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Phosphorylated microcapsules containing natural oil for potential self-healing use

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Abstract

This work reports on the preparation of oil-filled microcapsules for self-healing purposes. Biopolymeric microcapsules loaded with vegetable oils as green corrosion inhibitors were formulated using ethyl cellulose and phosphorylated ethyl cellulose as encapsulating materials. Chemical structure, thermal stability and surface morphology of microcapsules were characterized by Fourier transform infrared (FTIR) spectroscopy, thermal gravimetric analysis (TGA) and scanning electron microscopy (SEM). FTIR and TGA analysis confirmed the presence of oil core and polymer shell in the formulated microcapsules. The scanning electron microscopy was used to evaluate the shape and morphology of the prepared microcapsules. The obtained results revealed the spherical-like shape of the obtained capsules with diameters ranging from 10 up to 170 μm . Thus, the current study shows the potential application of phosphorylated ethyl cellulose for the development of new environmentally friendly microcontainers bearing corrosion inhibitors for end use in anti-corrosion self-healing coatings.

Keywords: Microencapsulation; Phosphorylation; Ethyl cellulose; Self-healing; Anti-corrosion coating; Core-Shell microcapsule.

1. Introduction

Over the last decade, the study and development of integrated chemical structures have attracted the attention of researchers. One of these structures are microcapsules made using different microencapsulation techniques. The main objective of preparing capsules is to envelope a core material by a shell material in order to be protected from the surrounding environment. Compounds storage and the possibility of controlling the release of the core material have made the use of microcapsules possible in different commercial applications, such as drug delivery systems, food preservatives, electronic devices, cosmetic products, and self-healing materials. [1]–[4]

Among the various techniques of self-healing materials development, the extrinsic method based on encapsulation strategy is the most considered approach. It is based on the encapsulation of a healing agent in a polymeric shell material. Then capsules have to be embedded into a matrix material allowing their release during a rupture event and therefore promoting self-healing. [5]

Corrosion inhibitors-loaded microcapsules for the application in self-healing coatings were the main objective of various studies. This application was based on the concept of extrinsic self-healing system firstly initiated by White et al. in 2001.[6] Conceptually, a self-healing anticorrosion coating is considered as a combination of the passive component, represented by the conventional matrix coating, and the active component represented by the corrosion inhibitor-containing micro/nano capsule. This concept has been used in different studies to develop anticorrosion coatings. For instance, linseed and tung oils were mainly encapsulated using urea-formaldehyde as the shell material, and the prepared microcapsules were incorporated into epoxy-based coatings in order to study and understand their effect on corrosion inhibition and healing performance. [7], [8]

In this study, various oil-filled microcapsules were prepared via solvent evaporation method. Ethyl cellulose and phosphorylated ethyl cellulose were used as polymeric shell materials to encapsulate lavender oil (LO), black seed oil (BSO), prickly pear oil (PPO) and argan oil (AO). The prepared microcapsules were characterized and the effect of the phosphorylated shell on the properties of the microcapsules has been discussed. The obtained microcapsules are destined to be used in our upcoming work to develop anti-corrosion self-healing coatings, but, can be explored in additional key applications (e.g., biomaterials). [9]

2. Experimental

2.1 Materials

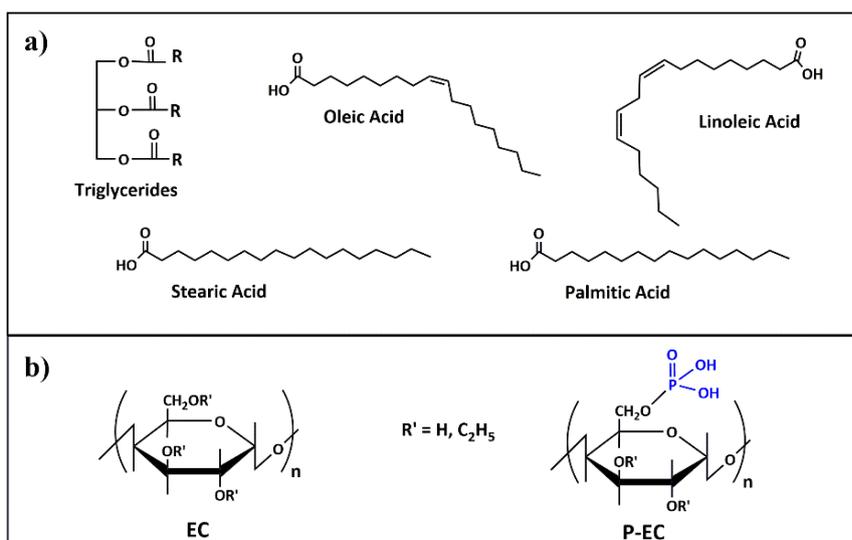
Ethyl cellulose (EC) powder, sodium dodecyl sulfate (SDS) and urea powder were purchased from Sigma Aldrich. Orthophosphoric acid (85 %) and methanol were obtained from Merck KGaA. The ethyl acetate (EA) was supplied by Somaprol, and Sodium hydroxide was provided by VWR. Lavender oil (LO), black seed oil (BSO), prickly pear oil (PPO) and argan oil (AO) were purchased from a drugstore in order to be used as core materials for the microcapsules. All chemicals were analytical reagents grade and were used without any further purification.

