

Microencapsulation of n-hexadecane phase change material by ethyl cellulose polymer

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Abstract Microencapsulation of phase change materials (PCMs) is an attractive opportunity for broadening their applications. In this respect, a novel encapsulating polymer, ethyl cellulose (EC) was used to entrap n-hexadecane (HD) PCM by an emulsion-solvent evaporation method. Emulsifiers strongly influenced the size and morphology of the forming EC-HD composite microcapsules, and they also had a great impact on their thermal properties. All of the three emulsifiers were suitable to prepare quasi core-shell microparticles, though the high porosity of shells resulted in serious leakage in composites prepared by Tween 80, and permeability of particles manufactured by poly(vinyl alcohol) (PVA), as can be stated from scanning electron microscopy and differential scanning calorimetry analysis. Interfacial tension measurements and spreading coefficient analysis enabled the prediction of preparation conditions for usable core-shell microcapsules. Volume weighted mean diameters of the microparticles were 319 μm , 92 μm and 85 μm formed by Tween 80, PVA and poly(methacrylic acid sodium salt) (PMAA), respectively. A significantly higher HD content and latent heat storage capacity could be achieved using PVA and PMAA than with Tween 80. The thermal cycling test indicated good thermal reliability of microcapsules prepared by PMAA, while the energy-storing capacity of composites prepared by PVA decreased substantially, and a dramatic reduction was found in microparticles using Tween 80.

Keywords: Phase change material, microencapsulation, ethyl cellulose, latent heat, thermal reversibility

Introduction

Thermal energy storage systems provide the potential to attain energy saving, which reduces the environmental impact of energy utilization. The use of latent heat storage is one of the most efficient ways of storing thermal energy. Unlike sensible heat, latent heat allows much higher storage density, with a smaller temperature difference between storing and releasing heat. Phase change materials are latent heat storage materials. Most of the organic PCMs are non-corrosive and chemically inert, stable, recyclable and compatible with numerous building materials. They have desirable cohesion, a high latent heat per unit weight, low vapour pressure, no supercooling, and offer congruent melting and self-nucleation. They have disadvantages such as low thermal conductivities, flammability and high changes in volume during phase change. In order to overcome these problems, their microencapsulation can be an efficient tool. The main benefits of microencapsulation are the increase of the heat transfer area, the reduction of PCM reactivity towards the outside environment and the improvement of cycling stability [1]. Paraffin waxes are versatile PCMs, since they melt and solidify at wide temperature ranges, have large latent heat capacity, negligible supercooling, low vapour pressure, good thermal and chemical stability, and self-nucleating behaviour. Because of its low melting point microencapsulated n-hexadecane can be used e.g. in smart textiles and thermo-regulated fibers.

Ethyl cellulose (EC) is an environmentally friendly polymer which, according to our knowledge, has not been used for the encapsulation of PCMs so far. It is a favourable encapsulating compound mainly used in pharmaceutical technology e.g. for modifying drug release, enhancing the efficacy of active pharmaceutical ingredients, compressing microcapsules, reducing the toxicity and improving stability and processability; furthermore, some taste and odour masking, nutraceutical, agricultural, dental, printing, clothing and cosmetic applications are also known [2]. Since EC is a soft polymer, it may be a favourable wall material for the preparation of PCM containing microcapsules [3]. Although plant oils have already been microencapsulated by ethyl cellulose [4,5], the purpose of those researches was completely different, and thus energy-storing capability was not studied. Phadungphatthanakoon et al. demonstrated n-eicosane PCM microencapsulation into a blend of EC and methyl cellulose [6]. According to these studies [4-6] ethyl cellulose could be predicted to be a suitable shell material for HD microencapsulation.

The emulsion-solvent evaporation method has been rarely used for the encapsulation of organic PCMs [7,8], probably because of the high organic solvent demand. However, it is a simple, easily up-scalable method, which

might provide several important benefits such as high yield and encapsulation efficiency. Loxley and Vincent investigated the emulsion-solvent evaporation process thoroughly [8], whilst they entrapped n-hexadecane in poly(methylmethacrylate) (PMMA) shell. Poly(vinyl alcohol), poly(methacrylic acid), sodium dodecyl sulfate and cetyltrimethylammonium bromide were investigated as potential surfactants in the water phase. The morphology of microcapsules formed by solvent evaporation is substantially determined by the interfacial energies. Torza and Mason [9] described the equilibrium morphology of forming drops as a function of interfacial tensions in the presence of three immiscible liquids. Briefly, if droplets of immiscible liquids (phases 1 and 3) are brought in contact with a third mutually immiscible liquid (phase 2), the final equilibrium morphology can be deduced by determining the various interfacial tensions between the phases (γ_{12} , γ_{23} , and γ_{13}). The spreading coefficients S_i for each phase can be defined as

