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Urea-Formaldehyde Microcapsules Containing an Epoxy Resin: Influence of Reaction Parameters on the Encapsulation Yield

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Summary: In this work urea-formaldehyde microcapsules containing an epoxy resin are prepared by in situ polymerization of monomers in an oil-in-water emulsion. Scanning electronic microscopy (SEM) was performed to investigate on microcapsule size and surface morphology. Calorimetric and spectroscopic analyses were carried out with the aim of evaluate the encapsulation yield and the shell features. Factors determining the microencapsulability of the core material were described. In particular, our interest was devoted to a better understanding of the influence of the reaction parameters on the microcapsule properties. It was found that the encapsulation yield as well as the extent of urea-formaldehyde polymerization depends on the reaction temperature and the stirring speed.

Keywords: emulsion polymerization; epoxy resin; microencapsulation; poly(urea-formaldehyde); Raman spectroscopy

Introduction

Microcapsules are tiny microparticles with diameters in the range of nanometers or millimeters that consist of core materials and covering membranes (also called walls).[1–3] Microcapsules can encapsulate various substances, such as gases, liquids, and solids; coating substances can be also selected from a wide variety of natural or synthetic polymers, depending on the material to be coated and on the characteristics desired in the final microcapsules. Through selection of the composition materials (core material and membrane), it is possible endow microcapsules with a variety of functions.

Since 1960 microcapsules have found application in a number of commercial fields ranging from chemicals[4] and pharmaceuticals[5] to cosmetics[6] and printing[7] and a widespread interest has developed.

Nowadays the microencapsulation technology exhibits significant promise for providing new ‘‘smart'' functionality for applications in advanced fields of intelligent microstructures and microsystems,[8] as well as for applications in the phase change materials (PCM's)[9] and in the self healing composites.[10]

In this paper we prepared urea-formaldehyde microcapsules containing an epoxy resin to be used as fillers in self-healing materials. In particular, our interest was devoted to a better understanding of the influence of the reaction parameters on the microencapsulability of the core material.

The wall material was selected in order to avoid leakage and diffusion of the encapsulated agent for considerable time. Moreover, high bond strength to the host polymer combined with a moderate strength microcapsule shell are required to remain intact during processing of the polymeric matrix.[10,11]

Epoxy resin was chosen as the encapsulated agent of interest thanks to its extreme

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versatility,[12,13] as it has found use in many advanced fields, ranging from electrical/ electronic to aircraft/aerospace and automotive industries.[14]

In order to evaluate the relation between the experimental conditions and the encapsulation yield, a set of urea-formaldehyde microcapsules containing an epoxy resin was prepared in which reaction time and temperature and stirring speed were modulated.

Scanning electronic microscopy (SEM) was performed to investigate on microcapsule size and surface morphology. Calorimetric and Raman analyses was carried out with the aim of evaluate the encapsulation yield.

Experimental

Materials

Urea (supplied from Fluka), formaldehyde 37 wt% solution in water, ammonium chloride and resorcinol (purchased from Aldrich Milan, Italy) were used for the preparation of microcapsules.

Ethylene maleic anhydride (EMA) copolymer was used as emulsifier and purchased from Aldrich Milan, Italy. As the encapsulated agent, a commercial available Bisphenol–F-type epoxy resin (PY306) was selected and supplied by Huntsman/Vantico (Italy).

All these products were used without further purification.

Preparation of Microcapsules

Formation of urea-formaldehyde microcapsules was achieved by *in situ* polymerization in an oil-in-water emulsion. In a typical procedure 2.5 g urea, 0.25 g ammonium chloride and 0.25 g resorcinol were dissolved in water (150 ml), under magnetic stirring and at room temperature.

Ammonium chloride acts as hardeners whereas resorcinol is a further brancher involved in the co-condensation reaction with urea and formaldehyde.[15] The incorporation of resorcinol also improves the low resistance of UF bonds to the influence of water.

Since in some cases it may be desirable to use an emulsion stabilizer, a 2.5 wt% aqueous solution of EMA copolymer (50 ml) was added to the reaction mixture. The emulsion stabilizers has the function to form thin layer around the capsule core entities and thereby to stabilize the emulsion. The pH was adjusted to 3.5 using sodium hydroxide (NaOH) and hydrochloric acid (HCl). 30 ml of PY306 were added to the solution to form an emulsion and allowed to stabilize for 10 min. 6.3 g of 37 wt.% aqueous solution of formaldehyde were added to the emulsion to obtain a 1:1.9 molar ratio of formaldehyde to urea. The temperature was raised to the selected value.