2.2 Preparation of microcapsules

Oil-filled microcapsules were prepared using a two stage solvent evaporation method as described elsewhere. [10], [11] Both, ethyl cellulose (EC) and phosphorylated ethyl cellulose (P-EC) were used as shell materials for the microcapsule's preparation (Scheme 1). The P-EC used as shell material was obtained through phosphorylation reaction of commercial ethyl cellulose (EC). The chemical modification of EC was performed using orthophosphoric acid in molten urea, following previously reported procedure. [10], [12] EC powder or P-EC powder were dissolved in ethyl acetate for 2 hours under room temperature and magnetic stirring at 650 rpm. The oil was then added to the solution stirring for 30 minutes more. In parallel, a 1wt.% sodium dodecyl sulfate aqueous solution was prepared. The polymeric solution (oil phase) was then added dropwise to the aqueous solution (water phase) under continuous mechanical mixing at a temperature of 60 °C for 90 minutes. The obtained mixture was freeze-dried, rinsed with distilled water, filtered, and then dried to generate the final native microcapsules (MC) and phosphorylated-microcapsules (P-MC).

To investigate the effect of shell materials and different oils on the microencapsulation process, the preparation was conducted using EC and P-EC as shell materials and lavender, black seed, prickly pear and argan based oils as core materials (Scheme

1).



prickly
pear and
based oils as
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Scheme. 1. a) Structure of major components in different vegetable oils (Lavender oil, Prickly pear oil, Black seed oil and Argan oil). b) Structure of Ethyl cellulose (EC) and phosphorylated ethyl cellulose (P-EC).

2.3 Characterization

Fourier Transform Infrared (FTIR) analysis was performed for initial raw materials, phosphorylated ethyl cellulose and prepared microcapsules to identify the core and shell materials. The FTIR spectra were recorded by a PerkinElmer FTIR spectrophotometer (Wellesley, MA, United States) using attenuated total reflection (ATR) technique and collecting 16 scans in the $4000\text{--}600\text{ cm}^{-1}$ range with a resolution of 4 cm^{-1} .

Thermogravimetric analysis (TGA) was carried out using a thermogravimetric analyzer (Model –TGA 5500, Discovery series, TA Instruments, United States) to evaluate the thermal stability of the initial raw materials, phosphorylated ethyl cellulose and the prepared oil-filled microcapsules. The analysis was performed under a nitrogen atmosphere with a heating rate of 10 °C/min from room temperature up to 700 °C .

The surface morphology and the shape of the prepared microcapsules were observed using a scanning electron microscope ((Philips XL 40 ESEM). Before analysis, the microcapsules were coated with gold to improve imaging.

3. Results and discussion

3.1 Characterization of microcapsules

Fourier transform infrared (ATR-FTIR) spectroscopy was used to characterize the core materials (LO, BSO, PPO and AO), the shell materials (EC and P-EC) and the prepared oil-filled microcapsules. The FTIR spectra of the core, shell and microcapsules are reported in Fig. 1. The obtained results revealed that the FTIR spectra of microcapsules have been found

matching with all the encapsulated oils spectra. The structure of major components in the different vegetable oils used in this study are presented in scheme 1-a).

