



Flame retardancy of rigid polyurethane foams containing thermoregulating microcapsules with phosphazene-based monomers

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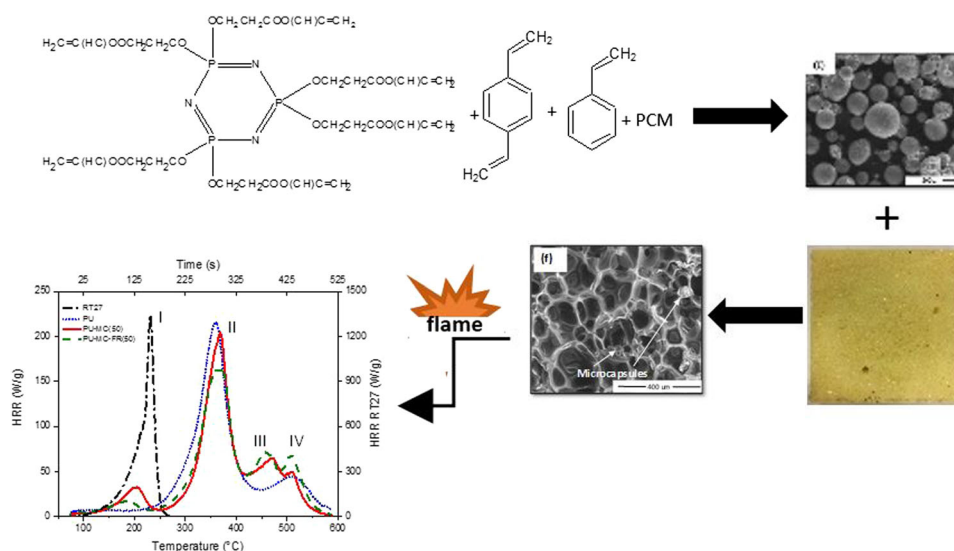
ABSTRACT

Thermoregulating microcapsules (MC) with flame-retardant properties were used to produce polyurethane (PU) foams. Thermogravimetric analyses of the microcapsules performed under atmospheric air and nitrogen confirmed that the hexa(methacryloylethylenedioxy) cyclotriphosphazene (PNC-HEMA) monomer raised the amount of residue after exposure to high temperature, proving the formation of a thermally stable char layer. Additionally, the flame-retardant properties of the microcapsules were analyzed by micro-combustion calorimetry (MCC), and the PU foams were tested by both MCC and cone calorimetry. The total heat release and maximum heat release rate were lower for microcapsules containing the flame-retardant PNC-HEMA. The composition of the microcapsules has been proved by MCC and TGA, where the release of the encapsulated phase change material (PCM) occurred at the expected temperature. However, in PU foams, the release of PCM is shifted to higher temperatures. Accordingly, these materials can be considered as an important alternative to commonly used microcapsules containing phase PCMs, where a lower flammability is required for their future application.

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GRAPHIC ABSTRACT



Introduction

The total energy consumption is increasing quickly every year whereas the production of environmentally friendly energy is not enough to ensure the energy demand, which results in undesired environmental consequences. In order to address these issues, passive solar systems implemented in various building parts can be a partial but effective solution to reduce the energy consumption. Since the source of the solar energy is time dependent and affected by weather conditions, an effective solar system requires utilization of compounds which absorb, store and release energy. One of the compounds that fulfills these requirements is phase change materials (PCM), which are thermal energy storage materials. PCMs are divided into organic, inorganic and eutectics compounds [1]. However, utilizing bulk quantities of organic PCMs such as paraffin or fatty acids results in low thermal conductivity, flammability, solidification around the edges, and diminished heat transfer [2, 3]. In order to solve these problems, microencapsulation can be employed. The shell of the microcapsules prevents leakage of the encapsulated PCMs, and interactions with the building materials. In addition, it improves the heat transfer area per microcapsule

unit volume and ensures the ability to withstand volume change during phase change [4]. Unfortunately, drawbacks such as lower thermal conductivity and increased flammability limit the application of these thermoregulating microcapsules.

Improved fire resistance and decreased flammability of microencapsulated paraffin are important for many applications. Several methods have been suggested to reduce the flammability of building materials containing PCMs. Building blocks containing PCMs can be surrounded on all sides with non-combustible concrete without changing the strength of the block [5]. Kośny et al. [6] developed ignition-resistant microencapsulated PCM using fatty acids esters with a phase change enthalpy of approximately 170 J/g, covering the surface of the microcapsules with a flame-retardant agent. PCM has also been applied to two fiber-based insulation systems: PCM-enhanced cellulose insulation [7] and a blend of PCM with blown fiberglass [8]. These insulations are designed to be used in residential walls and attics. Cellulose-based insulation containing PCM with a total phase change enthalpy of 121 J/g has provided an average reduction of cooling-dominated loads of 42 and 5% at sites in Tennessee and South Carolina, respectively. Banu et al. [9] tested gypsum wallboards impregnated with approximately 24% organic

PCM, and discussed the possibilities of reducing the flammability. Cai et al. [10–16] explored how to improve the flame retardancy of a form-stable PCM based on paraffin and high-density polyethylene with and without ethylene–vinyl acetate. Different types of fire retardants such as expandable graphite, ammonium polyphosphate, zinc borate, pentaerythritol, brominated fire-retardant, melamine phosphate, antimony oxide, melamine cyanurate, organophilic montmorillonite, magnesium hydroxide and red phosphorus microencapsulated with melamine formaldehyde were used. The phase change enthalpies of these materials are up to 100 J/g. Furthermore, possible synergistic effects between these fire retardants were examined. TGA analyses showed that the addition of these compounds improved the thermal stability of paraffin in form-stable PCM with little influence on thermal energy storage.

Nitrogen and phosphorus elements have flame-retardant properties, and they can be found in molecules such as hexachlorophosphazene (PNC) which has gained a great interest as a flame-retardant agent, since it can be considered as an environmentally friendly alternative to the existing halogenated compounds [17]. PNC was previously utilized to modify the fire-retardant properties of epoxy resins [18, 19]. The PNC-HEMA (hexa(methacryloylethylenedioxy)cyclotriphosphazene) monomer containing rings consisting of alternating phosphorus and nitrogen atoms in their chemical structure exhibits excellent flame-retardant properties due to the larger bonding energy compared to homoatomic bonds [20, 21]. It is believed that the thermal decomposition of the phosphazene-based polymers is an endothermic process in which phosphate, metaphosphate and polyphosphate are generated, forming a non-volatile protective film on the polymeric surface thereby isolating it from the air. Additionally, non-flammable gases such as CO₂, NH₃ and N₂ are released, preventing the supply of oxygen [22]. The objective of the current work is to improve flame retardancy of thermoregulating microcapsules by incorporating PNC for application in the production of polyurethane (PU) foam with thermal energy storage (TES) capability.

Polyurethane foams with phase change materials enhance the energy storage properties [23–25]. Additionally, polyurethane foams with flame-retardant modifications have been extensively reported in the literature [26–28]. Modified products revealed

significantly improved flame-retardant performance, i.e., reduced total heat release, longer time to ignition and higher amount of residue. However, none of the utilized products combined both thermal energy storage and flame retardancy. Since the PCMs behave as additional fuel in the foam, polyurethane foams containing flame-retardant PCM-microcapsules are not directly comparable with previous literature. In a previous work, thermoregulating microcapsules from PNC-HEMA were developed, and their enhanced flame retardancy properties were confirmed [20]. The current work explores the flame-retardant abilities that such microcapsules induce into the thermoregulating polyurethane foams. This material is expected to exhibit enhanced thermal energy storage for energy-saving purposes, combined with flame retardancy for use in building applications. This study opens a door for designing and development of flame-retardant thermal energy storage materials.