After a fixed time of reaction under continuous stirring chosen as an experimental variable, the mixer and hot plate were switched off. Once cooled to room temperature, the suspension of microcapsules was separated under vacuum filtration and then washed with chloroform to eliminate the residual (non encapsulated) epoxy resin. The microcapsules were isolated by filtration and vacuum dried at 40 °C for 24 hours.

Instrumental

Scanning electronic microscopy (SEM) was used to study the morphology of microcapsules, using a Leica Cambridge Stereoscan microscope model 440. Prior to being observed, samples were metallized with a gold layer.

Differential scanning calorimetry (DSC) (TA Instruments model 2920) was used to confirm the epoxy microencapsulation as far as to the qualitative evaluation of encapsulation yield. For each sample, a single scan from 0 °C to 300 °C at a rate of 10 °C/ min, under nitrogen atmosphere, was carried out.

All Raman spectra were collected on a Nicolet Nexus NIR FT-Raman spectrometer from Thermo Nicolet (Madison, WI, USA), equipped with a diode pumped Nd-YAG laser ($\lambda = 1064$ nm) as an excitation source operating at 0.85–1.05 W of power, and a room temperature InGaAs photoelectric detector. The backscattered radiation was collected at 180° to the laser beam direction. Typical spectra were recorded in the range 3800–200 cm^{-1}, at a resolution of 4 cm^{-1}, co-adding 500 scans to improve the signal-to-noise ratio. The specimens, in the form of finely ground powders were sampled in glass vials. Raman spectroscopy was used for the quantitative evaluation of the encapsulated epoxy resin.

To separate the individual peaks in the case of unresolved, multicomponent bands, a curve resolving algorithm was employed, based on the Levenberg-Marquardt method.[16] In order to reduce the number of adjustable parameters and to insure the uniqueness of the result, the band shape and the number of components were fixed. The number of components and their initial positions were estimated by looking at the negative peaks of the second-derivative spectra. To account for the fluorescence effect the baseline was simulated by a third-order polynomial function. The program was allowed to calculate, by a non-linear curve fitting of the data, the height, the full width at half height (FWHH) and the position of the individual components. The peak function used throughout was a mixed Gauss-Lorentz line shape.[17]

Results and Discussion

Urea-formaldehyde microcapsules were synthesized as described in the *Experimental part*. In particular, five different samples were prepared by varying the experimental conditions, such as reaction time and temperature and stirring rate, as summarized in Table 1.

Neat urea-formaldehyde was also preparared in the same condition of sample A.

Microcapsule Morphology

In order to examine the morphological features of synthesized microcapsules, SEM analysis was carried out, as reported in the micrographs of Figures 1–3.

Table 1.
Reaction parameters (temperature, time and stirring rate) selected for the preparation of urea-formaldehyde microcapsules.

sample	reaction temperature (°C)	reaction time (hour)	stirring rate (rpm)
Neat UF	60	4	2000
A	60	4	2000
B	60	6	2000
C	40	4	2000
D			1600
E			1200

All the samples exhibit a complex morphology, characterized by micro-sized beads with a partially rough outer surface (single oil droplets), and/or clusters of nanocapsules. This particular morphological feature could be ascribed to the reaction mechanism which leads to the formation of microcapsules.

Encapsulation proceeds via liquid-liquid phase separation. Polymerization between urea and formaldehyde is initiated in the water phase where a low molecular weight pre-polymer forms. As the molecular size increases, the polymer deposits at the organic-aqueous interface, in which the organic phase is constituted by the epoxy monomer.[18–20] The polymerization continues to give a cross-linked urea-formaldehyde capsule wall in the presence of resorcinol and ammonium chloride. The formation of urea-formaldehyde nanoparticles is attributed to precipitation of higher molecular weight pre-polymer in the aqueous solution and their aggregation and deposition on the capsule surface.

Due to the mechanism proposed above, for the sample composed by pure UF (Figure 1) clusters of nanocapsules formed by precipitation of the cured, high-molecular weight portions were found.

No evidence of micro-sized particles was detected. In this case, the reaction between the urea and formaldehyde occurred exclusively in the aqueous phase, since the epoxy-based droplets, acting as substrate for the interfacial polymerization, were absent.

