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Abstract

Two types of microcapsules of di-ammonium hydrogen phosphate (DAHP) with respectively polyether-polyurethane shell and polyester-polyurethane shell were evaluated as intumescent flame retardant (FR) in a commercial polyurea coating for textiles. The expected advantages of this new concept of encapsulated FR agent are to be compatible with a polymeric matrix in order to give a permanent FR effect and to be itself an efficient FR intumescent formulation for many materials. The thermal degradation for the two types of DAHP microcapsules shows characteristics of an intumescent formulation. The reaction to fire of cotton fabrics coated by FR polyurea loaded with neat or microencapsulated DAHP was studied with the cone calorimeter as the fire model. Both types of DAHP microcapsule present in the polyurea coatings on cotton fabric give an efficient FR effect, although the char developed with microcapsules is a little less heat resistant than that developed with the pure DAHP. Coatings containing microcapsules with polyester-polyurethane shells evolve the smallest quantity of smoke and CO.

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1. Introduction

Polyurethane/urea (PU) is a unique polymer with a wide range of physical and chemical properties such as abrasion resistance, water repellency, leather appearance, etc. These properties provided by PU coating to cotton or

cotton-polyester blended fabrics are very attractive in many textile applications: transportation (e.g. car seats), apparel (e.g. waterproof breathable jackets), and furnishings (e.g. artificial leather upholstery). But these PU coatings have poor flame retardancy.

The addition of a flame retardant to PU coatings is necessary to improve the fire behaviour of the coating and the underlying material. Polyurethane-phosphate combinations are known to form flame retardant (FR) intumescent systems [1–4]. The intumescent formulation is not permanent because of the water solubility and migration of the phosphate. This problem might be

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solved by the technique of microencapsulation. Microencapsulation [5–7] is a process of enveloping microscopic amounts of matter (solid particles, droplets of liquids or gas bubbles) in a thin film of polymer which forms a solid wall. This core/shell structure allows the isolation of the encapsulated substance from the immediate surroundings and thus protects it from any degrading factors such as water. We have synthesized microcapsules containing di-ammonium hydrogen phosphate (DAHP) with a polyurethane shell [8,9]. It is of interest to study microencapsulation with a polyurethane shell for two main reasons. First, we can expect that microcapsules with PU shells will be compatible with the final PU coating on the textile and also with other polymeric matrices. Secondly, combination of the encapsulated ammonium phosphates and the PU shells should be an intrinsic FR intumescent formulation. Microcapsules are obtained by two different techniques, microencapsulation by interfacial polymerization (IP) [10] and microencapsulation by evaporation of solvent (ES) [11]. In a previous work [12], we demonstrated that the concept of using IP microcapsules of phosphate in a polyurethane coating was efficient in providing flame retardancy for cotton fabrics.

In this paper, the IP microcapsules, the new ES microcapsules and their components (neat DAHP and neat PU shell) are examined by thermal analysis in air. Interactions between DAHP and the two types of PU shell were studied due to thermal gravimetric curves of microcapsules and their components. Cotton fabric was coated by several formulations of polyurea resin with either different loadings of microencapsulated DAHP (IP and ES types) or neat DAHP. The reaction to fire of these different textile coatings (in particular with ES microcapsules) is studied using the cone calorimeter as fire model [13,14].

2. Experimental

2.1. Materials

Raw materials were used without further purification.

The synthesis of IP and ES microcapsules of DAHP (μ PI and μ ES) was described in previous papers [8,9]. The polyurethane shell of IP microcapsules is synthesised from diphenyl methylene diisocyanate (blend of MDI isomers, principally 4,4'-diphenyl methylene diisocyanate), polyethylene glycol with a number average molecular weight of 400 g mol⁻¹ (PEG 400) and some water. The polyurethane shell of ES microcapsules is synthesised from pure 4,4'-diphenyl methylene diisocyanate, poly(hexamethylene adipate) glycol with a number average molecular weight of 3800 g mol⁻¹ (PHMA 3800) and ethylene diamine (EDA). We characterized the two types of microcapsules [8,9]. Their

Table 1
Physicochemical characteristics of IP and ES microcapsules of DAHP

Measured properties	IP microcapsules	ES microcapsules
Diameter	Number average: 3.35 μ m	Between 20 and 100 μ m
Chemical characteristics of the shell	Poly(ether/urethane/urea) crosslinked	Poly(ester/urethane/urea) crystallized soft segment
Weight percentage of DAHP	3%	1%
Weight percentage of lost DAHP for microcapsules dispersed in water (7days)	0.09%	0.03%

physicochemical characteristics are summed up in Table 1. While, weight percentages of encapsulated DAHP are certainly low, nevertheless it is interesting to note that PU shell is an efficient barrier to reduce DAHP dissolution in water especially for ES microcapsules. We also synthesised two types of microcapsule with the same PU shells but without DAHP in order to study their thermal behaviour.

