

Development of thermoregulating microcapsules with cyclotriphosphazene as a flame retardant agent

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Abstract. Thermoregulating microcapsules containing phase change material (Rubitherm® RT27) was produced by using the suspension-like polymerization technique with styrene (St), divinylbenzene (DVB) and hexa(methacryloylethylenedioxy) cyclotriphosphazene (PNC-HEMA) as co-monomers. The effect of PNC-HEMA for improving the flame retardant properties of the microcapsules were analyzed by scanning electron microscopy (SEM), differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA). It was found that the thermal energy storage (TES) capacity of the microcapsules increased in the presence of PNC-HEMA. However, the morphology of the microcapsules became irregular when the content of monomer with flame retardant properties was increased. Thermogravimetric analysis performed under atmospheric air confirmed that the PNC-HEMA raised the amount of residue after the burning process, proving the formation of thermally stable char. Thus, these materials could be considered as an important alternative to commonly used microcapsules containing phase change materials (PCMs), where a lower flammability is required for their application.

1. Introduction

Thermal energy storage (TES) is considered as one of the most important alternative for commonly used fossil fuels energy systems. A lot of attention has been paid to latent heat thermal energy storage, in which phase change materials (PCMs) are key compounds. PCMs are able to adsorb, store and release energy during heating and cooling cycles in wide range of melting temperatures [1, 2]. Various kinds of PCMs suitable for building applications can be found in the literature. Paraffins are interesting PCMs due to a high heat of fusion, low supercooling and vapor pressure in the molten stage, good chemical stability, no phase segregation, and a reasonable price. These properties promote the applicability as thermal energy storage systems [1, 3]. Nevertheless, paraffins also present several disadvantages such as: low thermal conductivity, low density, high volatility, flammability, and volume change. The most common ways to combine these PCMs with building materials are direct incorporation and microencapsulation. The leakage of PCM is an important problem, that appears during direct incorporation of PCM materials into building materials. In order to avoid the leakage of PCM, microencapsulation of PCM can be performed. Microencapsulation can improve heat transfer efficiency, prevent reactivity of PCM with the immediate surroundings, increase heat transfer areas, and limit the volume changes during phase change [2, 4]. Several techniques of microencapsulation have been reported. They are divided in two main groups: chemical and physical methods [4]. The drawbacks such