Experimental

Material

Polyol R-4520 (Repsol YPF S.A., Spain) and polymeric methylene diphenyl diisocyanate (PMDI) (AISMAR S.A., Spain) were used for the synthesis of rigid polyurethane foam. Tegoamin 33 and Tegostab B8404 (supplied by Evonik Degussa International AG) were utilized as catalysts and surfactants, respectively. Microcapsules were synthesized by suspension-like polymerization. The synthesis consists of a continuous phase containing water and the suspending agent, and a discontinuous phase containing monomers, PCM, porogen and initiator. The synthesis of microcapsules (MC) was performed in the same way as in previously reported procedures [20, 29]. The PCM (Rubitherm®RT27; denoted as RT27) content of the prepared microcapsules varied from 0 to 68 wt%, and the flame-retardant monomer (FR) PNC-HEMA was utilized at 0 or 10 part per hundred of monomer. The composition and basic properties of the samples are shown in Table 1. The materials have been denoted MP (microparticles without RT27) and MC (microcapsules containing RT27). The presence of flame-retardant monomer PNC-HEMA is denoted by FR, and the content of RT27 is given in the parenthesis. The presence of PNC-HEMA in the shell of the

Table 1 The compositions, mean volume average particle diameter, $d_{v0.5}$ (representing the value where 50% of the sample is less or equal to $d_{v0.5}$), and latent heat of the studied microcapsules

Sample name	RT27 (wt%) ^a	PNC-HEMA pph ^b	$d_{v0.5}$ (μm)	ΔH (J g^{-1})	C_{PCM} (%)
MP	0	0	324	-	-
MP-FR	0	10	305	-	-
MC(32)	32	0	283	48.73	28.46
MC-FR(32)	32	10	224	47.25	27.60
MC(50)	50	0	268	78.01	45.57
MC-FR(50)	50	10	188	79.40	46.38
MC(68)	68	0	249	101.80	59.46
MC-FR(68)	68	10	112	109.00	63.67

^aBased on monomer and RT27 amounts^bBased on monomer amounts

microcapsules was confirmed by EDAX-analysis (data not shown).

Polyurethane foam preparation

Initially, all components of rigid polyurethane foams were weighted using an analytical digital balance according to the formulation shown in Table 2. The desired masses of the polyol, water, amine, silicone and microcapsules were stirred for 1 min. The corresponding amount of isocyanate was added to the mixture and stirred for 5 s until the foam started to grow. The obtained foams were cured at room temperature for at least 24 h. As a first approach to explore the effect of thermoregulating microcapsules on the flame retardancy properties of polyurethane foams, MC(50) and MC-FR(50) have been chosen. In previous works, it was confirmed that 10 wt% microcapsules favor a nucleating effect, i.e., the mechanical properties remained at a similar level as for polyurethane foams without fillers [30, 31]. Hence, polyurethane foams were prepared with 10 wt% of microcapsules with and without PNC-HEMA.

Table 2 Formulation of the polyurethane foam

Compound	PU	PU-MC/PU-MC-FR (g)
Polyol R-4520	40.00 g	40.00
H ₂ O	0.66 g	0.66
Tegoamin 33	0.73 g	0.73
PMDI	58.21 g	58.21
Tegostab B8404	0.66 g	0.66
Silicone	0.13 g	0.39
Microcapsules (MC(50) or MC-FR(50))	0.00	11.18

Characterization

Density

The apparent density of the PU foam samples was measured according to ASTM D 1622–03. The size of the specimen was 25 × 25 × 25 mm (length × width × thickness). The apparent densities of three specimens per sample were measured, and then the average values are reported.

Scanning electron microscopy

Quanta 250 (FEI Company) with a tungsten filament operating at a working potential 10.0 kV or 15 kV was used for studying the morphology and surface features of the microcapsules. The Secondary Electron detector (LFD—Large Field Detector) was applied.

Differential scanning calorimetry

The latent heat storage capacity of synthesized and used reagents was determined by a differential scanning calorimetry model DSC Q100 of TA Instruments equipped with a refrigerated cooling system and nitrogen as the purge gas. Measurements

were conducted in the temperature range -40 to 80 °C at a heating or cooling rate of 3 °C/min.

The PCM content (C_{PCM}) in the microcapsules was determined by the changes in enthalpy:

$$C_{PCM}(\%) = \frac{\Delta H_{MC}}{\Delta H_{PCM}} \times 100\% \quad (1)$$

where ΔH_{MC} and ΔH_{PCM} are the latent heat of fusion for the microcapsules and pure PCM, respectively.

Thermogravimetric analysis

The thermal stability of the synthesized microcapsules was obtained using a TA instruments SDT Q600 Simultaneous DSC-TGA from room temperature to 600 °C at a heating rate of 10 °C/min under a nitrogen or air atmosphere. This equipment has a calorimetric precision of $\pm 2\%$ (based on metal standards) and a balanced sensitivity of 0.1 µg.

Microscale combustion calorimetry

Micro-combustion calorimetry (MCC) was performed in the FTT Micro Calorimeter (Fire Testing Technology Ltd., United Kingdom) at Lund University. Ca. 6 mg of each sample was weighed with an analytical balance and placed in an MCC for rapid pyrolysis. Samples were heated from 75 to 600 °C at a heating rate 1 °C/s in a stream of nitrogen. After pyrolysis, the volatilized decomposition products were transferred to a combustion furnace set at 900 °C and the oxygen/nitrogen flow rate was set at $20/80$ ml/ml. The amount of spent oxygen was measured with an oxygen analyzer and used to calculate the heat release rate (HRR). Three specimens of each material were analyzed, and the average result is reported. Heat release rate dQ/dt (W) is proportional to the mass generation rate (g/s) of volatile fuel, i.e., the mass loss rate of the solid. The total heat release (THR) is the heat of complete combustion of the pyrolysis gases per unit initial mass of solid material, and the heat release capacity (HRC) is a derived quantity that represents the maximum capability (capacity) of a material to release combustion heat per degree of temperature rise during pyrolysis or burning [32].