As far as the microcapsules containing the epoxy resin concerns, a different and more complex morphology is evident in the

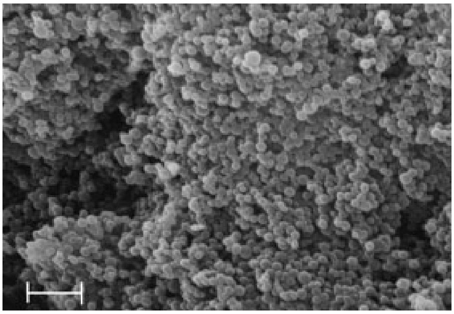

Figure 1.
SEM micrograph of neat urea-formaldehyde.

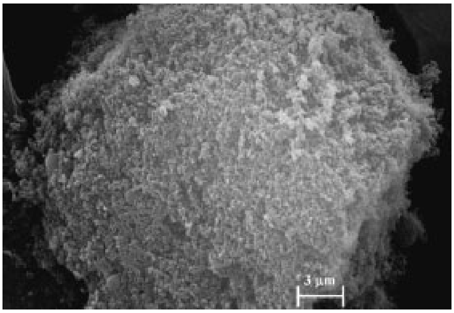

Figure 3.
SEM micrograph of sample E.

SEM micrographs. Figure 2 shows the SEM image of samples A which is very similar to that observed for the samples B and C, differing respectively on the reaction time and temperature used for their preparation (see Table 1).

The microcapsule diameters are in the range between 5 and 15 microns in all cases and the morphology is characterized by the presence either of microcapsules and agglomerates of nanoparticles.

Figure 3 shows the SEM image of samples E which is very similar to that observed for the sample D. Both samples have been prepared at a reaction temperature of $T = 40\,^\circ C$ and by decreasing the stirring rate (see Table 1).

It can be observed that the morphology was very similar to that observed for the sample composed by pure UF and it was characterized by the widespread amount of agglomerated nanosized particles.

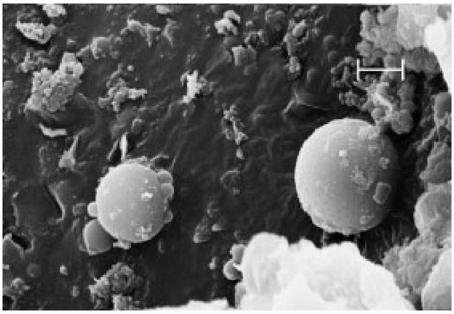

Figure 2.
SEM micrograph of sample A.

Most probably, in both cases, due to the lower reaction temperature and stirring rate the organic phase was not well dispersed in the aqueous medium and the urea-formaldehyde system reacted predominantly in the water phase.

Thermal Analysis

In order to investigate on the presence of the epoxy resin into the capsules, a thermal analysis by DSC was carried out. The DSC curves of prepared samples are reported in Figure 4 in comparison with the thermogram of hollow UF capsules with the aim to evaluate the effect of the reaction temperature on the encapsulating capability. For this purpose, the peak centred at $T = 225\,^\circ C$ was taken into account since it was not possible to refer to the melting point of the epoxy resin as a diagnostic peak indicating the achievement of the encapsulation. In fact, once the epoxy resin was melted to be added to the reaction solution, it was not able to recrystallize, retaining its viscous state for a long time.

The peak at $T = 225\,^\circ C$ is likely to be attributed to the homopolymerization of the epoxy monomer. It is known that epoxies are reactive towards self-polymerization to polyethers at high temperatures ($T \approx 200\,^\circ C$) and in the presence of impurities, such acidic and basic compounds.[21] These species most probably were captured into the capsules during the wall formation.

Since the ΔH associated to the homopolymerization reaction is unchanged for

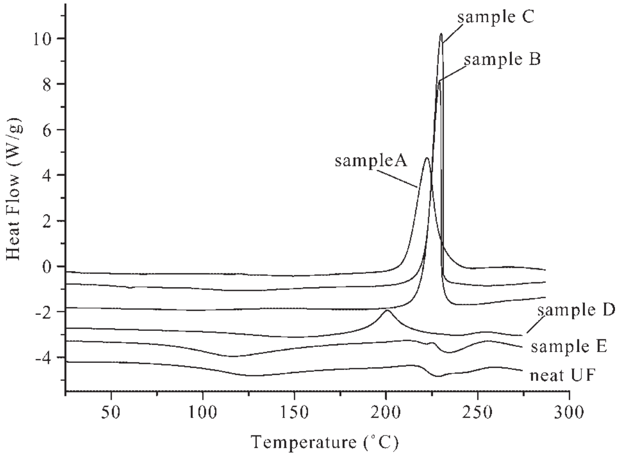

Figure 4.
DSC curves of neat UF and UF/PY306 microcapsules.

sample A and B, that differ only on the reaction time used for their preparation (see Table 1), it can be concluded that the reaction time do not affect the encapsulation yield.