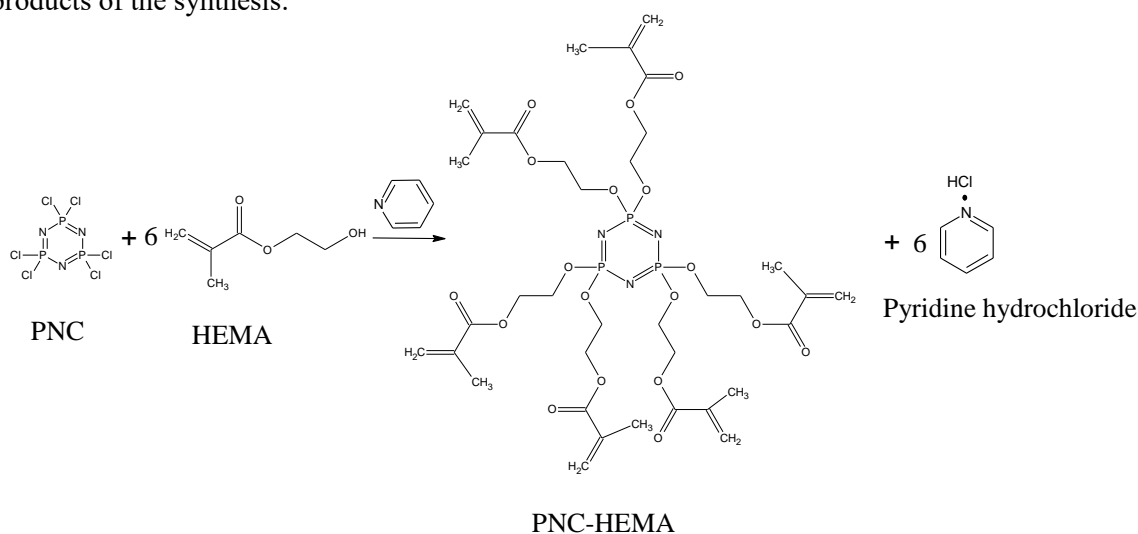


as low thermal conductivity and flammability properties have limited the application of these materials, especially in the building industry. Several methods have been described to reduce the flammability of building materials containing PCM. One of them involved addition of the PCM to the building block and surrounding on all sides with non-combustible concrete without changing the strength properties of the block [5]. Kośny et al. [6] developed microencapsulated fire-resistive PCM using fatty acids esters, which are less flammable than paraffins, and by covering the surface of the microcapsules with a flame retardant agent. That PCM was applied into two insulations systems: PCM-enhanced cellulose insulation [7] and a blend of PCM with blown fiberglass [8]. Those insulations are designed to be used in residential walls and attics. Banu et al. [9] tested ordinary gypsum wallboard impregnated with approximately 24% organic PCM and discussed the possibilities to reduce its flammability. Accordingly, improved fire resistant properties and decreased flammability of microencapsulated paraffins is an important issue for many applications.

Monomers with heteroatomic bonds in their chemical structure have good fire resistant properties due to the larger bonding energy compared to homoatomic bonds. Compounds of phosphazene having a P-N bond linked with other organic groups, inorganic or semiinorganic compounds, exhibit high heat resisting properties [10].

In this paper, a monomer exhibiting flame retardant properties, hexa(methacryloyl ethylenedioxy)cyclotriphosphazene (PNC-HEMA), was synthesized to improve the thermal stability and flammability of thermoregulating microcapsules from styrene and divinylbenzene containing Rubitherm®RT27. Microcapsules containing different amounts of PNC-HEMA were developed, and their effect on TES capacity, morphology and thermal stability were analyzed.

The following chemical structure represents the full substitution of hexachlorophosphazene (PNC) by hydroxyethylmethacrylate (HEMA), giving PNC-HEMA and pyridine hydrochloride as final products of the synthesis:



2. Materials and methods

2.1. Materials

Three reagents as co-monomers were used. Styrene of reagent grade (St, 99 wt.%, Sigma–Aldrich Chemical Co.) and divinylbenzene of technical grade (DVB, containing 80% DVB isomers, Sigma–Aldrich Chemical Co.) were purified by washing with an aqueous sodium hydroxide solution (1.25 N) and calcium chloride as desiccant. Hexa(methacryloyl ethylenedioxy) cyclotriphosphazene (PNC-HEMA) was synthesized in the Laboratory of Polymers Technology regarding the recipe published by Anzai et. al. [10]. Rubitherm®RT27 of commercial grade (Rubitherm GmbH), benzoyl peroxide (BPO, humidified with ~25% of H₂O pure, pharma grade, PanReac Co.) and polyvinylpyrrolidone (PVP, K30, Mw 40,000 g/mol, Sigma–Aldrich Chemical Co.) of reagent grade were used as core material, initiator and suspending agent, respectively. Toluene of analytical grade as inert diluent and ethanol as cleaner

were used. Water with a conductivity of 1 $\mu\text{S}/\text{cm}$ was produced in Laboratory of Polymers Technology by distillation and subsequent deionization using ion exchange resins. Nitrogen with high purity was utilized as an inert gas.

2.2. Polymerization

Microcapsules (MC) or particles (P) were prepared by a suspension-like polymerization technique by following the method described in a previous study [11], where weight percentage (wt. %) corresponds to a weight ratio between the PCM or monomer respect to the sum of PCM and monomers employed.

Table 1. The compositions of the flame retardant microcapsules with PCM.