The FTIR spectra of lavender oil showed sharp peaks at 620 cm⁻¹, 730 cm⁻¹ and 893 cm⁻¹ attributed to C-H vibrations. The peak at 997 cm⁻¹ was assigned to -CH₂ vibrations. The peaks at 1095 cm⁻¹, 1163 cm⁻¹ and 1238 cm⁻¹ were related to C-O stretching vibrations. The peaks at 1373 cm⁻¹, 1426 cm⁻¹ and 1456 cm⁻¹ belong to C-H bending vibrations. The peak at 1651 cm⁻¹ was due to C=C stretching vibrations. The peak at 1748 cm⁻¹ corresponds to C=O stretching vibrations and the peaks at 2861 cm⁻¹, 2921 cm⁻¹ and 3004 cm⁻¹ were associated with the -CH₂ stretching, while the band at 3300 cm⁻¹ was ascribed to -O-H stretching vibrations. Those values were close to the ones reported in a previous work. [13]

The FTIR spectra of EC showed characteristic peaks at 1056 cm⁻¹ assigned to -C-O-C- stretching vibrations. The peaks at 2878 cm⁻¹ and 2971 cm⁻¹ correspond to -CH stretching vibrations. The peak at 1373 cm⁻¹ was attributed to -CH bending vibrations and the peak at 3475 cm⁻¹ was associated to -O-H stretching vibrations. [14]

New small peaks appeared in the FTIR spectra of phosphorylated ethyl cellulose as well as phosphorylated microcapsules. The peaks observed at 810 cm⁻¹ and 1630 cm⁻¹ were attributed to P-O-C and O=P-OH groups, respectively. [10] These new peaks appeared thanks to the presence of phosphorus in the P-EC shell material.

The infrared spectra of the microcapsules revealed all the characteristic peaks of the core material and the shell material for all the encapsulated oils using EC or P-EC as shell material (in yellow in Fig. 1), which confirmed clearly that the encapsulation was correctly carried out using different oil core and polymer shell materials. Furthermore, for all prepared microcapsules, no peaks related to the free chemicals used in the encapsulation process have been identified, so the efficiency of the capsule cleaning process has been demonstrated.