$$S_i = \gamma_{jk} - (\gamma_{ij} + \gamma_{ik}) \quad (1)$$

and designating phase 1 to be that for which $\gamma_{12} > \gamma_{23}$, then $S_1 < 0$. Then, there are only three possible combinations of S_i , that is,

$$S_1 < 0; S_2 < 0; S_3 > 0, \quad (2)$$

$$S_1 < 0; S_2 < 0; S_3 < 0, \quad (3)$$

$$S_1 < 0; S_2 > 0; S_3 < 0. \quad (4)$$

When the conditions in Eq. (2) are satisfied the particles take on core-shell structure with a phase 1 core within a shell of phase 3. When Eq. (3) is accomplished, “acorn”-shaped particles are formed, and when Eq. (4) is performed, two separate droplets remain (Fig. 1)

This approach was also applied by Loxley and Vincent [8] with the difference that relationship was given for one solid and two liquid phases. The structure of the formed microcapsules was predicted by analysing the interfacial tension between the core-oil and the various aqueous surfactants as well as between the encapsulating polymer and the emulsifier solutions. These calculations presaged core-shell structure only for using poly(methacrylic acid), and acorn shape in the case of the other three emulsifiers. However, in the experiments PVA also provided microcapsules consisting of HD core and PMMA shell. Taking into account these results [8], *Smith* prepared PMMA microcapsules containing Rubitherm® RT20 phase change material [7]. He also found that poly(methacrylic

acid) was more suitable for attaining core-shell structure, since with PVA the size distribution of the microcapsules contained multiple peaks due to the instability of the emulsion that results in incomplete encapsulation or agglomeration.

In our study EC was used for embedding n-hexadecane PCM by an emulsion-solvent evaporation method applying PVA, Tween 80 or PMAA emulsifiers. Size, morphology, yield, PCM content and thermal properties of the forming composite particles were investigated. EC-HD composites produced by PMAA were found to be the most appropriate for energy storage with respect to each of the studied properties.

Materials and methods

Materials

Dichloromethane, polyvinyl alcohol ($M_w=30,000-70,000$, 87-90 % hydrolysed), Tween 80, poly(methacrylic acid sodium salt) ($M_w=9500$) and poly(methyl methacrylate) ($M_w\sim 15,000$) were obtained from Sigma Aldrich, and n-hexadecane was purchased from MOL Hungarian Oil and Gas Company (Hungary). Ethyl cellulose (viscosity: 4 mPa s, 5 wt% in 80:20 toluene/ethyl alcohol, 25 °C) was a kind gift from Dow Deutschland Anlagengesellschaft mbH (Germany).

Emulsion-solvent evaporation technique

The phase change material was entrapped by the carrier polymer using an oil-in-water emulsion, solvent evaporation method. 200 mg EC was dissolved in 5 ml dichloromethane and 0.52 ml (400 mg) n-hexadecane was added during magnetic stirring. The oil-in-water emulsion was formulated by pouring the organic phase into 20 ml distilled water containing 2 % PVA emulsifier, and was stirred magnetically (IKA RET B) for 150 min with 800 rpm under atmospheric pressure at room temperature in order to remove the organic solvent. In another experiment 200 mg EC was dissolved in 5 ml dichloromethane while being stirred magnetically, and 0.26 ml (200 mg) n-hexadecane was added. The formed organic solution was emulsified in 20 ml distilled water containing 2 % Tween 80 surfactant at 800 rpm, and stirring was continued for 150 min under atmospheric pressure at room temperature. Finally, 250 mg

EC was dissolved in 5 ml dichloromethane and 0.975 ml (750 mg) n-hexadecane was added during magnetic stirring. The oil-in-water emulsion was formulated by pouring the organic phase into 20 ml distilled water containing 1 % PMAA surfactant, and was stirred magnetically for 150 min with 800 rpm under atmospheric pressure at room temperature. Composite microcapsules were filtered by a 3 μm cut-off filter (Macherey-Nagel 640 d) for the determination of yield and PCM content.