Sample name	RT27 (wt. %)	PNC-HEMA (wt. %)
MC-FR(0.0)		0.00
MC-FR(1.5)		1.50
MC-FR(3.2)	68.50	3.20
MC-FR(6.3)		6.30
MC-FR(9.5)		9.50
P-FR(0.0)	0.00	0.00
P-FR(3.2)		3.20

Polymerization reactions were performed in a 0.5 L jacketed glass reactor equipped with a reflux condenser, a nitrogen gas inlet tube, a digital control of stirring and a thermostatic bath to keep the reaction at the required conditions. A continuous phase constituted mainly by water and PVP at a mass ratio of 0.07 PVP/water. A discontinuous phase containing styrene, divinylbenzene, PNC-HEMA (FR), PCM and toluene with the weight percentages shown in Table 1. St/DVB, toluene/PCM and monomers/BPO mass ratios were kept constant, being 1.00, 1.92 and 4.43, respectively.

2.3. Characterization

2.3.1. Yield of microcapsules. The microcapsules yield (η_r) was determined on the basis of the total amount of the product (W_{MC}):

$$\eta_r = \frac{W_{MC}}{RT27_{\text{feed}} + (St - DVB)_{\text{feed}}} \quad (1)$$

where $RT27_{\text{feed}}$, $(St - DVB)_{\text{feed}}$ are the weights of the Rubitherm[®]RT27 and monomers fed to the reactor (g), respectively, W_{MC} is the total amount of MC obtained during the polymerization process.

2.3.2. Differential scanning calorimetry. Melting point and latent heat storage capacities of the microcapsules were performed by a differential scanning calorimetry model DSC Q100 of TA Instruments equipped with a refrigerated cooling system and nitrogen as the purge gas. Each sample with the weight between 5 and 10 mg was heated and cooled in the temperature range from -40 to 80 $^{\circ}\text{C}$ with heating and cooling rate of 3 $^{\circ}\text{C}/\text{min}$. The PCM content (C_{PCM}) in the microcapsule was determined by the enthalpy changes values:

$$C_{PCM} (\%) = \frac{\Delta H_{MC}}{\Delta H_{PCM}} \times 100\% \quad (2)$$

where ΔH_{MC} and ΔH_{PCM} are the latent heats of fusion for the analyzed microcapsules and pure PCM (J/g), respectively.

The encapsulation efficiency (EE) can be determined from the Rubitherm[®]RT27 inside the total microcapsules ($RT27_{MC}$) and the Rubitherm[®]RT27 fed ($RT27_{\text{feed}}$):

$$EE (\%) = \frac{RT27_{MC}}{RT27_{feed}} \times 100\% \quad (3)$$

$$RT27_{MC} = W_{MC} \times C_{PCM} \quad (4)$$

2.3.3. Thermogravimetric analysis. Decomposition behavior and thermal stability of microcapsules were analyzed by the TA instruments SDT Q600 Simultaneous DSC-TGA. The measurements were performed from room temperature to 700 °C at a heating rate of 10 °C/min under air atmosphere.

2.3.4. Scanning electron microscopy. The morphology and the physical aspect of the microcapsules were analyzed by Quanta 250 (FEI Company) Scanning electron microscope with a tungsten filament operating at a working potential 10 kV or 15 kV.

2.3.5. Particle size and particle size distribution. Particle size distribution (PSD) with mean volume ($dv_{0.5}$) and number ($dn_{0.5}$) particle sizes of the microcapsules were determined by Low Angel Laser Light Scattering (LALLS) utilizing a Malvern Mastersizer 2000 equipped with a Scirocco 2000 unit providing the dispersions of the particles in the air and a software based on the Mie theory to analyze the experimental data.

3. Results and discussion

3.1. Morphology and particle size of products

The morphology of synthesized products was characterized by SEM and it is shown in Figure 1. Increasing the amount of PNC-HEMA resulted in poorer shape and higher agglomeration of the microcapsules. Irregular shape and agglomeration were mainly observed for products having a content of PNC-HEMA higher than 3.2 wt.% (Figure 1c). This is contrary to the expected results in which higher crosslinker contents improve the appearance of the polymer surface [12], in this case a broken product was obtained. However, particles synthesized by using 3.2 wt.% of PNC-HEMA without PCM (Figure 1f) depict smooth and spherical surfaces. Thus, the morphology of microcapsules is affected by the PCM content and also by the presence of the monomer with flame retardant properties.