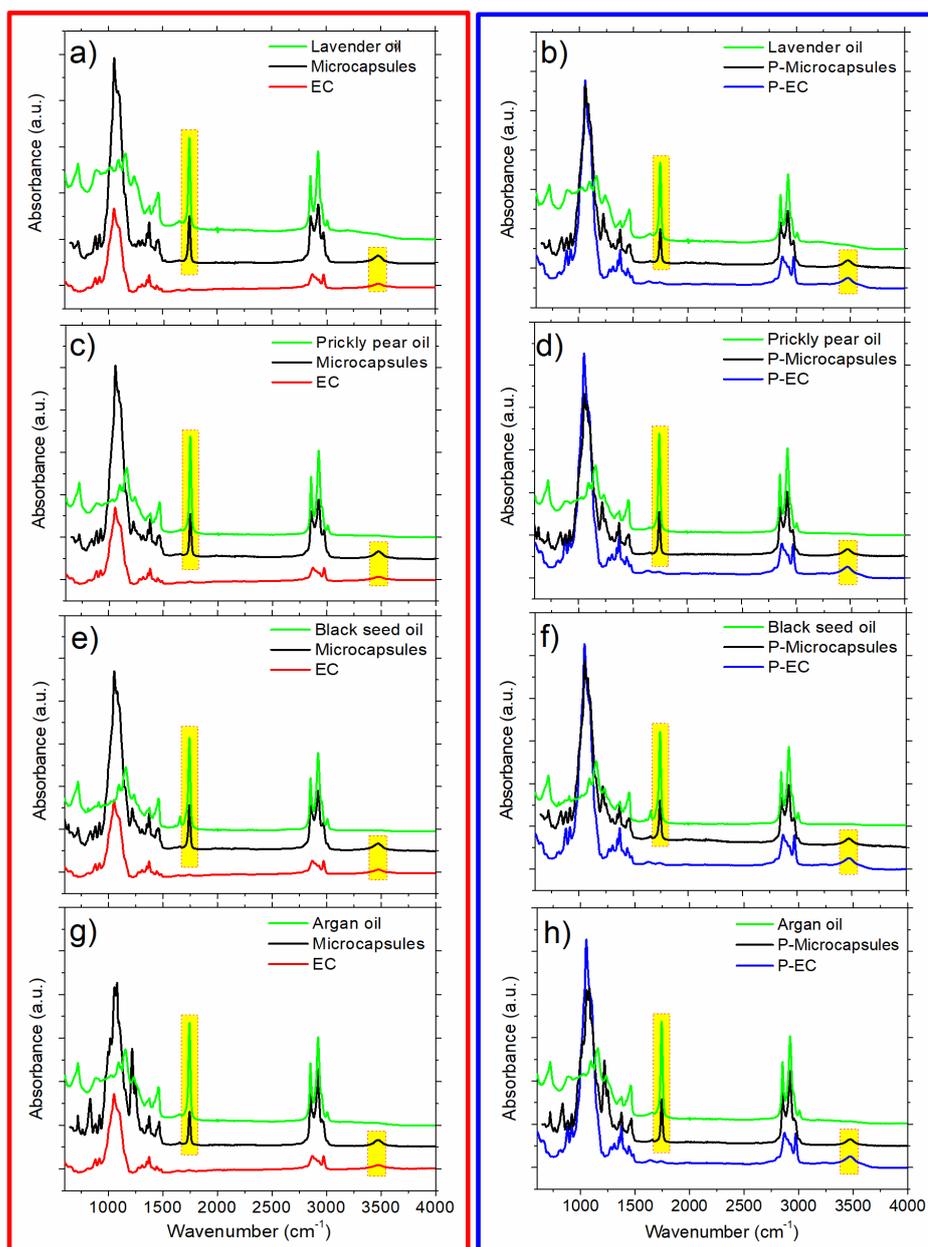


Fig. 1. (a) FTIR spectra of (a, b) lavender oil, (c, d) prickly pear oil, (e, f) black seed oil, (g, h) argan oil, ethyl cellulose (a, c, e, g), phosphorylated ethyl cellulose (P-EC) (b, d, f, h)) and the corresponding oil filled microcapsules.

3.2 Microcapsules thermal characteristics and content

Thermogravimetric analysis (TGA) has been used to investigate the thermal stability of the prepared microcapsules, the encapsulated oils (LO, PPO, BSO and AO) and the shell materials (EC and P-EC). The obtained results are shown in Fig. 2.

The phosphorylated and non-phosphorylated oil-filled microcapsules (MC and P-MC) exhibited two stages of weight loss. For instance, lavender oil microcapsules show two stages at 180–285 °C and 285–480 °C, corresponding to the decompositions of ethyl cellulose shell and the lavender oil core, respectively. In the case of prickly pear oil

microcapsules, the two stages related to the decomposition of EC and PPO were observed at 195-285 °C and 285-475 °C, respectively. The black seed oil microcapsules and argan oil microcapsules also exhibit two stages of weight loss related to EC and the encapsulated oils (Table 1). The thermogram of the phosphorylated microcapsules filled with lavender oil shows a first stage weight loss at 165–280 °C related to the decomposition of phosphorylated ethyl cellulose. The second stage of weight loss related to the lavender oil decomposition was observed between 280 °C and 505 °C. The decomposition of phosphorylated microcapsules containing prickly pear oil was observed through two stages of weight loss at 170-280 °C and 280-520 °C. The phosphorylated microcapsules containing black seed oil and argan oil show two stages of weight loss as well (Table 1).

Table 1. Thermogravimetric analysis (TGA) results of the prepared microcapsules.

Sample	1 st region		2 nd region		Final residue (%) at 600 °C
	Range °C	Peak* °C	Range °C	Peak* °C	
LO microcapsules	180–285	192	285–480	381	4.67
LO P-microcapsules	165–280	178	280-505	393	3.62
PPO microcapsules	195-285	201	285-475	391	4.93
PPO P-microcapsules	170-280	183	280-520	402	4.02
BSO microcapsules	215-290	220	290-490	391	7.43
BSO P-microcapsules	165-280	180	280-525	377	6.70
AO microcapsules	190-290	202	290-513	386	10.9
AO P-microcapsules	170-283	187	283-590	384	4.47

* From derivative thermogravimetry (DTG) curve of all samples

The thermal degradation shows an overlapping temperature range of the core and shell materials which limits the accurate determination of the percentage of each component. This limitation led us to determine the percentages of encapsulated oils and polymeric materials used as shell materials for encapsulation via the solvent extraction method. Thus, a determined weighed mass (m_1) of each prepared microcapsule was mixed with n-hexane and sonicated for 10 min. The suspension was filtrated, and the obtained solid filtrate was dried in an oven at 50 °C until the generation of a constant weight (m_2). The oil content of the microcapsules was then determined using the following equation (1):

$$\text{Oil content (\%)} = \frac{(m_1 - m_2)}{m_1} 100\% \quad (1)$$

The obtained results are summarized in Table 2.

Table 2. Oil content of the prepared microcapsules.