Cone calorimetry

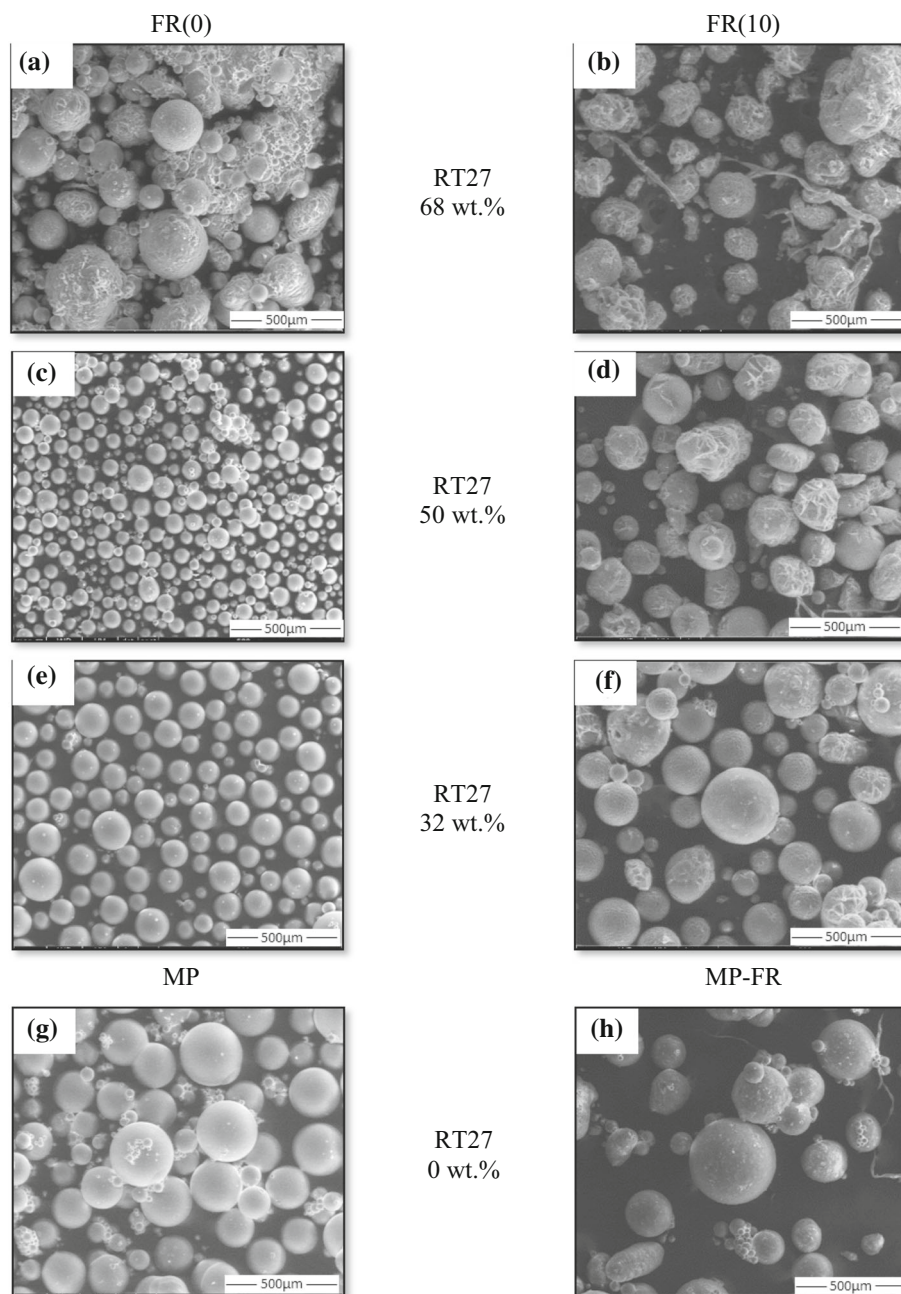
In order to determine the influence of microcapsules on the flammability of the rigid polyurethane foams, a cone calorimeter at Lund University (supplied by Fire Testing Technology Ltd., United Kingdom) was used. The specimens were exposed to a heat flux of 35 kW/m², corresponding to approximately 650 °C at the cone surface. The tests were performed according to ISO 5660. Samples with a size of $10 \times 10 \times 2.5$ cm were analyzed in a horizontal position, with the exhaust duct flow rate set at 0.024 m³/s. The duration of each test was set until 2 min after any flaming or combustion signs ceased. Before testing, the samples were wrapped in a single layer of aluminum foil, covering the unexposed surfaces with the shiny side toward the specimen. For each polyurethane foam, three specimens were tested.

Results and discussion

Microcapsules with flame-retardant properties

The microcapsules with various amounts of the paraffin Rubitherm®RT27 (RT27) as the core and a copolymer of styrene (S), divinylbenzene (DVB) and hexa(methacryloylethylenedioxy)cyclotriphosphazene (PNC-HEMA) as a shell were synthesized by suspension-like polymerization. The synthesis was performed with 0 , 32 , 50 and 68% RT27. The SEM images of the resulting microcapsules and particles without RT27 are presented in Fig. 1. Products with a shell of S-DVB copolymer (P(S-DVB)) always exhibited a perfectly smooth and spherical shape. On the other hand, shells of S, DVB and PNC-HEMA terpolymer (P(S-DVB-PNC-HEMA)) resulted in a morphology varying according to RT27/monomer and S-DVB/PNC-HEMA mass ratios. For low RT27/monomer mass ratios, the morphology of the microcapsules was spherical with smooth surfaces, while higher mass ratios resulted in a rougher surface. Furthermore, particles synthesized by using PNC-HEMA without RT27 exhibit smooth and spherical surfaces. Similar results were observed by Luo et al. [33] who reported improved morphology with increasing monomer content. In the presence of PNC-HEMA, the morphology might be affected by unsubstituted hydroxyl groups that remain in the

Figure 1 SEM images for synthesized microcapsules and particles: **a** MC(68), **b** MC-FR(68), **c** MC(50), **d** MC-FR(50), **e** MC(32), **f** MC-FR(32), **g** MP and **h** MP-FR.



HEMA and do not react with the six active sites of PNC, or by the high compressive strength of the copolymer which leads to a higher hardness of the shell. Particles exhibiting high hardness can be broken due to the vigorous stirring required in the suspension-like polymerization process [20]. Accordingly, the morphology of the microcapsules from P(S-DVB-PNC-HEMA) is strongly affected by the PCM content.

Figure 2 presents the TG and DTG curves of neat PNC-HEMA monomer, and particles with (MP-FR) and without (MP) PNC-HEMA obtained under air

atmosphere. The neat PNC-HEMA revealed a thermo-oxidative degradation of the monomer over a wide temperature range from 280 to 700 °C with a final residue of 66.33 wt%. The residue contains thermo-oxidative products from the phosphazene fraction. The phosphorous compound promotes char formation at the surface of the condensed phase. This prevents the diffusion of oxygen to the internal part, rendering the internal polymer unavailable for burning. Further burning of the residue could be potentially activated at higher temperatures. The

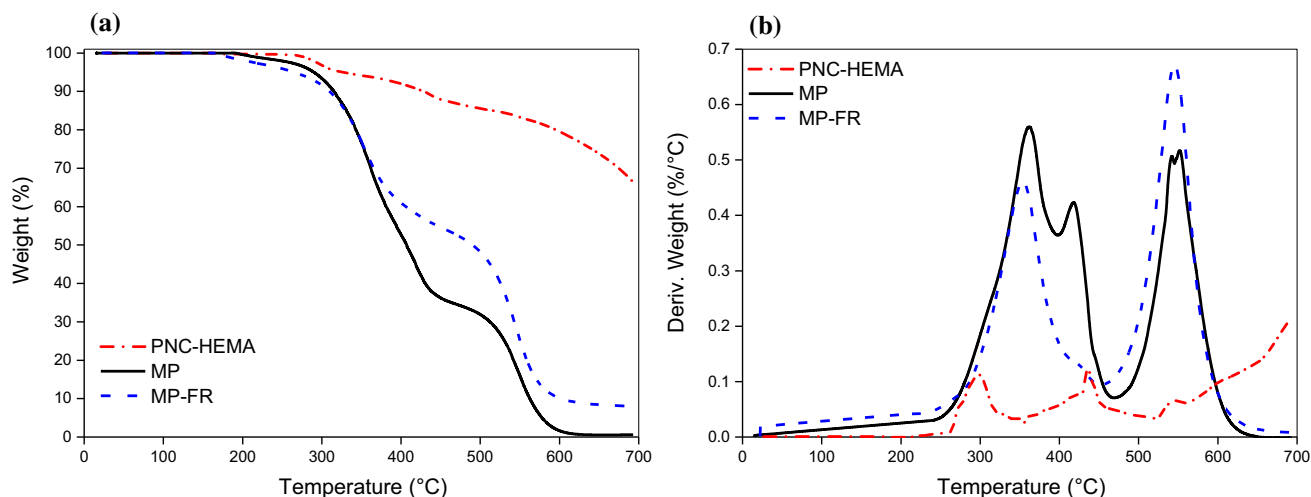


Figure 2 Degradation curves of neat PNC-HEMA and particles with (MP-FR) and without (MP) PNC-HEMA, under air atmosphere: **a** thermogravimetry (TG) and **b** derivative thermogravimetry (DTG).