On the other hand, a decrease of the ΔH associated to the homopolymerization reaction has been observed by decreasing the reaction temperature and the stirring rate. This can be explained in terms of a less efficient dispersion of the core agent with reducing the temperature and the agitation speed. In fact, at $T = 40\,°C$ the epoxy resin is below its melting point and its high viscosity does not favours the homogeneous emulsification throughout the aqueous phase. Moreover the lower stirring rate reduces the epoxy resin/water interfacial surface and the UF polymerization occurred predominantly in the water phase.

The results obtained from DSC analysis are summarized in Table 2.

From these findings it can be presumed that only the temperature and the stirring rate affect the epoxy resin encapsulability. Low reaction temperature and stirring rate force the monomer to react in the aqueous rather than at the epoxy/water interface, leading to a decreased encapsulation yield.

Raman Spectroscopic Analysis

The Raman spectra of the microcapsules prepared in the present study are reported in Figure 5, along with the spectra of the pure components for comparison.

The epoxy resin gives rise to an intense Raman scattering, thus producing an essentially noise-free spectrum. Prominent peaks are present in the 3065–2830 cm^{-1} range, due to the stretching modes of the aromatic and aliphatic C–H bonds. Of particular relevance for the present investigation is a well resolved triplet with maxima at 1609,

Table 2.
ΔH and temperature values associated to the epoxy resin homopolymerization in the microcapsules.

Sample	$T_{rection}$ (°C)	$t_{reaction}$ (h)	*stirring rate* (*rpm*)	$\Delta H_{homopol}$ (J/g)	$T_{homopol}$ (°C)
Neat UF	60	4	2000	–	–
A	60	4	2000	390	223
B	60	6	2000	391	228
C	40	4	2000	330	229
D	40	4	1600	101	200
E	40	4	1200	13	212