According to Anzai et al. [10, 13], the PNC-HEMA polymer presents small polymerization shrinkage, large hardness and a small coefficient of thermal expansion. These properties are attributed to the inorganic P_3N_3 ring and its hetero bonding effects [14]. There are two possible factors that can influence the final morphology of the obtained microcapsules. Firstly, unsubstituted chloride ions that remain in the PNC-HEMA, and avoid the whole reaction of the six active sites of PNC. Secondly, the compressive strength of the copolymer rises in the presence of PNC-HEMA, leading to a higher hardness of the shell. It is possible that during the reaction, the particles having high hardness are broken due to the vigorous stirring required in the suspension polymerization process. It can be concluded, based on the SEM analysis, that the PNC-HEMA employed as a monomer should be maximum 3.2 wt.%, which provide spherical morphology and not a damaged structure.

Volume and number particle size distributions of the microcapsules are shown in Figure 2. The volume particle size distributions are bimodal, except for microcapsules without PNC-HEMA monomer or PCM. However, the number average distributions are unimodal for all types of microcapsules. The volume particle size distribution decreases by increasing content of flame retardant monomer and follow this order: MC-FR(6.3) < MC-FR(9.5) < MC-FR(3.2) < MC-FR(1.5) < MC-FR(0), having average values of 57, 64, 112, 145 and 213 μm , respectively. This trend can be related to the irregular morphology and damage of microcapsules in the presence of PNC-HEMA. Regarding the number average particle size, the values are very close and within 7 and 14 μm . The differences between the number and volume distributions are due to the cubic influence of the particle size and also the morphology on the $dv_{0.5}$ whereas $dn_{0.5}$ is only dependent on the density distribution which is defined as the number of particle per particle size [15]. Accordingly, the volume average is biased towards large particles. The huge

difference between number and volume averages indicates that most of the particles are quite small (number average), but that there are a few very large particles present (which will contribute strongly to the volume average). The large sizes are probably due to agglomeration.