Sample	LO MC	LO P-MC	PPO MC	PPO P-MC	BSO MC	BSO P-MC	AO MC	AO P-MC
Oil content (%)	63.60	72.14	67.16	72.02	51.31	69.60	44.38	67.56

It is worth to mention that the thermal degradation of the microcapsules resulted in a final residue higher in the case of MC compared to the P-MC for each encapsulated oil; this fact could be related to the oil content of the microcapsules. The TGA analysis reported the absence of the other materials used for the encapsulation, especially the sodium dodecyl sulfate (SDS) material usually characterized by a degradation temperature range between 162 °C and 218 °C.

The thermal degradation of the prepared P-MC exhibits a flame retardancy behavior due to the phosphorylated ethyl cellulose on the microcapsules shell. the phosphorous groups on the P-EC shell cause an early degradation of the microcapsules outer surface, which promote the protection of the entire microcapsules through the formation of a protective layer on the polymeric shell.

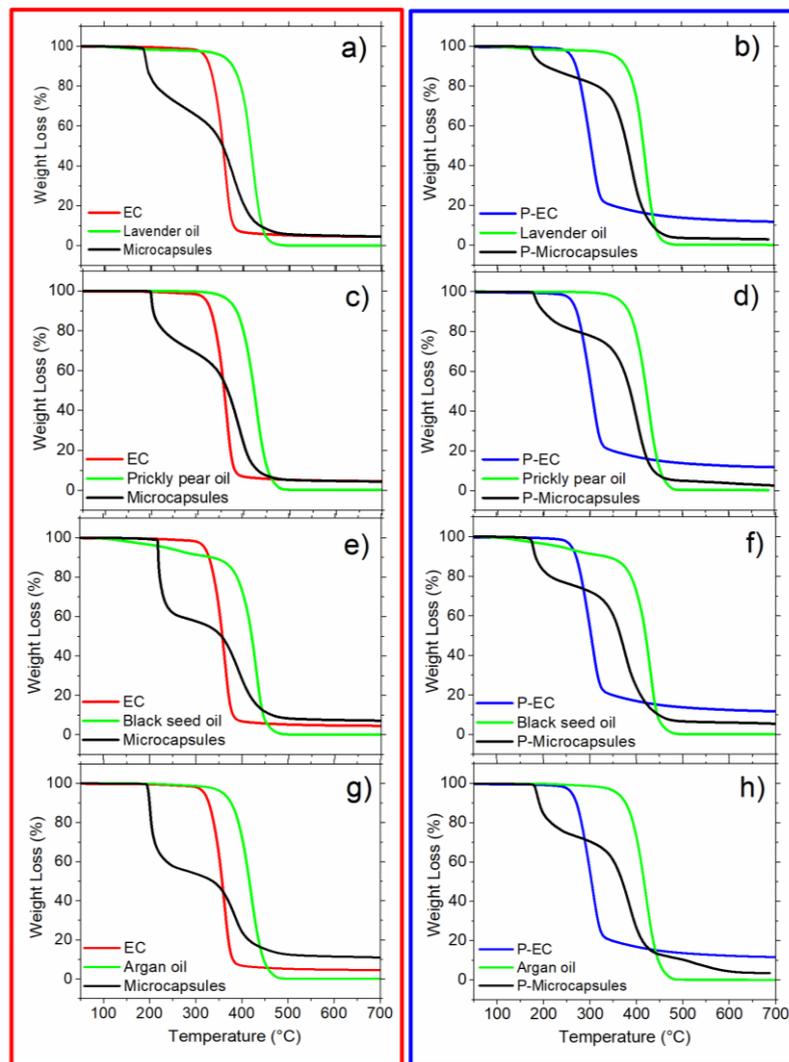
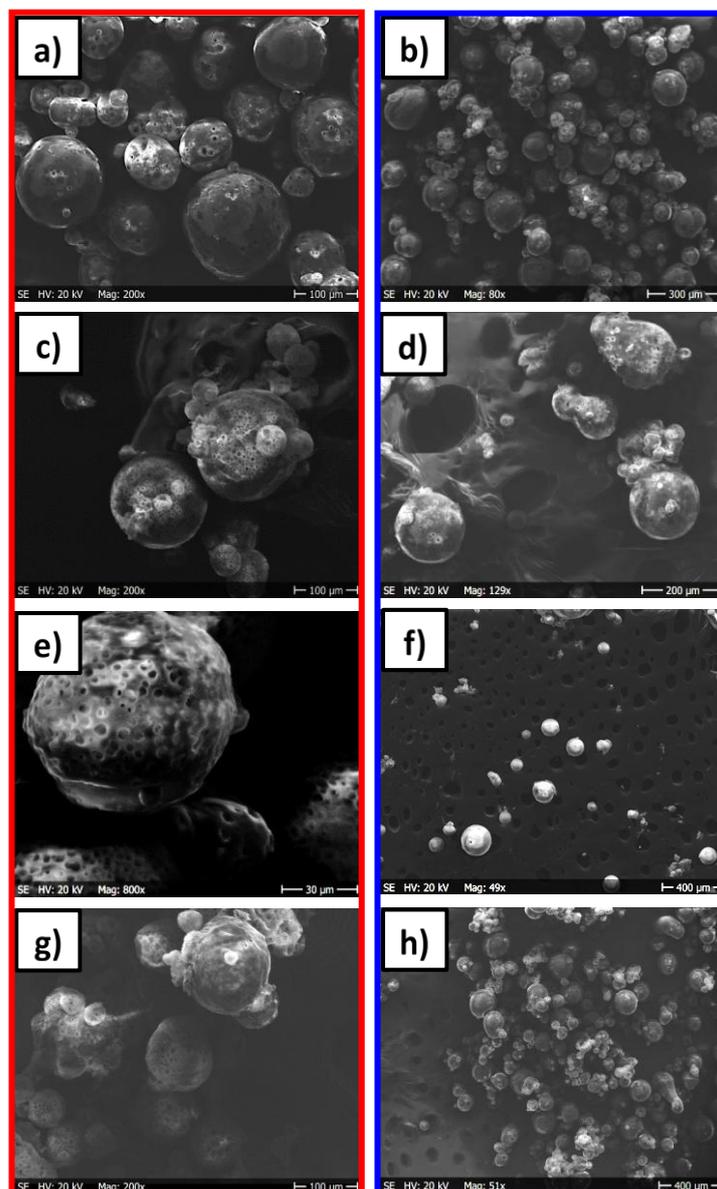