A pure cotton fabric (146 g m⁻²) was coated by a commercial polyurea paste from Allrim obtained from a mixture of 20 parts of polyamine (BD021 AW; aromatic diamine) and 100 parts of polyisocyanate (BD021 BY; blend of diphenyl methylene diisocyanate isomers). We incorporated in this paste 20 and 30% (by weight) of solid DAHP, (NH₄)₂HPO₄ (purity 99% minimum) from Riedel-de Haën AG, or 20% of DAHP microcapsules (IP or ES types) synthesised in our laboratory.

2.2. TGA experiment

All TGA tests were carried out using TGA 2950 from TA Instruments at a linear heating rate of 10 °C min⁻¹ in air (60 ml min⁻¹; Air Alphagaz 1 from Air Liquide). The weight of all samples was kept within 9–10 mg. The temperature range was from ambient to 800 °C. Concerning thermal analysis of IP and ES microcapsules, curves of weight difference between the experimental and theoretical TG curves are computed as follows:

$$\Delta(M(T)) = M_{\text{exp}}(T)_{[\text{microcapsule}]} - M_{\text{theo}}(T)_{[\text{PU shell/DAHP}]}$$

where $\Delta(M(T))$ is the curve of residual mass difference, $M_{\text{exp}}(T)_{[\text{microcapsule}]}$ is the experimental residual mass of IP or ES microcapsules (variation by temperature T), $M_{\text{theo}}(T)_{[\text{PU shell/DAHP}]}$ is the theoretical residual mass of the same microcapsules computed by linear combination between the experimental residual masses of DAHP and PU shell (IP or ES types):

$$M_{\text{theo}}(T)_{[\text{PU shell/DAHP}]} = xM_{\text{exp}}(T)_{[\text{DAHP}]} + (1-x)M_{\text{exp}}(T)_{[\text{PU shell}]}$$

where x is the weight percentage of DAHP, $M_{\text{exp}}(T)_{[\text{DAHP}]}$ is the experimental residual mass of DAHP, $M_{\text{exp}}(T)_{[\text{PU shell}]}$ is the experimental residual mass of PU shell (IP or ES types).

The $\Delta(M(T))$ curves allow the observation of an eventual increase or decrease in the thermal stability of the microcapsules compared to the combination of components analysed separately.

2.3. Coating processing

Coatings were carried out by using a coating table K Control Coater (Erichsen). This coating technique replicates coating with a blade, except the coated support is not moving and the coating paste is spread out with a threaded rod. The coating thickness increases with the thread size of the rod. We used a rod with a medium thread in order to obtain an expected coating thickness of about 36 μm . The weight of deposited coating was about 220 g m^{-2} . The coated fabric was then put in a drying oven for 6 h at 50 $^{\circ}\text{C}$.

The various formulations of polyurea coating are described in Table 2. We compared the polyurea coatings including encapsulated DAHP, IP or ES types, with those including solid DAHP.

2.4. Cone calorimeter

Our samples were exposed in a Stanton Redcroft Cone Calorimeter following the procedure defined in ASTM E 1354. They were put in horizontal orientation between two cut steel sheets and the surface exposed to the external heat flux was $9 \times 9 \text{ cm}^2$. The external heat flux chosen was 35 kW m^{-2} because it corresponds to the heat flux in a mild fire. Data on the principal fire properties included rate of heat released (RHR), cumulative heat released (total heat evolved: THE), FIGRA (fire growth rate) index [15], volume of smoke production (VSP) [16], and CO and CO_2 production. FIGRA, computed as $\text{FIGRA} = \text{RHR} (\text{W})/\text{time} (\text{s})$,

Table 2
Different coating formulations tested

Formulation name	Composition of coating on cotton fabrics
Co[PUe]	Polyurea reference sample
Co[PUe–20% μ PI]	PUe with 20 wt% IP microcapsules of DAHP
Co[PUe–20% μ ES]	PUe with 20 wt% ES microcapsules of DAHP
Co[PUe–20%DAHP]	PUe with 20 wt% neat DAHP
Co[PUe–30%DAHP]	PUe with 30 wt% neat DAHP

provides an estimation of both the spread (rate) and the size of a fire. VSP measures the flow of smoke in a ventilated room. The experiments for each sample were in triplicate. When measured at 35 kW m^{-2} flux, RHR and VSP values are reproducible to within $\pm 10\%$ and weight loss, CO, CO_2 are reproducible to within $\pm 15\%$. The results presented hereafter are the average of three measurements.