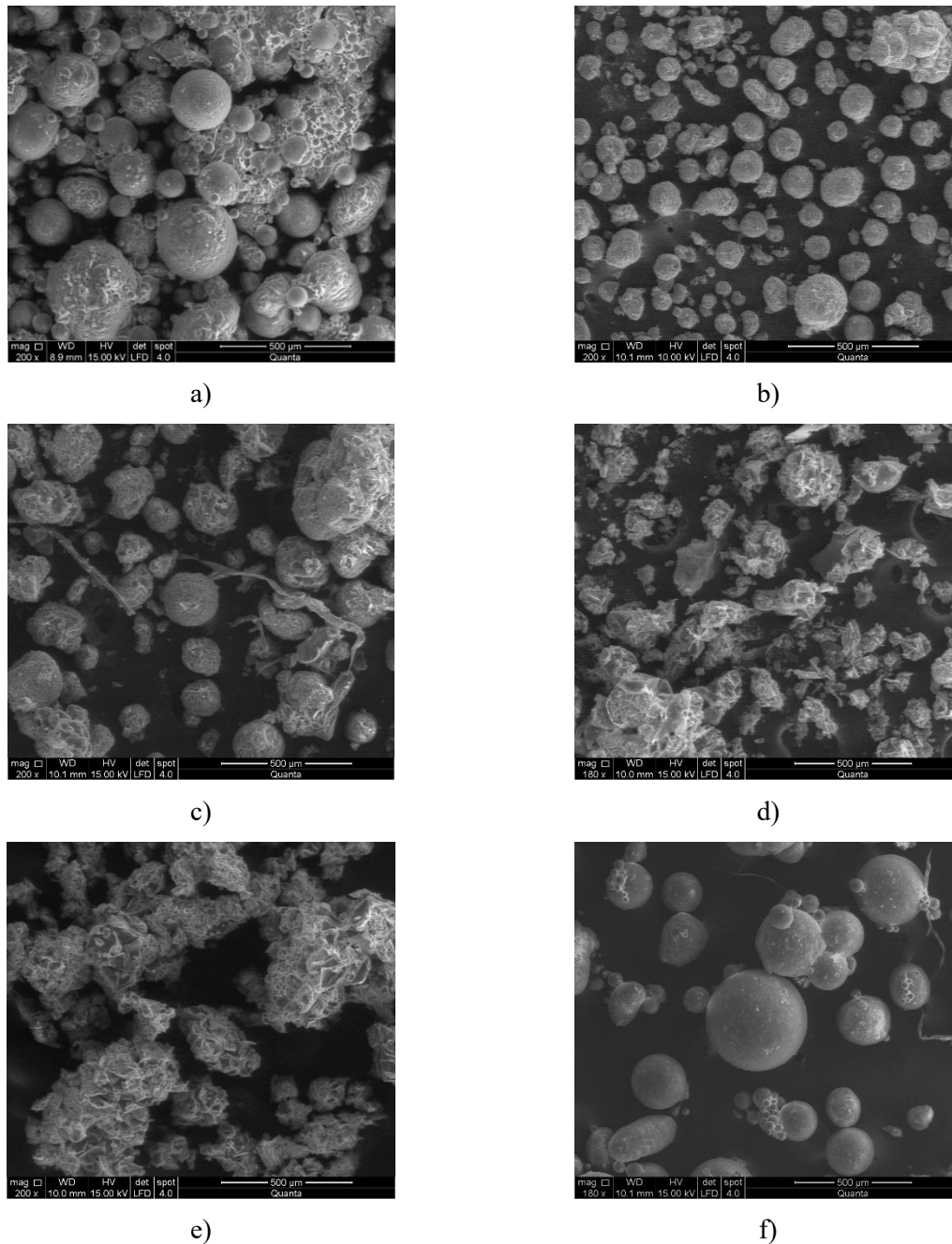


Figure 1. SEM images for microcapsules containing different amount of PNC-HEMA and particles a) MC-FR(0); b) MC-FR(1.5); c) MC-FR(3.2); d) MC-FR(6.3); e) MC-FR(9.5); f) P-FR(3.2).

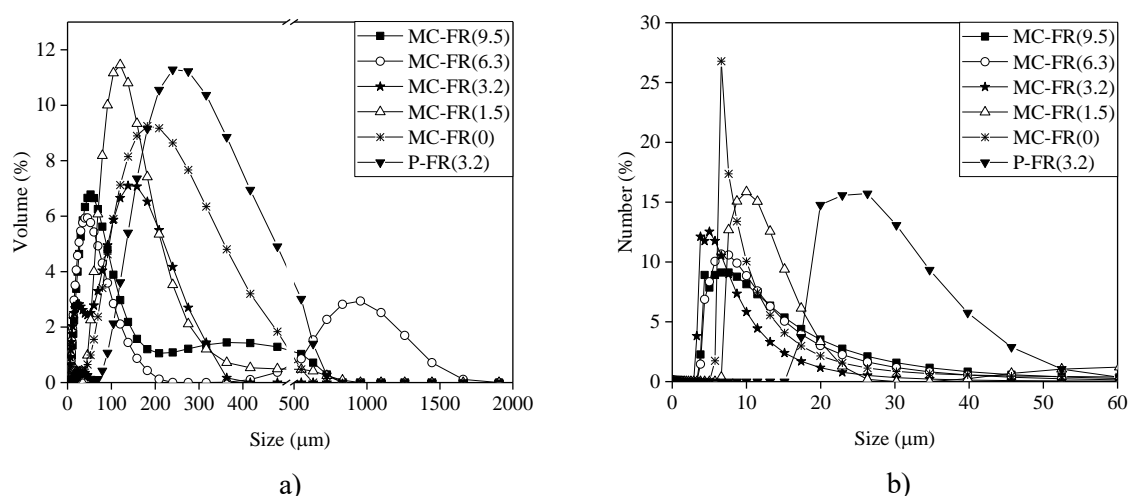


Figure 2. Particle size distribution for microcapsules containing different amount of PNC-HEMA and particles a) volume average, b) number average.