Fig. 2. TGA weight loss curves of (a, b) lavender oil, (c, d) prickly pear oil, (e, f) black seed oil, (g, h) argan oil, ethyl cellulose (a, c, e, g), phosphorylated ethyl cellulose (P-EC) (b, d, f, h)) and the corresponding oil filled microcapsules.

3.3 Microcapsules morphology

The morphology of the prepared oil-filled microcapsules was investigated by SEM. The obtained micrographs are illustrated in Fig. 3. It was clearly shown that the obtained microcapsules are spherical in shape with some roughness and cavities on the surface which may induce a better compatibility effect with the coating matrix. The freeze-drying performed as the last step in the microcapsule's preparation could be the source of the observed cavities and some broken capsules as well. [15]

As expected, micrometric size distribution of the generated capsules can be clearly observed from the micrographs in Fig. 3, indicating the efficiency of the preparation method using both native ethyl cellulose and phosphorylated ethyl cellulose with the four encapsulated oils (lavender, black seed, prickly pear and argan based oils). Furthermore, a wide size distribution of the microcapsules was extracted from the micrographs and estimated to be in



the range up to 170 µm.

Fig. 3. SEM micrographs of oil-filled microcapsules using ethyl cellulose (a, c, e, g) and phosphorylated ethyl cellulose (b, d, f, h) as shell material. The microcapsules core material are based on (a, b) lavender oil, (c, d) prickly pear oil, (e, f) black seed oil, (g, h) argan oil.

4. Conclusions

In this study, oil-filled microcapsules were successfully prepared via solvent evaporation method. Native ethyl cellulose and phosphorylated ethyl cellulose were used as polymeric shell materials to encapsulate four different oils (lavender, black seed, prickly pear and argan based oils). As far as we know, this was the first time to encapsulate the above-mentioned oils using phosphorylated ethyl cellulose as a shell-forming polymer. The microcapsules composition was evaluated by FTIR, and the obtained results proved that the microcapsules were only composed of the studied oil core material (lavender, black seed, prickly pear or argan based oil) and the shell material (ethyl cellulose or phosphorylated ethyl cellulose). TGA analysis was used to investigate the thermal stability of the microcapsules and it confirmed the flame-retardant aspect induced to the P-MC through the use of P-EC as a shell material. The oil content was determined for the obtained microcapsules. More exploration of the oil's properties effect on the final capsules needs to be investigated. The SEM micrographs further confirmed the efficiency of the preparation method and showed the spherical shape of the microcapsules with a particles size range of 10-170 μm . The main objective of this study was to proof the concept of oil encapsulation using P-EC as a shell; the prepared microcapsules will be destined for the preparation of anti-corrosion self-healing coatings.

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