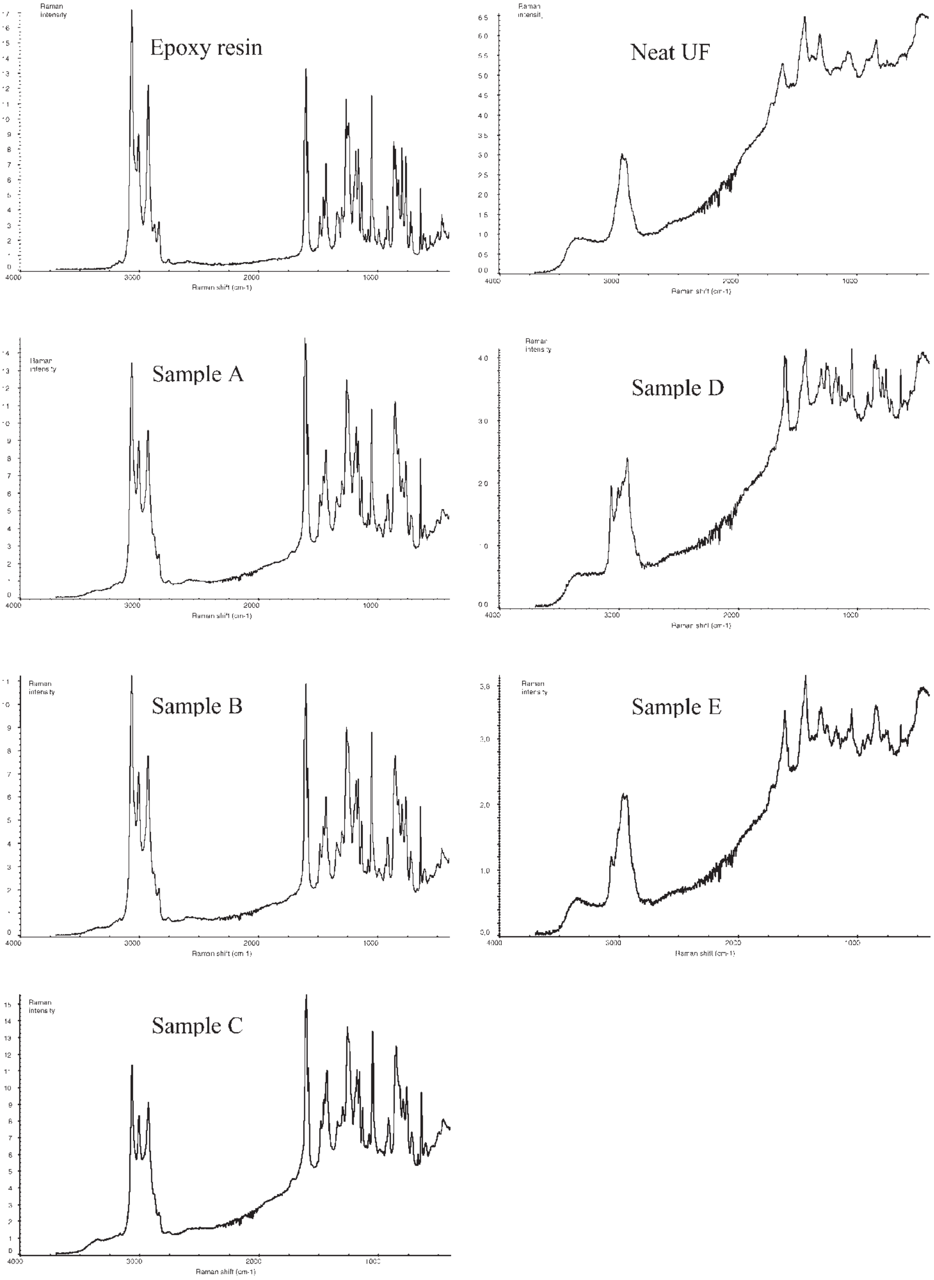

Figure 5.
Raman spectra of epoxy resin, neat urea-formaldehyde and UF/PY306 microcapsules.

1600 and 1587 cm^{-1}, assigned to the quadrant ring stretching modes of the aromatics. The epoxy group gives rise to several characteristic peaks at 1263, 917 and 864 cm^{-1}.[22,23]

The UF resin produces a much lower amount of Raman scattering with respect to the epoxy, and a correspondingly worse spectrum, characterized by intense fluorescence, as indicated by the steep slope of the baseline. In spite of the low intensity and the poor signal-to-noise ratio, several peaks can be identified and assigned. A broad band in the region 3050–2800 cm^{-1} originates from the methylene groups, while the amide carbonyls produce an unresolved multiplet with maxima at 1716 and 1623 cm^{-1}. The complex profile observed in the carbonyl stretching region reflects the multiplicity of molecular structures formed upon curing.[22,24]

Two bands at 1470 (shoulder) and 1438 cm^{-1} are assigned, respectively, to the bending mode of methylene units in the N–CH$_2$–N and in the CH$_2$–OH structures.[22,23] The spectra of samples A, B and C are very similar to the spectrum of the epoxy resin. However, the fluorescence increases in going from sample A to sample C, which reflects the growing contribution of the UF phase to the overall scattering process. Spectra of samples D and E closely resemble the spectrum of the UF resin, thus indicating that in these two cases the UF component is largely predominant. Nevertheless, the more intense peaks of the epoxy resin, notably those in the 1660–1560 cm^{-1} range, remain readily detectable.

Raman spectroscopy is well established as a quantitative analytical technique. In fact, by assuming a direct proportionality between the normalized intensity of a characteristic Raman peak and the concentration of the scattering species, we may write:

$$\frac{I_{UF}}{I_{EPO}} = \frac{I_{1722}}{I_{1585}} = k\frac{C_{UF}}{C_{EPO}} \tag{1}$$

from which

$$\left(\frac{C_{EPO}}{C_{UF}}\right)_S = \left(\frac{I_{1722}}{I_{1585}}\right)_{STD} \cdot \left(\frac{I_{1585}}{I_{1722}}\right)_S \cdot \left(\frac{C_{EPO}}{C_{UF}}\right)_{STD} \tag{2}$$

where I_{1722} and I_{1585} are the intensities of two peaks characteristic, respectively, of the UF and the epoxy resins and C_{EPO} and