3.2. Thermal energy storage properties of microcapsules

Figure 3 shows PCM content, encapsulation efficiency and microcapsules yield. The latent heat of the microcapsules with flame retardant monomer increases significantly compared with the ones without (101.8 J/g), being 107.8, 109.0, 111.2 and 110.4 J/g for MC-FR(1.5), MC-FR(3.2), MC-FR(6.3) and MC-FR(9.5), respectively. These values correspond to PCM contents ranged between 62.97 and 64.95%. Accordingly, the latent heat of the thermoregulatory materials is very similar to the theoretical value (68.5%). These results indicate that employment of PNC-HEMA as a monomer in the microencapsulation process favors the PCM encapsulation. When using only St and DVB as monomers, the PCM content reaches 59.46%. Considering the interfacial tension influence the encapsulation process [16], the higher hydrophilicity of water/PNC-HEMA than those of water/styrene or water/divinylbenzene, favors the formation of core/shell morphologies using PNC-HEMA as a monomer [17]. It can be noticed that the PCM content becomes higher with increasing amount of PNC-HEMA, while the encapsulation efficiency and microcapsule yield decrease.

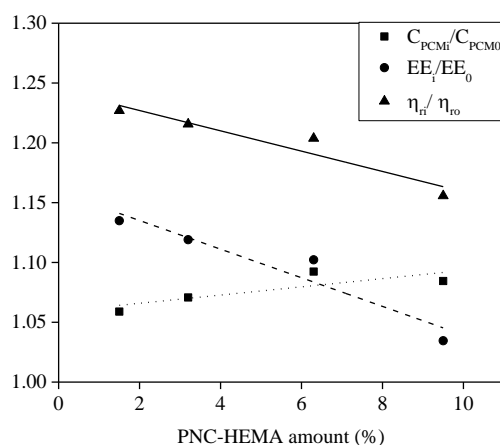


Figure 3. Effect of PNC-HEMA amount on microcapsules yield (η_r), paraffin content (C_{PCM}) and encapsulation efficiency (EE).

3.3. Thermal degradation study of products

Figure 4 shows TG and DTG curves of particles (P-FR(0.0) and P-FR(3.2)) and microcapsules containing different amount of PNC-HEMA as well as neat PNC-HEMA under air atmosphere. Neat PNC-HEMA presents weight loss up to 200 °C, which is related to toluene evaporation and thereafter wide monomer combustion with a final residue of 13.39%. For the particles, two weight losses can be distinguished. The first one corresponds to the polymer combustion and the second one is the degradation of char layer formed at high temperatures. The temperature at which 50% of sample's weight has been lost rises from 398°C to 482 °C in presence of 3.2 wt.% of PNC-HEMA. Furthermore, the char amount formed by P-FR(3.2) was 10% higher than for the product without flame retardant properties.