3. Results and discussion

3.1. Thermal degradation study of microcapsules

TG curves of the neat DAHP, the IP and ES microcapsules of DAHP and their virgin PU shells (IP and ES microcapsules without DAHP) are reported in Fig. 1.

The thermal degradation of ammonium phosphates has been already studied [17–20]. The weight loss of neat DAHP starts at 90 $^{\circ}\text{C}$ and corresponds to release of adsorbed water. The two peaks at 160 and 205 $^{\circ}\text{C}$ of the weight loss rate can be assigned respectively to water and ammonia. At higher temperature, DAHP is transformed into polyphosphoric acid (PPA). From 500 $^{\circ}\text{C}$, PPA dehydrates to phosphorus oxides (P_4O_{10} type) which then sublime.

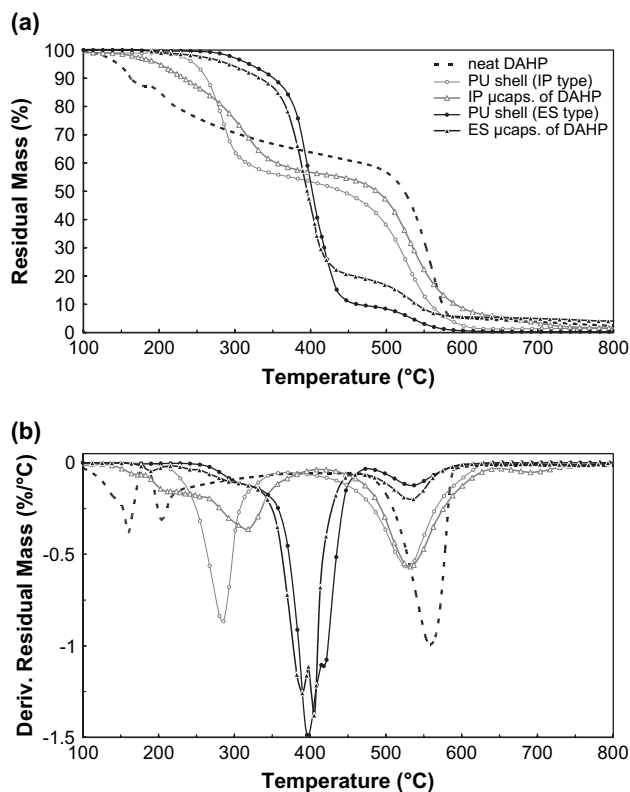


Fig. 1. TG and DTG curves of neat DAHP, IP and ES microcapsules of DAHP, and PU shells of IP and ES microcapsules without DAHP.

The PU shell alone of IP microcapsules without DAHP degrades in two main steps. The first starts at 200 °C with a peak of weight loss rate ($9\% \text{ min}^{-1}$) at 280 °C and the second starts at 400 °C with a peak of weight loss ($6\% \text{ min}^{-1}$) at 530 °C. No residue is observed at 600 °C. According to previous studies [18,19,21] on thermal degradation of PU, the first step corresponds to the depolymerisation of PU to produce the starting monomers. Under atmospheric pressure, the monomers volatilise only slowly from the condensed phase and undergo a series of further reactions. In the case of PU synthesised with MDI [21–23], most of these reactions lead to the formation of crosslinked compounds with urea groups. Above 500 °C, all urethane groups are decomposed and the last degradation corresponds to the decomposition of urea groups.