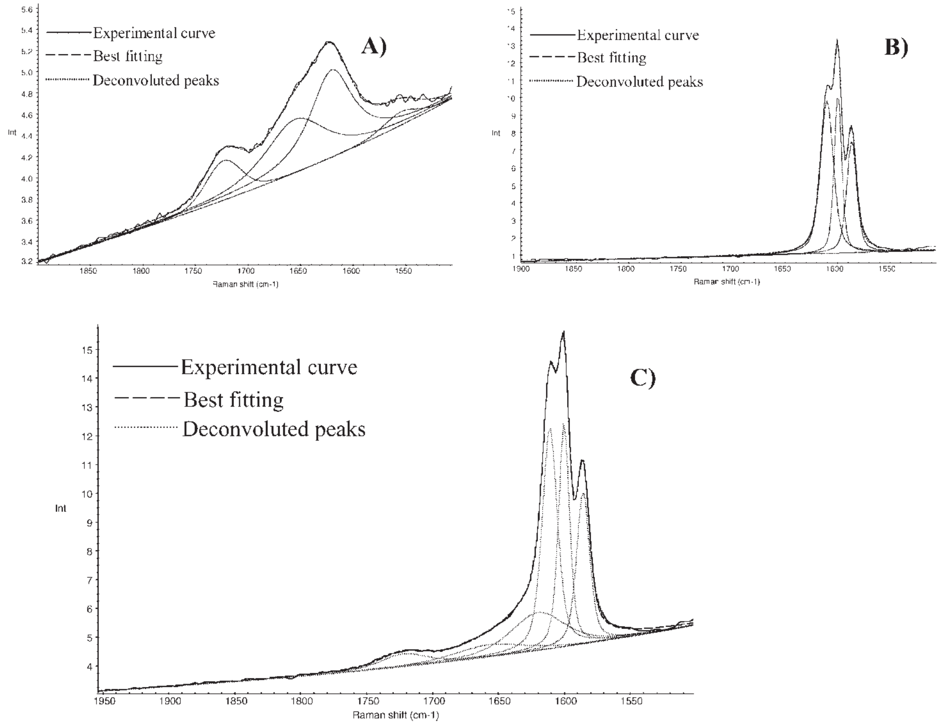

Figure 6.
Curve fitting of A) neat urea-formaldehyde, B) epoxy resin and C) sample C.

Table 3.
Summary of quantitative analysis by Raman spectroscopy.

Sample	*I*(1722)(*A.U.*)	*I*(1585)(*A.U.*)	*I*(1722)/*I*(1585)	W_{epo}/W_{UF}	*%epoxy resin*
Epoxy resin	–	93.5	–	–	100
Neat UF	21.34	–	–	–	0
A	15.22	96.09	0.16	2.72	73.1
B	13.5	72.6	0.19	2.32	70
C	23.95	80.21	0.3	1.43	59
D	8.65	6.94	1.25	0.34	25.6
E	11.84	3.68	3.22	0.13	11.8

C_{UF} refer to their concentration, expressed in weight %. The subscripts S and STD indicate, respectively, the sample being analysed and a standard mixture of known composition prepared by mechanical mixing of the two resins.

Because of severe peak overlapping in the region of interest, a curve fitting analysis was performed to evaluate I_{1722} and I_{1585}. The results are displayed in Figure 6A for the UF resin, Figure 6B for the epoxy resin and in Figure 6C for a representative microcapsule sample (sample C). In all cases the correspondence between the simulated and the experimental profiles is excellent and the peak parameters, i.e. the full width at half height (FWHH), the position and the band-shape, as evaluated from the spectra of the pure reins closely correspond to those obtained for the composite spectra. This confirms the reliability of the method.

The percentage of epoxy resin over the total sample weight, as evaluated from Equation 2 for all the investigated specimens is reported in Table 3.

Conclusions

A series of UF/PY306 epoxy resin microcapsules has been prepared by in situ polymerization in an oil-in-water emulsion and the influence of experimental parameters on the encapsulation yield has been evaluate by means DSC and Raman spectroscopy.

The calorimetric and spectroscopic results indicate that a decrease of the reaction temperature, as well as of the stirring rate has a great influence on the encapsulation yield.

In particular, the main factor responsible for the epoxy resin microencapsulability seems to be related to the stirring rate. Most probably, the dispersion of the organic phase in the water, which is made progressively adverse by decreasing the reaction temperature, i.e. by passing from sample A to sample C, is further reduced by lowering the stirring rate, i.e. by passing from sample C to samples D and E. As a consequence of the low epoxy/water interfacial surface, the reaction between urea and formaldehyde occurs predominantly in the aqueous phase, according to the same mechanism proposed for the UF sample.

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