Among microcapsules with PCM, all samples present three degradation stages. The first one corresponds to the release of encapsulated PCM, and the lowest maximum degradation temperatures ($T_{\max 1}$) occurs for MC-FR(0) and the highest for MC-FR(3.2). The second ($T_{\max 2}$) and third ($T_{\max 3}$) weight losses can be assigned to combustion of copolymer and degradation of char, respectively. The char layer obtained after combustion of PNC-HEMA protect the internal part of the material and delay the degradation rate. Accordingly, the thermal stability of the microcapsules at high temperatures is improved. Finally, the MC-FR(0) were completely degraded at 700 °C whereas the obtained char yield was 1.35, 3.84, 3.26 and 3.76% for MC-FR(1.5), MC-FR(3.2), MC-FR(6.3) and MC-FR(9.5), respectively. Microcapsules with PNC-HEMA concentrations higher than 3.2 wt.% did not show significant additional change. This can be explained by a large amount of unreacted PNC-HEMA, leading to a lower particle yield. The results are in agreement with those reported by Qu et al. [18], in which epoxy composites with poly(phosphazene-co-bisphenol A)-coated boron nitride were prepared and analyzed by TGA in nitrogen and air atmospheres. It was reported that the presence of phosphazene and boron nitride improved thermal stability and thermal conductivity of the composites, as well as decreased flammability, yielding a residue around 5%.

Regarding the thermal degradation results, MC-FR(3.2) seems to be the most suitable product for the production of thermoregulating microcapsules with flame retardant properties. It can be concluded that the presence of PNC-HEMA promotes char formation and enhances the thermal stability and the flame retardant properties of microcapsules.

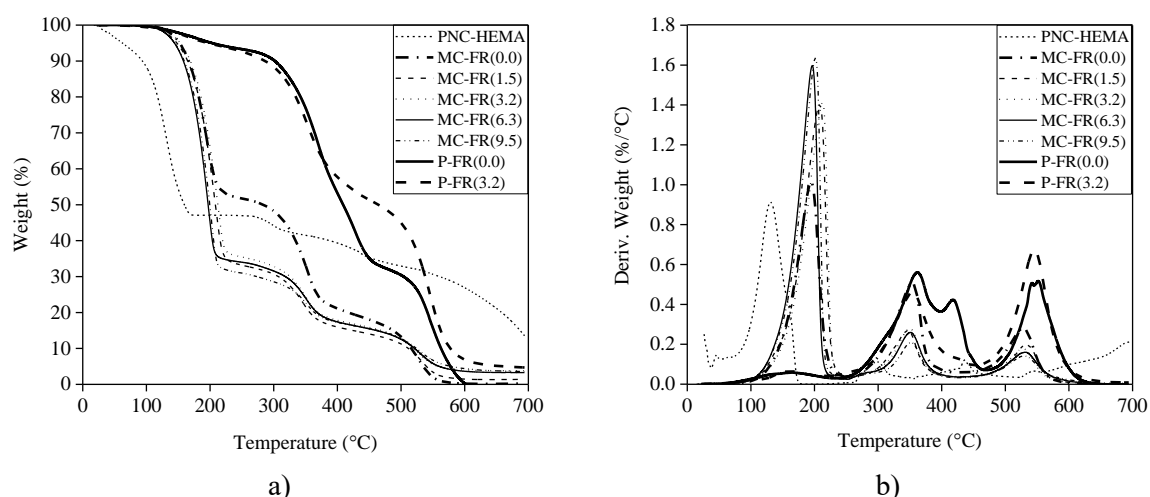


Figure 4. Degradation curves of microcapsules and particles under air atmosphere a) TG, b) DTG.

4. Conclusions

Thermoregulating microcapsules from PNC-HEMA, styrene and divinylbenzene as co-monomers were manufactured. It was observed that a high content of PNC-HEMA is deleterious for the morphology of the microcapsules. Nevertheless, all the thermal properties of the microcapsules such as TES capacity,

thermal stability and fire resistance were improved with the content of PNC-HEMA. According to the physical and thermal results the use of 3.2 wt.% of PNC-HEMA respect to the other monomers was the optimal concentration for obtaining microcapsules with the best morphology and the highest TES capacity and thermal stability. MC-FR(3.2) presented an spherical shape with relatively small particle size (112 μm), a TES capacity of 109.0 J/g and a charred residue of 3.84 wt.%. Thus, it was confirmed that the phosphazene compound was able to create a dense and stable char at high temperature improving the flame retardant properties of microcapsules. Therefore, it is possible to improve the fire-resistive of the materials by incorporating flame retardant monomers as shell constituents.

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