particles exhibited two different weight loss regions, corresponding to the polymer thermal-oxidative degradation and further degradation of the char layer formed at high temperatures. The thermo-oxidative degradation temperature of 50% of the samples shifts from 404 °C to 482 °C in the presence of PNC-HEMA, and the char yield was 10% higher for PNC-HEMA containing microparticles (MP-FR) than for corresponding particles without PNC-HEMA (MP). This illustrates that the addition of PNC-HEMA improves the carbon forming process and that the formed carbon layer was beneficial to prevent heat diffusion and heat transfer to the whole material, and effectively hinder further combustion [34].

The TGA and DTG curves under the nitrogen atmosphere of flame-retardant particles and microcapsules are shown in Fig. 3. Contrary to the measurement performed under air, the thermal degradation temperature of flame-retardant particles (MP-FR) was one step between 150 °C and 450 °C, showing the fracture of the crosslinked polymer network. The microcapsules containing different amounts of RT27 exhibited two weight losses. The first one corresponds to the RT27 evaporation. As expected, the RT27 weight loss increases when the amount of RT27 in the microcapsules is raised (Fig. 3c). The second weight loss is related to the shell decomposition, which decreases when the amount of RT27 in the capsules becomes higher since this reduces the weight fraction of polymer shell in the capsules. The RT27 and polymer weight losses are in good agreement with the composition of the

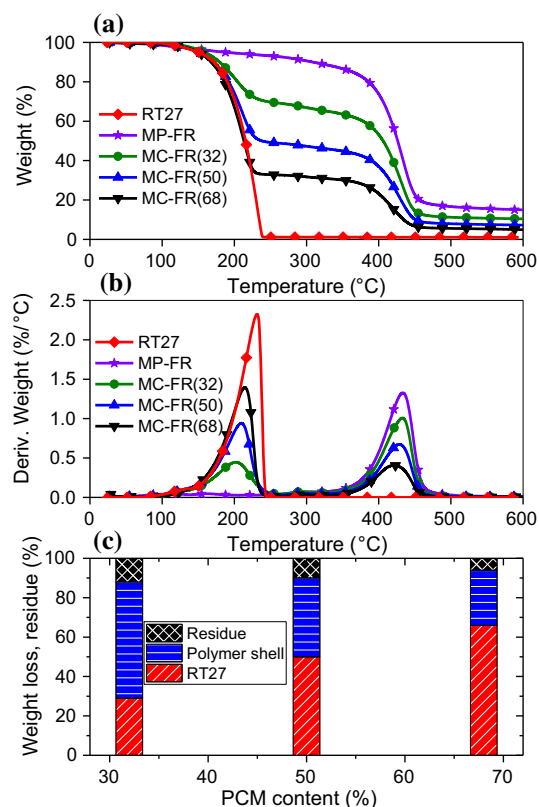


Figure 3 Degradation curves of microcapsules containing PNC-HEMA and pure RT27 core material under nitrogen atmosphere: **a** thermogravimetry (TG), **b** derivative thermogravimetry (DTG) and **c** residue, and weight loss of the RT27 and polymer shell.

microcapsules obtained by DSC. The residue (Fig. 3c) increased with the amount of polymer in the composition (lower RT27 content).

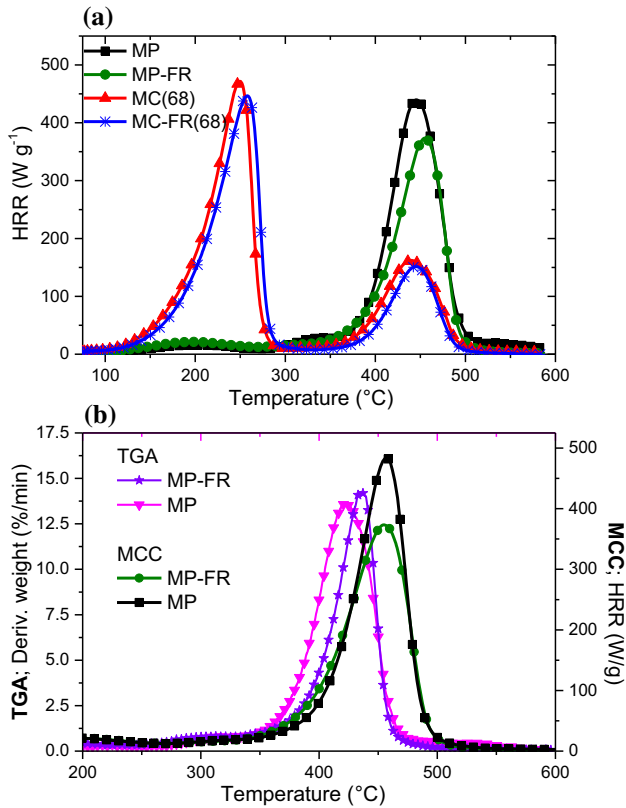


Figure 4 **a** Heat release rate (HRR) of microcapsules with RT27 (MC(68)), flame-retardant microcapsules with RT27 (MC-FR(68)), microparticles without RT27 (MP) and flame-retardant microparticles without RT27 (MP-FR), and **b** comparison of micro-combustion calorimetry (MCC) and thermal gravimetric analysis (TGA) for microparticles with and without PNC-HEMA (MP-FR and MP).

Micro-combustion calorimetry (MCC) is a useful technique to investigate the effect of microcapsule composition relating the chemical structure of the compounds to the combustion behavior based on oxygen consumption theory and quite often at higher heating rates. This analysis was carried out for all materials (microcapsules and microparticles). Figure 4a shows heat release rate curves as a function of temperature for microparticles without RT27 with and without PNC-HEMA (MP-FR; MP) compared to the corresponding microcapsules with the highest RT27 content (MC-FR(68); MC(68)), illustrating the RT27 influence on the MCC released energy as well as the effect of PNC-HEMA. The heat release rate (HRR) curves for microparticles without RT27 (MP-FR; MP) revealed one peak, representing polymer pyrolysis. Whereas the microcapsules with RT27 (MC(68); MC-FR(68)) exhibit an additional RT27 peak

at lower temperatures. The HRR curves for the samples with PNC-HEMA (MP-FR; MC-FR(68)) are significantly lower than for the corresponding samples without (MP; MC(68)). Accordingly, the energy released during the pyrolysis of microparticles and microcapsules with PNC-HEMA is lower. Comparing results from MCC with TGA (both carried out under nitrogen atmosphere) illustrates a shift of the degradation peak of the polymer toward higher temperatures in MCC than in TGA (Fig. 4b). This is probably due to the differences in heating rates (60 $^{\circ}C/min$ for MCC and 10 $^{\circ}C/min$ for TGA).