The IP microcapsules of DAHP show degradation with more than two stages. The weight loss starts at 140 °C with evolving water. Then the second step of weight loss corresponds to evolving ammonia from DAHP and at the same time the degradation of PU. The IP PU shell of DAHP microcapsules degrades earlier than pure IP PU shell. Indeed the depolycondensation is catalysed by acidity from decomposition of DAHP. Several studies [24–27] have shown the intumescent mechanism between phosphorus compounds and polyurethane. Polyphosphoric acid accelerates and increases the formation of char by carbonisation processes and additional crosslinking reactions; also the quantity of non flammable volatile products is decreased. Thus, for the IP PU shell of DAHP microcapsules, the first peak of weight loss rate is delayed at 320 °C instead of 280 °C for pure IP PU shell and the peak of weight loss rate is smaller ($4\% \text{ min}^{-1}$) for the former than the latter ($9\% \text{ min}^{-1}$). The thermal stability is slightly enhanced (temperature range 300–800 °C) and a residue of 5 wt% is observed at 650 °C.

The neat PU shell of ES microcapsules degrades with two main stages. The first stage starts at 250 °C. The degradation rate increases slowly between 250 and 350 °C, then it rises steeply between 350 and 400 °C to reach $15\% \text{ min}^{-1}$. The transient residue is 10% at 450 °C. The second stage starts at 500 °C with a weight loss rate of $1.3\% \text{ min}^{-1}$. No residue is observed at 600 °C. The beginning of the first stage can be associated with the depolymerisation of PU. The first stage corresponds especially to the degradation of polyester segments. Polyester segments (PHMA 3800) represent about 84% of the total mass of ES PU shell. Polyesters like PHMA undergo several scission reactions [28] and products stemmed from scission and rearrangement reactions are decomposed during the second stage.

For the degradation of ES microcapsules of DAHP, one again finds the two main stages described previously for the neat PU shell of ES microcapsules. Nevertheless ES microcapsules of DAHP decompose slightly faster at

a lower temperature (200 °C) than the pure ES PU shell. In the same way as is the case for IP microcapsules of DAHP, depolycondensation of ES PU is catalysed by acidity from decomposition of DAHP. After the first stage at 450 °C, residual mass of ES microcapsules of DAHP (20%) is twice the residual mass of neat ES PU shell and a residue of 5 wt% is observed at 650 °C. This char residue of ES microcapsules of DAHP shows an interesting thermal stability even above 800 °C (4% at 800 °C).

If we compare the thermal behaviour of two types of DAHP microcapsules at low temperature (before 300 °C), it is worth noting that ES microcapsules of DAHP are much less decomposed than IP microcapsules of DAHP. At 300 °C, residual mass and degradation rate are respectively 75% and $3\% \text{ min}^{-1}$ for IP microcapsules against 94% and $1\% \text{ min}^{-1}$ for ES microcapsules. Our aim is to obtain with microcapsules of DAHP an intumescent formulation for PU textile coating and even other polymer materials. With the good thermal stability of ES microcapsules of DAHP up to 300 °C, these microcapsules could be added in polymers even if the processing temperature of these polymers is higher than 200 °C.

Fig. 2 shows the weight difference curves (explained in the part of TGA experiment) for the two types of DAHP microcapsules. These curves allow investigation of interactions between DAHP and the PU shell. Intumescent mechanism always starts by acceleration of degradation of material (thermal destabilisation), and then char with good thermal stability is produced. Acidic sources will accelerate degradation of the material in order to produce foamed cellular charred layers which protect the underlying material from the heat flux. The weight difference curves for the two types of microcapsules show characteristics of intumescent development. Indeed, we can observe a first temperature range with a thermal destabilisation followed by an improvement in thermal stability. Thermal destabilisation for ES microcapsules (over the temperature range

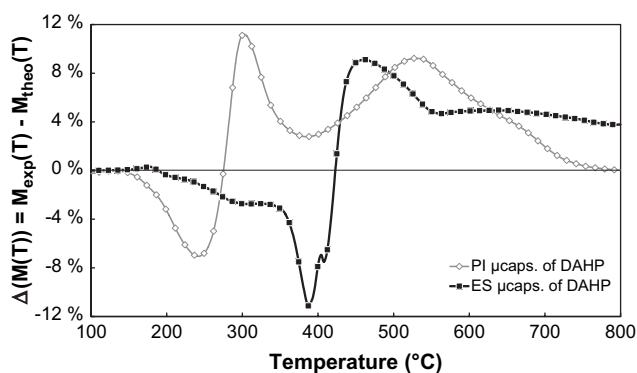


Fig. 2. Curves of residual mass difference for IP and ES microcapsules of DAHP.