Analysis of microcapsules

The size of particles was measured by Mastersizer 2000 (Malvern Instruments, Malvern, UK) operated upon laser diffraction method. Their morphology was investigated after centrifuging and redispersing the microparticles in distilled water, dropping onto a grid, and drying at room temperature. Then, the capsules were vacuum-coated for 3 min with a mixture of gold and palladium and examined with a Philips XL-30 environmental scanning electron microscope (ESEM) at 25 kV.

The yield of the product was determined by weighing the microcapsules after filtration, rinsing with distilled water and drying at 60 °C. 100 mg of each sample was weighed, and the PCM content was calculated after the n-hexadecane was extracted 3 times from the microparticles by each 5 ml n-hexane.

The thermal properties of the microcapsules were determined using a Setaram $\mu\text{DSC3evo}$ differential scanning microcalorimeter. The samples were weighed into 100 μL aluminium crucibles, and were gently pressed to the bottom of the crucible in order to improve the thermal contact between the sample and the crucible, and then the system was hermetically closed by crimping a cap. The samples were three times cycled from 5 to 35 °C, with a scanning rate of 0.6 °C/min. The results were processed by using the thermoanalyzer's Calisto Processing (v1.12) software. The corresponding melting/freezing enthalpies, and onset temperatures were determined by the baseline integration method (Tangential sigmoid baseline type). Melting/freezing enthalpies were given for the total mass of microcapsules (EC+HD).

Accelerated thermal cycling tests were carried out to determine the thermal reliability of the microencapsulated PCM. One thermal cycling test consisted of exposing microcapsules to a melting and freezing process. The tests were performed consecutively up to 1000 thermal cycles. The microcapsules were warmed by a heating circulator

(Julabo EH, Germany) up to 29 °C and cooled down to 9 °C by a Peltier element. DSC analysis was employed to check the thermal reliability of the composite PCMs after thermal cycling.

Determination of interfacial tensions and spreading coefficients

Polymer films were prepared from a 4 % and a 5% (w/v) solution of the ethyl cellulose polymer in DCM. A glass microscope slide, previously cleaned with ethanol, was immersed in the polymer solution. It was allowed to be wetted by the solution and after five minutes the solution was drained by 1 ml/min. Finally, the freshly prepared film was dried overnight.

The surface tensions of the liquid phase components of the systems were measured by the pendant drop method using an FTA 1000 B tensiometer (First Ten Angstroms, Inc., USA). The interfacial tensions between hexadecane and the surfactant solutions were also determined by the pendant drop method using a quartz cuvette filled with the oil (light phase). A drop of the surfactant solution was pictured when immersed in hexadecane in a quartz cuvette [10]. The interfacial tensions between each surfactant solution, oil and ethyl cellulose polymer were calculated from the measured contact angle against a film of ethyl cellulose on the base of Young's Force Balance for the sessile drop.

$$\gamma_{LV} \cdot \cos(\theta) = \gamma_{SV} - \gamma_{SL} \quad (5)$$

where LV: liquid - vapour interface, SV: solid(polymer) - vapour interface, SL: solid - liquid interface and θ : contact angle between polymer film and liquid phase.

The surface tension of the ethyl cellulose polymer (32 mN/m) was taken from the pertinent literature [11]. Interfacial tension values were determined from at least ten independently formed drops. The temperature of experiments was 22 ± 1 °C.

Results and discussion

Size, yield, PCM content

Loxley and Vincent successfully used PVA and PMAA emulsifiers in a system [8] similar to ours; however, by using PMMA as the encapsulating polymer. Furthermore, in our previous studies PVA was found to be a very effective surfactant for emulsifying EC containing organic droplets in the aqueous phase [12-14]. Nevertheless, we also examined the usability of other emulsifiers, such as Tween 80, polyvinylpyrrolidone and poloxamer (Pluronic F68) beside PMAA. The use of PVA, Tween 80 and PMAA resulted in well-treatable composite microcapsules; with the other two emulsifiers a significant amount of immense aggregates also formed. As shown in Fig. 1, the type of emulsifier had a great impact on the size of microcapsules. Using Tween 80, the size of forming microcapsules was much larger (volume weighted mean: 319 μm) than with PVA (volume weighted mean: 92 μm) or PMAA (volume weighted mean: 85 μm). PVA and PMAA were similarly effective surface active agents, nevertheless, microparticles manufactured by PMAA had a wider size distribution. It can also be observed that neither of the microparticles had monomodal distribution, since each obtained size distribution contained another little peak in the region below 10 μm , 20 μm and 40 μm with PMAA, PVA and Tween 80, respectively; however, less than 10 % (w/w) of each sample fell into these small size ranges.