As expected, microcapsules with encapsulated RT27 exhibit two peaks, the heat released during the pyrolysis of RT27 and polymer, respectively. Peak heat release rate I (PHRR I) is the heat released during the pyrolysis of RT27, and is therefore absent for the samples without RT27, and increases with RT27 content (Fig. 5a). Peak heat release rate II (PHRR II)

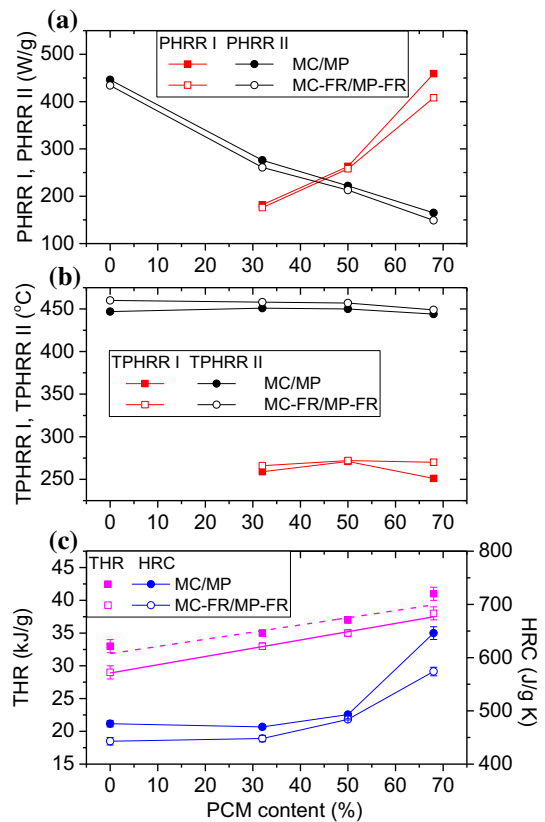


Figure 5 **a** Peak heat release rate I (PHRR I) for RT27 pyrolysis and peak heat release rate II (PHRR II) for pyrolysis of polymer shell, **b** the temperatures associated with RT27 (TPHRR I) and polymer (TPHRR II) pyrolysis and **c** the total heat release (THR) and heat release capacity (HRC), for microparticles (MP) and microcapsules (MC) with and without PNC-HEMA.

represents the pyrolysis of the polymer shell, and decreases with RT27 content (Fig. 5a) since a higher RT27 content corresponds to a lower amount of polymer shell. Both peaks are lower in the presence of PNC-HEMA (Fig. 5a), confirming that the flammability of the material is reduced. In addition, the temperatures associated with RT27 and polymer pyrolysis (TPHRR I and TPHRR II) are shifted to higher values for microcapsules containing PNC-HEMA (Fig. 5b).

As illustrated in Fig. 5c, the total heat release (THR) and heat release capacity (HRC) are both reduced for the samples containing the flame-retardant PNC-HEMA, thereby providing the desired flame-retardant properties. The lower THR of microcapsules with PNC-HEMA compared to microcapsules without indicates that more volatile products are carbonized to participate in the charring process [35]. The heat release capacity (HRC) can be used as a reliable indicator of a polymer's flammability [36]. The presence of the flame-retardant PNC-HEMA as a co-monomer in the microcapsules and microparticles leads to a decrease of HRC, suggesting a lower flammability. The phosphazene in the PNC-HEMA located at the microcapsules surface is expected to promote the polymer decomposition toward char products and inhibit heat transfer to the internal part of the material. In addition, non-flammable gases such as CO_2 , NH_3 and N_2 could be released [34].

In order to evaluate the validity of the utilization of micro-combustion calorimetry for microcapsules analysis, the deviation of the energy released by RT27

and both polymer shells was compared in Fig. 6. Neat RT27, MP and MP-FR (lines) are plotted against released energy calculated for microcapsules (points). The peak area that corresponds to RT27 is in good agreement with values obtained for all microcapsules. Similarly, in Fig. 6b, the energy released by the polymer is scattered between both types of shell. The results illustrate that the method is suitable for the evaluation of the microcapsules.

Application of microcapsules in polyurethane foam

With the aim to evaluate the effectiveness of the thermoregulating microcapsules in building materials, three different rigid polyurethane (PU) foams were produced. The microcapsules with 50% RT27 were selected to be incorporated in polyurethane foams, since these microcapsules exhibited optimal latent heat and improved flame-retardant properties, in addition to a spherical, non-damaged morphology. Polyurethane foams with and without microcapsules were characterized in terms of their thermal energy storage and the influence of microcapsules on the reaction to fire.

The apparent density of these PU foams are 74 kg/m^3 for PU, 95 kg/m^3 PU-MC(50), and 83 kg/m^3 for PU-MC-FR(50). As expected, the density increases with the addition of microcapsules. This is due to a higher total mass corresponding to the addition of microcapsules, combined with a reduction of the final foam height [30]. MC-FR(50) is smaller than MC(50) ($188 \mu\text{m}$ and $268 \mu\text{m}$, respectively). A lower particle size results in a better filler distribution in the PU

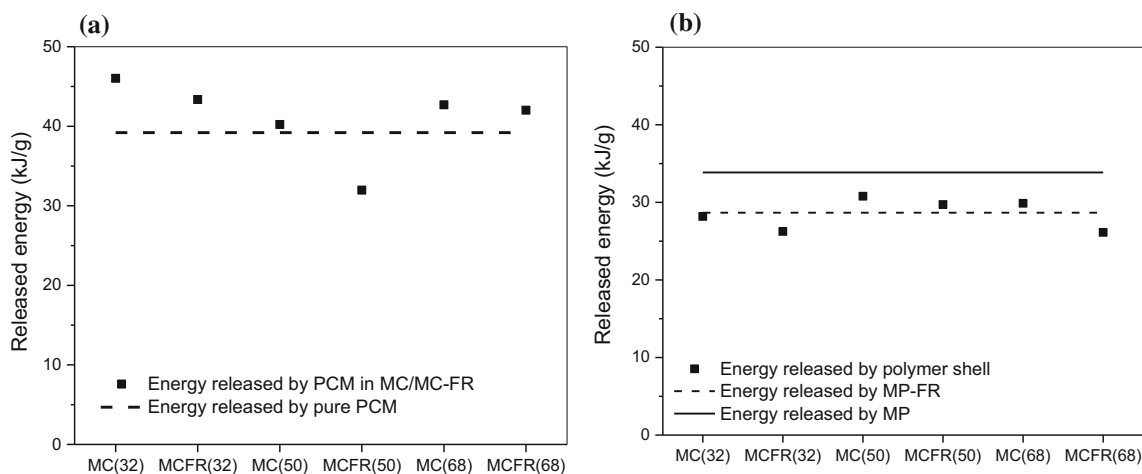


Figure 6 Deviation between energy released by neat RT27 and microcapsules **a**, and between polymer shell and microcapsules **b**.