from 200 to 420 °C, with a minimum of -12% at 390 °C) is more significant and higher than for IP microcapsules (with a temperature range from 150 to 270 °C, with a minimum of -7% at 245 °C). The intumescent mechanism takes place at a lower temperature for IP microcapsules than for ES microcapsules. Reactions between phosphoric acid (generated from DAHP) and products resulting from degradation of the PU shell allow similar thermal stabilisation at higher temperature ($+9\%$) for ES microcapsules (at 460 °C) and for IP microcapsules (at 530 °C). In the case of IP microcapsules (polyether polyurethane shell), thermal stabilisation decreases from 530 °C and becomes zero at 800 °C. In the case of ES microcapsules (polyester polyurethane shell), thermal stabilisation is constant ($+4\%$) from 530 °C to above 800 °C. Therefore, polyester PU is a better char former in intumescent formulations than polyether PU [1–3].

3.2. Reaction to fire of cotton fabrics coated by FR polyurea

The rate of heat release (RHR) is recognized to be the most important factor quantifying the size of fire [16]. RHR curves of different polyurea coatings on cotton fabric are presented in Fig. 3. The coating with 30% of untreated DAHP has the smallest RHR peak (170 kW m^{-2}). It is decreased by 30% compared to the RHR peak of virgin polyurea coating (242 kW m^{-2}). The two types of microencapsulated DAHP also indicate an efficient FR effect. In that, RHR peaks of Co[PUe-20% μ PI] and Co[PUe-20% μ ES] are respectively decreased by 20 and 19% with regard to the RHR peak of Co[PUe]. The coatings with 20% of microcapsules have a slightly better fire performance than that with 20% of neat DAHP for which the RHR peak is decreased by 16% in respect to the RHR peak of Co[PUe]. However RHR responses of coatings with microcapsules are wider than that of Co[PUe-20% DAHP]. Moreover a second small RHR peak is

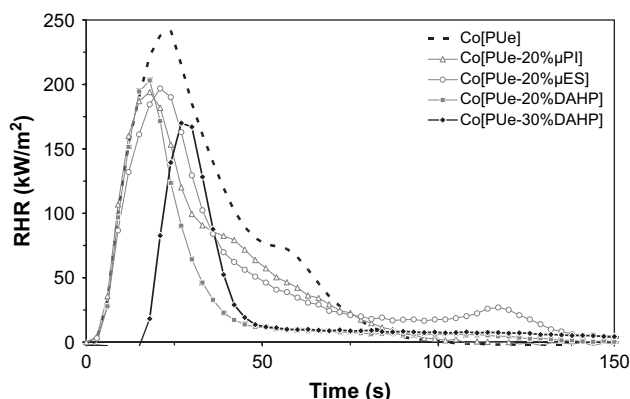


Fig. 3. RHR curves of different polyurea coatings on cotton fabrics.

observed for coatings with microcapsules as for virgin polyurea coating. In the case of Co[PUe], this second peak appears quickly followed by the total decomposition of the sample. This second peak occurs at 42 s for Co[PUe-20% μ PI] and at 117 s for Co[PUe-20% μ ES]. We can assume that the intumescent system within the microcapsules is less resistant to heat and flame stresses than that with DAHP alone. This second RHR peak corresponds to a crack of the intumescent char with a partly resumption of the combustion. It is also very important to remind the reader that 20% of IP and ES microcapsules correspond respectively only to 0.55% and 0.24% of pure DAHP.

The difference between coatings with microcapsules and coatings with DAHP alone is more distinguishable considering the total heat evolved (THE) curves (Fig. 4). At the end of combustion, virgin polyurea coating has evolved a total heat of 67 kJ. For the other coatings THE decreases in this order: 58 kJ, 52 kJ, 35 kJ and 28 kJ, respectively, for Co[PUe-20% μ ES], Co[PUe-20% μ PI], Co[PUe-20%DAHP] and Co[PUe-30%DAHP]. Even if the intumescent systems within microcapsules are not as mechanically resistant, coatings with microcapsules present not only a flame retardant effect but also an enhancement of fire resistance with regard to virgin polyurea coating. Co[PUe-20% μ ES] has a slightly weaker resistance to fire than Co[PUe-20% μ PI] but Co[PUe-20% μ ES] has also half less quantity of pure DAHP.