The yield of the microparticles was moderately high with PVA and Tween 80 (Table 1), and PMAA provided very satisfactory results. Initial HD content was selected to be the highest (75 %) during preparation using PMAA, since in the case of the other two emulsifiers significant leakage could be observed at a higher initial HD ratio. The HD content in the microcapsules formed by PVA or PMAA was very close to its initial weighed ratio (66.6 % and 75 %, respectively); nevertheless with Tween 80 it was significantly lower (initial ratio: 50 %). This supports the fact that the Tween 80 was not as efficient emulsifier as PMAA or PVA, which was also observed upon size investigation.

Morphology

SEM observations (Fig. 2 a,c,f) confirmed what has already been pointed out at laser diffraction measurements: the particles were polydisperse because of the presence of some particles smaller by about one order of magnitude than the abundance. Most of the capsules were spherical, prepared by either of the emulsifiers. Scanning electron microscopy also showed that all the three composite types possessed more or less core-shell structure (Fig. 2); however, the cross-sections of the shells were porous to various extents (Fig. 2 b,d,g). Microcapsules formed by Tween 80 represented the highest porosity; moreover, some of the pores seemed to perforate the shell (Fig. 2 d,e),

which can result in the leakage of the PCM from inside. The wall of microparticles synthesized by PVA was also rather porous, and some holes could be observed on the shell of some microspheres (Fig. 2 a,b). Most compact structure was achieved by PMAA emulsifier (Fig. 2 f,g).

Interfacial tensions

The fulfilment of conditions in Eq.(2) results in a core-shell morphology with phase 1 appearing as the core within a shell of phase 3. The interfacial tension between each emulsifier solution and the air, and then between the n-hexadecane and each surfactant solution had to be measured in order to determine the equilibrium morphology. Table 2 shows the measured surface tensions (mN/m) (liquid-vapour of surfactant solution and HD, liquid-liquid of surfactant solution and HD) and contact angle (degrees) data (EC film - surfactant solution and EC film - HD), as well as calculated interfacial tensions and spreading coefficients (solid-liquid of EC film - surfactant solution and that of EC film - HD).

Analyzing the data according to the theory of Torza and Mason [9], spreading coefficients vary in quite a wide range as a function of applied emulsifiers. As expected, when the HD-surfactant liquid-liquid interfacial tension was the smallest with Tween 80, the spreading coefficient S_3 was the highest negative value. When the liquid-liquid interfacial tension was the biggest with PMAA, the S_3 became positive. This means the core-shell structure is most likely to be formed using PMAA, while the acorn shape is probable with Tween 80 and PVA. However, some authors found that this analysis does not result in the experienced morphologies in every case [8,15]. In our investigations, the morphologies obtained by SEM showed quasi core-shell structure with Tween 80 as well as PVA, though the interfacial tension analysis did not predict it. Nevertheless, the porousness of their shell queries the reality of the core-shell morphology. In this respect it is emphasized that this analysis only considers the interfacial energies for calculating the probable morphology; and it does not take into consideration other important influencing parameters such as the volume ratio of the core and shell material, speed of evaporation, the time frame of solvent content in the organic phase, and so on. In our case the capsules do not get to the equilibrium morphology during the process. In the initially forming emulsion droplets the solubility of ethyl cellulose decreases via the evaporation of dichloromethane. Thus, in the emulsion droplets ethyl cellulose-rich coacervates form, which are mobile enough to move to the surface and coalesce, although, due to the wetting condition they cannot constitute a continuous shell in

the presence of Tween 80 or PVA. The pores of the shell are filled by the droplets of n-hexadecane, though the energetic relations do not enable their movement into the water phase, hence they remain in the EC shell as smaller droplets. At the same time, the dichloromethane evaporates from the emulsion droplets, which issues in increasing viscosity and mechanical strength of the shell material. This inhibits the ooze of HD in bigger drops to the outward surface of the capsule wall and thus the formation of the acorn structure predicted by the model [8]. Nevertheless, small HD droplets can definitely leak out to the surface while Tween 80 emulsifier is used.