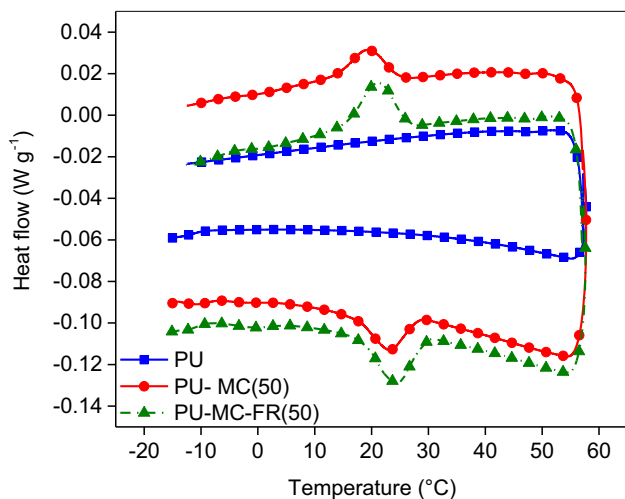


Figure 7 DSC curves of the polyurethane foam without microcapsules (PU), polyurethane foam with microcapsules without PNC-HEMA (PU-MC(50)), and polyurethane foam with microcapsules containing PNC-HEMA (PU-MC-FR(50)).

foam [37], which might explain the lower density of PU-MC-FR(50) compared to PU-MC(50).

In order to analyze thermal energy storage capacity of microcapsules in the polyurethane foam, DSC measurements were performed in the polyurethane foam, DSC measurements were performed and the thermograms are shown in Fig. 7. As expected, the polyurethane foam did not exhibit any heat absorption or release around the melting point of RT27. When microcapsules were added, peaks during heating and cooling were observed. The latent heat for PU-MC(50) and PU-MC-FR(50) was 4.36 and 5.26 J/g, respectively. Differences in the detected latent heat of polyurethane foams are influenced by the latent heat of the microcapsules, which in turn are associated with their morphology [29]. In the PU foam, we can observe a latent heat profile along with the height of the foams. The TES capacities are found to be higher at the bottom of the foams than at the top, indicating that the produced CO₂ was not enough to distribute the microcapsules through the whole foam and achieve a uniform microcapsules distribution. Accordingly, a deviation between the experimental and the theoretical TES capacities is observed. This effect has been previously reported in [37], where several samples from different zones were analyzed and the average value reported.

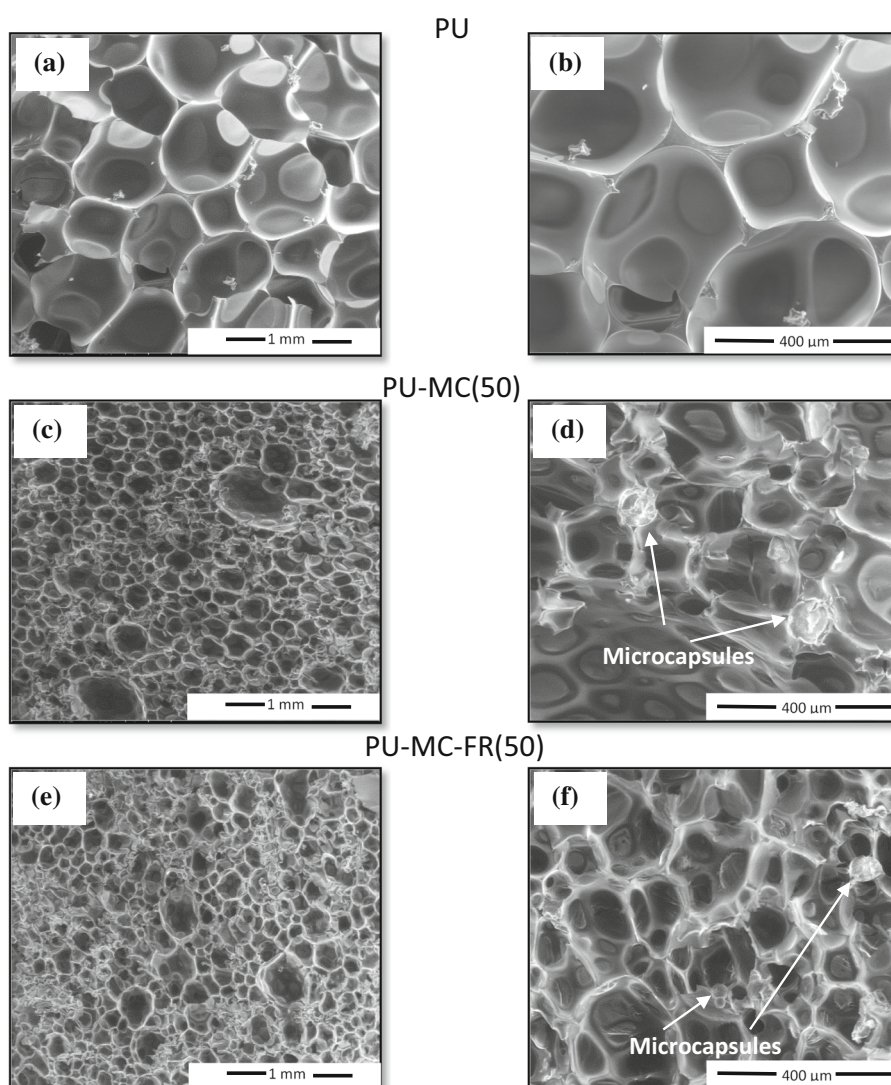
Scanning electron microscopy was used to evaluate the changes in the foam structure. Figure 8 displays the SEM images of the polyurethane foams. The rigid

polyurethane foams revealed porous, polyhedral closed-cell structures with pentagonal or hexagonal faces, similar to previous findings [30, 37]. Nevertheless, a significant difference in the cell size can be observed for foams with and without microcapsules. The cell size was reduced from 700 μm in the absence of microcapsules to about 162 μm in the presence of microcapsules. The decreased cell size can be attributed to the increased viscosity of the foam in the presence of microcapsules, and the enhancement of nucleation [37, 38]. Microcapsules (indicated with arrows) can be observed in the nodes of the cells. Some of them are broken; however, this might be due to cutting of the foam during sample preparation.

Micro-combustion calorimetry was performed with the aim to evaluate the influence of microcapsules on the fire properties of polyurethane foam as well as the effect of the flame-retardant PNC-HEMA as an additional monomer in the synthesis of the microcapsules. Figure 9 illustrates the heat release rate (HRR) curves versus the temperature of the synthesized polyurethane foams. Four peaks are distinguishable, two correspond to microcapsules (peak I—RT27 and peak III—shell) and another two related to polyurethane being the degradation of hard segments (peak II) and soft segments (peak IV) [39, 40]. For polyurethane foam without microcapsules, a small initial heat release was observed. This is probably due to low volatile compounds and/or unreacted monomers. The peak was integrated, and the polyurethane fraction of the heat release was subtracted from the RT27 peaks to estimate the heat release from RT27. The RT27 heat released decreased from 1111 J/s for the samples without PNC-HEMA (PU-MC(50)) to 233 J/s for the samples containing flame-retardant microcapsules (PU-MC-FR(50)). Although the flame-retardant microcapsules were not able to completely prevent the burning of the polyurethane foam, a fraction of the RT27 is trapped in the condensed phase, contributing to a lower total heat release.