The FIGRA index is a good indicator of the contribution to fire growth of a material. FIGRA curves of the polyurea coatings are shown in Fig. 5. All coatings have a peak at about 12 s except that of Co[PUe-30%DAHP] which is delayed by 15 s. After 75 s, their FIGRA values are close to zero meaning that they have no contribution to the propagation of fire. Nevertheless, we can observe that the contribution to the fire growth is less for coatings with neat DAHP (from 50 s) than for coatings with microcapsules. Co[PUe-30%DAHP] has the smallest FIGRA peak (6

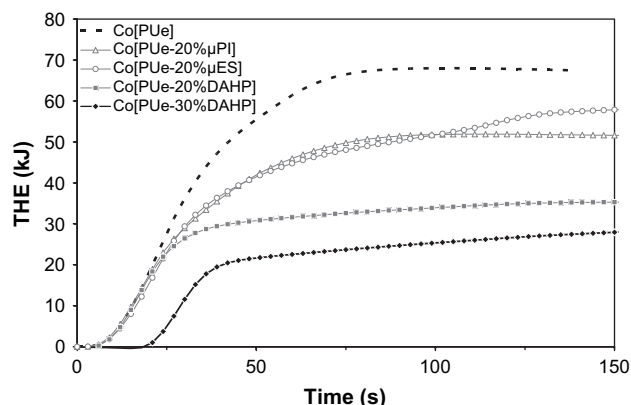


Fig. 4. THE curves of different polyurea coatings on cotton fabrics.

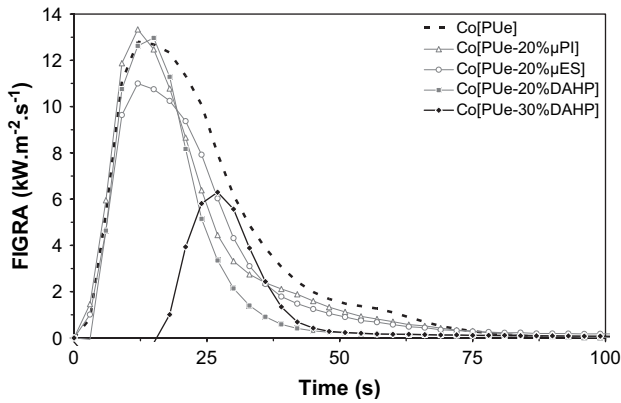


Fig. 5. FIGRA curves of different polyurea coatings on cotton fabrics.

$\text{kW m}^{-2} \text{s}^{-1}$). Even if the maximum FIGRA values for Co[PUe-20%DAHP] and Co[PUe-20% μ PI] are similar to the one for Co[PUe] ($13 \text{ kW m}^{-2} \text{s}^{-1}$), the peaks of Co[PUe-20% μ PI] and Co[PUe-20%DAHP] are less wide than that for Co[PUe]; thus Co[PUe-20% μ PI] and Co[PUe-20%DAHP] contribute less to fire growth than Co[PUe]. The FIGRA peak of Co[PUe-20% μ ES] is not only less wide but also much smaller ($11 \text{ kW m}^{-2} \text{s}^{-1}$) than that of Co[PUe].

The volume of smoke production (VSP) and the total VSP (T_{VSP}) evolved by the coated fabrics during combustion are illustrated in Figs. 6 and 7. All the coatings evolve smoke with a main peak at about 12 s except for Co[PUe-30%DAHP] (about 24 s). The Co[PUe-20% μ ES] sample evolves much less smoke than all other coatings, not only at the moment of the VSP peak ($0.0023 \text{ m}^3 \text{ s}^{-1}$) but also after; from 33 s onwards, the Co[PUe-20% μ ES] sample does not release any more smoke. Co[PUe-20% μ ES] is unique in that it produces a smaller total quantity of smoke (0.037 m^3) than Co[PUe] (0.051 m^3). Co[PUe] sample shows VSP peaks ($0.0039 \text{ m}^3 \text{ s}^{-1}$) slightly smaller than the one for Co[PUe-20% μ PI] ($0.0041 \text{ m}^3 \text{ s}^{-1}$) and more significant than Co[PUe-20%DAHP] ($0.0031 \text{ m}^3 \text{ s}^{-1}$) and Co[PUe-30%DAHP] ($0.0027 \text{ m}^3 \text{ s}^{-1}$). It is also

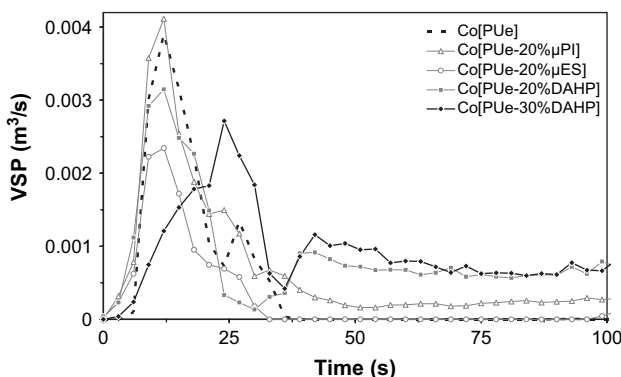


Fig. 6. VSP curves of different polyurea coatings on cotton fabrics.

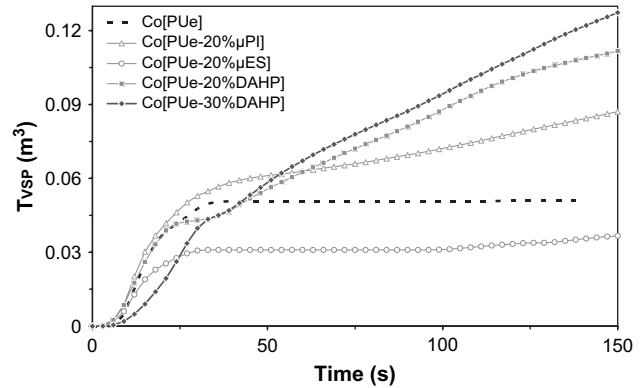


Fig. 7. Total VSP curves of different polyurea coatings on cotton fabrics.

observed that from about 60 s onwards T_{VSP} for Co[PUe-20% μ PI] is definitively smaller than for coatings containing DAHP. At 150 s, T_{VSP} is 0.087, 0.112 and 0.127 m^3 respectively for Co[PUe-20% μ PI], Co[PUe-20%DAHP] and Co[PUe-30%DAHP].

Figs. 8 and 9 present respectively the CO production versus time and the total quantity of CO (T_{CO}) evolved under the experimental conditions of the cone calorimeter. With regard to Co[PUe] with 21 cm^3 of final T_{CO} , coatings containing DAHP produce more CO (31 cm^3 for Co[PUe-20%DAHP] and 28 cm^3 for Co[PUe-30%DAHP]), while coatings with microcapsules produce less CO (18 cm^3 for the two types of microcapsules). It is interesting to see that at all times Co[PUe-20% μ ES] releases the smallest total quantity of CO.

Figs. 10 and 11 present respectively the CO_2 production versus time and the total quantity of CO_2 (T_{CO_2}) evolved. Between 27 s and 39 s, we observe the main peak of CO_2 for all the coatings. Co[PUe] shows the highest peak and evolves the highest total quantity of CO_2 (345 cm^3). CO_2 peaks of Co[PUe-20%DAHP] and Co[PUe-20% μ PI] are equivalent and slightly higher than the one for Co[PUe-20% μ ES]. Nevertheless at the end of their combustion, T_{CO_2} values of Co[PUe-20% μ

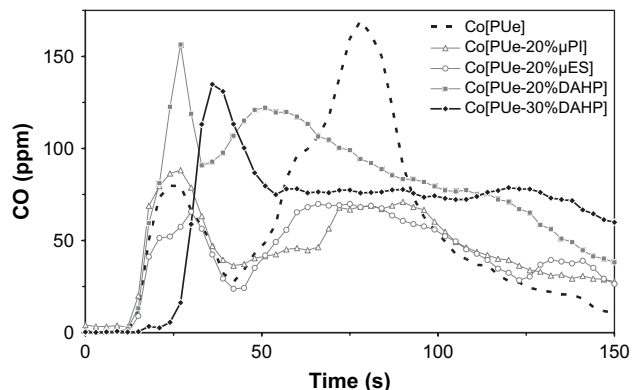


Fig. 8. CO curves of different polyurea coatings on cotton fabrics.

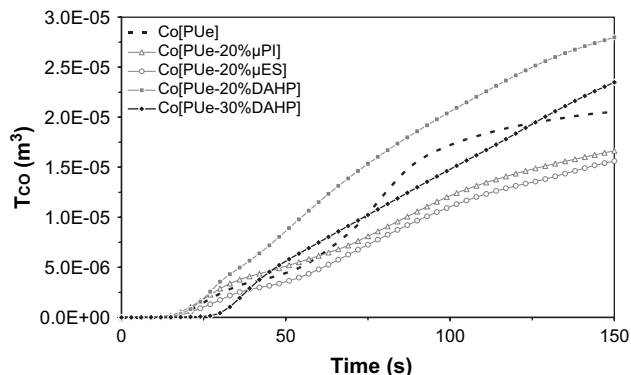


Fig. 9. Total evolved CO curves of different polyurea coatings on cotton fabrics.