As can be seen in both Figs. 9 and 10a, the main polyurethane foam peak (II) is lower in the presence of the microcapsules containing PNC-HEMA than for the other samples. The peak corresponding to the polymer shell is similar for both types of microcapsules (Fig. 10a), while the peak IV decreased for the polyurethane foam containing microcapsules without PNC-HEMA (PU-MC(50)). Lower PHRR I and II for the sample containing flame-retardant microcapsules indicate that the material pyrolysis was delayed,

Figure 8 SEM images of (a, b) polyurethane foam without microcapsules (PU), (c, d) polyurethane foam with microcapsules without PNC-HEMA (PU-MC(50)) and (e, f) polyurethane foam with microcapsules containing PNC-HEMA (PU-MC-FR(50)).



while PHRR III and IV are higher for the material containing PNC-HEMA. The flame-retardant microcapsules did not catalyze the pyrolysis of the polyurethane foam and were able to form a passive layer avoiding faster evaporation. Decreasing PHRR when fire retardants are added is in agreement with previous findings [41]. Similar changes were found for the temperatures at which peaks could be observed (Fig. 10b). The temperature of peak heat release of RT27 dropped in the presence of flame-retardant microcapsules, whereas the temperature corresponding to hard segments, polymer shell and soft segments heat release increased. As is evident from Fig. 10c, both the heat release capacity and total heat release are highest for the polyurethane foam containing microcapsules without PNC-HEMA, confirming that the flame-retardant microcapsules

prevent the polyurethane foam from becoming more flammable.

Cone calorimetry is based on the principle of oxygen consumption during combustion of a sample subjected to a given heat flux [42] and is, therefore, a very relevant technique to evaluate the flame retardancy of materials containing phosphazenes. Figure 11a shows the cone calorimetry heat release rate of the polyurethane without and with different types of microcapsules, and the results are summarized in Fig. 12. Generally, polyurethanes are easy to ignite due to the porous structure and low density. After ignition, the heat release rate of polyurethane foam without microcapsules (PU) and with microcapsules without PNC-HEMA (PU-MC(50)) increased significantly and reached a maximum peak value after, respectively, 10 and 15 s, after which the HRR

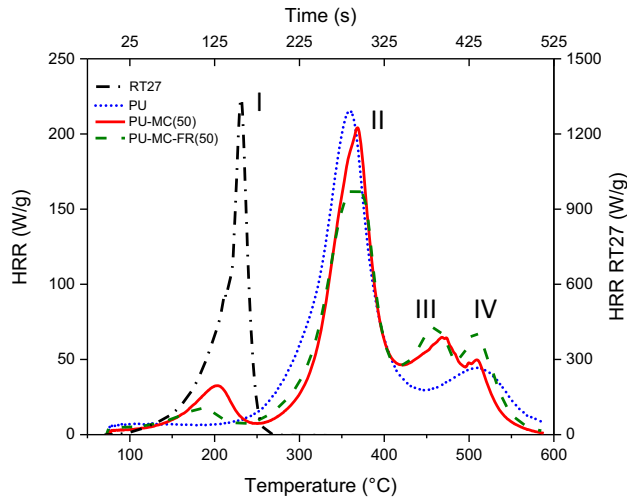


Figure 9 Micro-combustion calorimetry heat release rate (HRR) curves of polyurethane foam without microcapsules (PU), polyurethane foam with microcapsules without PNC-HEMA (PU-MC(50)), and polyurethane foam with microcapsules containing PNC-HEMA (PU-MC-FR(50)). The samples are compared to the RT27 used in the capsules.

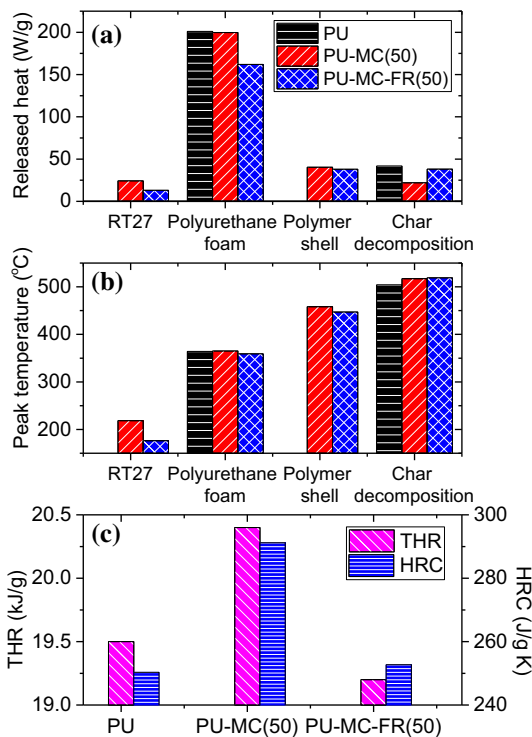


Figure 10 Micro-combustion calorimetry: **a** peak heat release, **b** peak heat release temperature and **c** the total heat release (THR) and heat release capacity (HRC), for polyurethane foam without microcapsules (PU), polyurethane foam with microcapsules without PNC-HEMA (PU-MC(50)), and polyurethane foam with microcapsules containing PNC-HEMA (PU-MC-FR(50)).

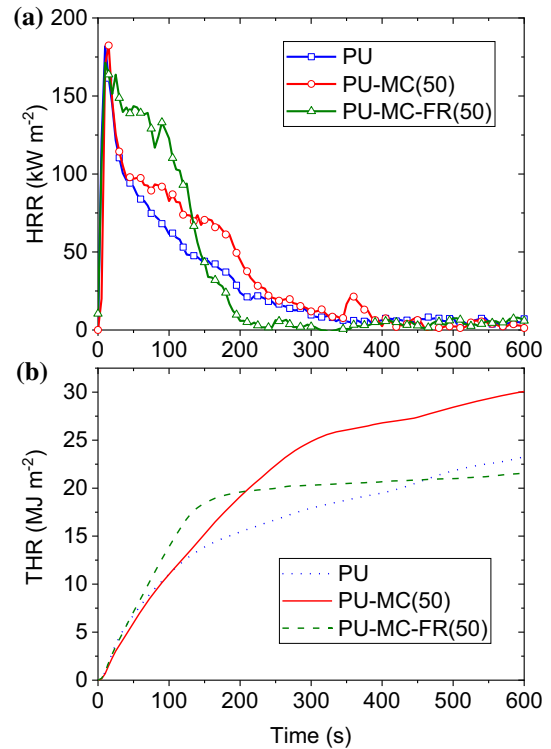


Figure 11 Cone calorimetry: **a** heat release rate and **b** total heat release, for polyurethane foam without microcapsules (PU), polyurethane foam with microcapsules without PNC-HEMA (PU-MC(50)), and polyurethane foam with microcapsules containing PNC-HEMA (PU-MC-FR(50)).

decreased gradually until extinguished. The polyurethane foam with microcapsules containing PNC-HEMA (PU-MC-FR(50)) formed char which busted under high temperatures, and the inside materials decomposed and released inflammable gases which is a common phenomenon in char-formation flame-retardant polymers [27].