PI], Co[PUe–20%µES] and Co[PUe–20%DAHP] are respectively 265, 220 and 152 cm³. Co[PUe–30%DAHP] shows the smallest peak and evolves the smallest total quantity of CO₂ (118 cm³).

4. Conclusions

Two types of microcapsules of di-ammonium hydrogen phosphate with polyether–polyurethane (IP microcapsules) and polyester–polyurethane (ES microcapsules) shells respectively were evaluated as intumescent FR agents in commercial polyurea coatings for textile fabrics. The expected advantages of this new concept of encapsulated FR agent lie in its being compatible with the polymeric matrix in order to give a permanent FR effect and while being an efficient FR intumescent formulation for many materials.

Microcapsules and their components (e.g. DAHP and PU shell alone) have been examined by thermal analysis in air. Curves of weight difference between the experimental and theoretical TG responses for the two types of microcapsules show evidence of interactions between DAHP and PU shell. The two types of

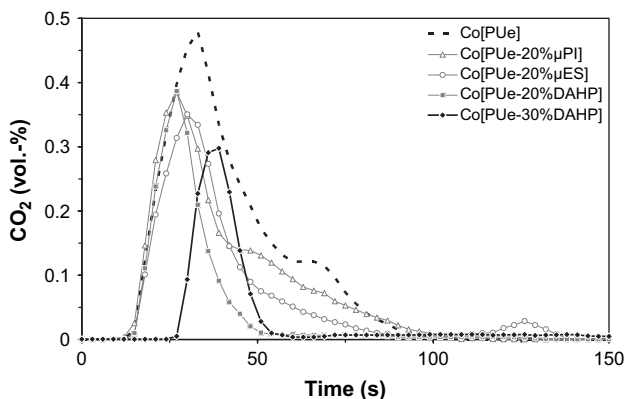


Fig. 10. CO₂ curves of different polyurea coatings on cotton fabrics.

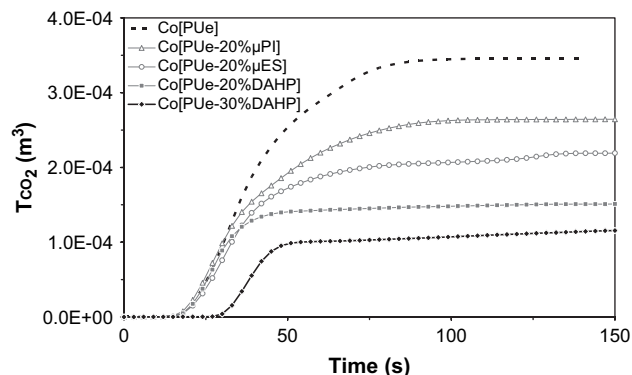


Fig. 11. Total evolved CO₂ curves of different polyurea coatings on cotton fabrics.

microcapsules exhibit a significant stabilization at high temperatures (above 450 °C) with production of thermal stable char that can be attributed to the development of an intumescent structure. In contrast to IP microcapsules, ES microcapsules could be added to materials at temperature above 150 °C because these microcapsules are thermally stable until 200 °C.

The reaction to fire of cotton fabrics coated by FR polyurea loaded with neat or microencapsulated DAHP was studied by cone calorimetry. The coatings with 20% of IP or ES microcapsules show decreases in propensity to spread flame with regard to virgin polyurea coating. Their decreases of RHR peaks are similar to that for a coating with 20% of DAHP only. But in comparison with encapsulated DAHP formulations, neat DAHP formulations present smaller total heat evolutions, and thus a greater enhancement in fire resistance. Microencapsulated DAHP does not develop a strong enough intumescent shield to resist heat and flame stresses and develops cracks in the intumescent structure. It is worth noting that coatings with ES microcapsules evolve smaller quantities of smoke and CO than virgin polyurea and all other FR coatings.

Future work will be needed to increase the encapsulation yield of DAHP. We will also evaluate whether the FR property of microencapsulated DAHP is permanent. The microcapsules of DAHP with PU shell will be studied as the intumescent flame retardant component in different polymers.

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