The cone calorimetry total heat release (Fig. 11b) of polyurethane foam without microcapsules (PU) and with microcapsules without PNC-HEMA (PU-MC(50)) exhibited continuous burning and increasing THR. However, the total heat release of the samples containing flame-retardant microcapsules (PU-MC-FR(50)) stabilized after approximately 120 s, illustrating improved fire resistance. The THR increases when non-flame-retardant microcapsules are added to the polyurethane foam (Fig. 12a). This is expected since microcapsules can be considered as an additional fuel. The presence of flame-retardant microcapsules reduced the THR (Fig. 12a), in agreement with the micro-combustion calorimetry (Fig. 10c). However, the difference is greater for cone

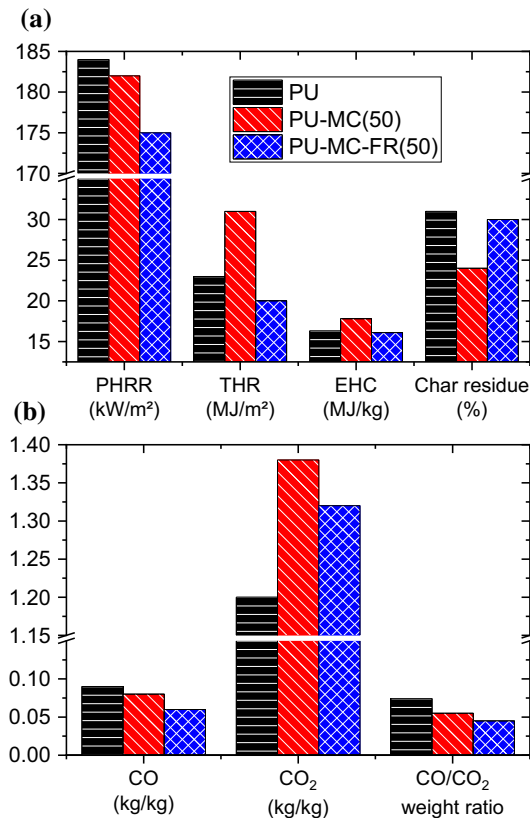


Figure 12 Cone calorimetry. Peak heat release rate (PHRR), total heat release (THR), effective heat of combustion (EHC), char residue, released CO per kg sample, released CO₂ per kg sample, and CO/CO₂ weight ratio for polyurethane foam without microcapsules (PU), polyurethane foam with microcapsules without PNC-HEMA (PU-MC(50)), and polyurethane foam with microcapsules containing PNC-HEMA (PU-MC-FR(50)).

calorimetry, indicating higher heat release reduction in the presence of flame-retardant microcapsules in cone calorimetry. This difference is related to the method and the different thermal stability of the materials depending on the presence of oxygen. In the cone calorimeter, thermo-oxidation can occur, and char is degraded leading to heat release rate, even without the flame. However, at micro-combustion calorimetry standard conditions, the pyrolysis atmosphere is nitrogen, and the char can therefore not undergo thermo-oxidation. Accordingly, the char residue (Fig. 12a) is expected to be higher and the THR lower in cone calorimetry [43].

It is important to note that the fire-retardant PNC-HEMA monomer significantly reduced the negative impact of microcapsules in the PU foam. Although, the sample containing flame-retardant microcapsules generated more heat compared to the other samples

up to approximately 100 s (Fig. 11b), the heat release diminished with the char formation on the material. This is in agreement with previous findings [44]. This can be due to earlier decomposition of PNC-HEMA than the rest of the polymers, resulting in the release of volatile molecules and potential carbonization reactions [45].

The effective heat of combustion (EHC) obtained for cone calorimetry (Fig. 12a) was compared to total heat release (THR) from MCC (Fig. 10c). Although MCC revealed higher values, the trend was similar. This could be related to the amount and exposure of the sample. In MCC, gasses (N₂ and O₂) can easily diffuse into the sample whereas in cone calorimetry only one surface is exposed to fire. Accordingly, it is easier to form a protective char layer in cone calorimetry. Good agreement between EHC from cone calorimetry and THR from MCC was reported elsewhere [46]. Attending to this, MCC could be used as a screening method for flame retardancy when only a small amount of sample is available.

As shown in Fig. 12a, incorporating the flame-retardant PNC-HEMA monomer in the microcapsules ((PU-MC-FR(50)) can significantly increase the char residue at the end of the burning process compared to utilizing non-flame-retardant microcapsules (PU-MC(50)). In addition, the average residue for PU-MC-FR(50) was similar to that of polyurethane foam without microcapsules (PU). This confirms that fire risk associated with the utilization of PCMs can be reduced by shell modification of the thermoregulating microcapsules.

The CO/CO₂ ratio (Fig. 12b) corresponds to the degree of complete combustion. The greater this ratio is, the lower the completeness of the combustion, which might increase the toxicity of the smoke [47]. The CO/CO₂ ratios are lower in the presence of microcapsules than without. Incorporating microcapsules in polyurethane foam both suppress the formation of CO and increase the CO₂ output (Fig. 12b). The highest amount of CO₂ was observed for PU-MC(50), indicating enhanced combustion of the polyurethane foam, leading to significantly lower char residue (Fig. 12a).

Figure 13 shows the SEM images for the residues of the polyurethane foams after combustion by the cone calorimeter. The compactness of the char in the presence of flame-retardant microcapsules (PU-MC-FR(50)) improved compared to that of neat polyurethane foam, with a tighter and denser structure

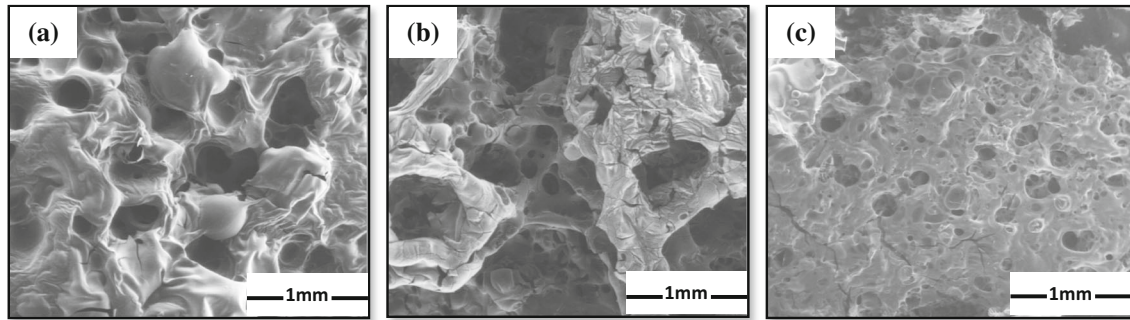


Figure 13 SEM images of char from polyurethane foams obtained after cone calorimetry: **a** polyurethane foam without microcapsules (PU), **b** polyurethane foam with microcapsules without PNC-

HEMA (PU-MC(50)) and **c** polyurethane foam with microcapsules containing PNC-HEMA (PU-MC-FR(50)).

contributing to improved barrier properties of the flame-retardant samples. This illustrates the flame-retardant efficiency of the microcapsules. However, a higher proportion of flame-retardant microcapsules is desired, since this would lead to a better thermal storage performance.

Conclusion

Thermoregulating microcapsules with a shell of the flame-retardant PNC-HEMA combined with styrene and divinylbenzene as co-monomers were successfully synthesized. Although a high RT27 content in the microcapsules provides the best thermal properties, these particles do not exhibit an optimal morphology. However, flame-retardant microcapsules with a lower RT27 content are spherical with a smooth surface.

Inclusion of the flame-retardant PNC-HEMA monomer in the shell of the microcapsules decreased the peak heat release rate (PHRR) and increased the PHRR temperature. A dense and stable char was formed at high temperatures, improving the flame-retardant properties of the microcapsules. After the addition of microcapsules to polyurethane foams, the total heat release and heat release capacity were significantly lower for polyurethane foams containing flame-retardant microcapsules than for the samples containing microcapsules without PNC-HEMA.

Accordingly, it is possible to improve the flame retardancy of materials by incorporating the PNC-HEMA monomer in the shell of microcapsules containing phase change materials. The presence of PNC-HEMA in the microcapsules shell offers a great potential for improvement of the flame retardancy

without affecting the thermal energy storage capacity.

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