Thermal properties

Melting and solidifying DSC curves of HD and EC-HD composites are shown in Fig. 3. The DSC curve of HD was taken as reference to evaluate the change in the thermal properties of the composite PCM. The phase transition intervals of the EC-HD microcapsules prepared with PVA and PMAA greatly overlapped with those of the HD, suggesting that the thermal properties of the composites were similar to those of the HD. However, the cooling DSC curve of the composites prepared with Tween 80 contained two peaks that denote the detachment of the two phases during crystallization. A similar phenomenon was observed by other authors [16-18]; however, the reason is not completely clear. *Zhang* attributed the peaks at higher and lower temperatures to heterogeneously and homogeneously nucleated liquid-crystal transitions, respectively [17]. Thus, the stirring rate affected the DSC crystallization and certainly the size of the microcapsules, which means that the degree of crystal subcooling increased with the decrease of microcapsule size. *He et al.* found that characteristic temperatures depended strongly on the DSC heating/ cooling rate [18]. In the melting process, an enlarged temperature range was observed as compared to the freezing process at the same rate. At a higher scanning rate one wider temperature peak, while at a slower scanning rate two peaks appeared, where the peak of low temperature was due to a solid-solid phase transition.

In our case, the melting and solidification temperatures are 18.9 °C and 15.4 °C for pure HD, 18.5 °C and 13.9 °C for the EC-HD by PVA, and 19.5 °C and 15.2 °C for the EC-HD by PMAA, respectively. At EC-HD by Tween 80, the melting and the first solidifying peaks with maxima of 18.4 °C and 14.2 °C, respectively, are a bit lower than for pure HD, while the second solidifying peak is 11.6 °C. When the phase transition temperatures of PCM and microcapsules synthesized by PVA and PMAA are taken into consideration comparatively, the melting temperatures are in compliance with the HD. This is due to the ordered structures of PCM in the solid phase gradually changed

towards the disordered structures in the liquid phase of HD [19]. Conversely, the entrapped impurities (e.g. trace of emulsifier) and the heterogeneous structure reduced the crystallization point [20].

The latent heats of melting and freezing were 208.4 J/g and 206.6 J/g for HD, 147.1 J/g and 140.8 J/g for the EC-HD microcapsules by PMAA, 137.8 J/g and 134.4 J/g for the EC-HD composite by PVA, and 46.6 J/g and 32.6 J/g for the EC-HD by Tween 80, respectively. Microcapsules manufactured by PVA and PMAA displayed almost as high heat storage capability as that follows from their HD content. The microcomposites formed by Tween 80 are capable to store much less energy than that which results from its HD concentration. This can be explained by the structure of the particles that indicated a significant likelihood of paraffin leakage from the capsules.

The PCMs designed for application must withstand repetitive cycles of heating and cooling without any degradation in their life period. Results of the DSC analysis after the thermal reliability study can be seen in Fig. 4. In accordance with expectations, the microcapsules with core-shell structure (by PMAA) could save their energy storing capacity to the highest extent (137.9 J/g and 132.3 J/g). Although the decrease ratio of latent heats of melting and freezing of composites formed by PVA were more considerable, their values remained still quite high: numerically 118.2 J/g and 115.3 J/g, respectively. However, melting and freezing enthalpy changes of microcapsules produced by Tween 80 were reduced substantially to 26.2 J/g and 18.6 J/g, respectively. This tendency can be explained by the various structures of shells noticed in SEM images and confirmed by interfacial tension measurements. The DSC analysis before and after thermal cycling verifies the observation that the PCM can ooze through the leaky shell considerably from the capsules produced by Tween 80, and noteworthy leakage can occur from microparticles prepared by PVA. The results also proved that the composite manufactured by PMAA, even at a high (3:1) HD/EC ratio was stable against the leakage of HD. It is also emphasized that the core-shell structure is desirable with respect to most potential applications; however, it is not sufficient except if it is attendant with leakage inhibition.

Conclusions

Ethyl cellulose was found to be a suitable polymer to entrap n-hexadecane phase change material. Microcapsules were encapsulated by the emulsion-solvent evaporation method using PVA, Tween 80 or PMAA emulsifier. With all of the surfactants quasi core-shell microcapsules could be formulated, although the shells showed porosity of

various extents. The structure of the forming microparticles can be predicted by determining the interfacial tensions between the phases, and analysing the spreading coefficients. According to these calculations core-shell particles had been expected only with PMAA. Nevertheless, the shells of capsules obtained by PVA and especially with Tween 80 were so porous that they suffered from substantial leakage, which was proved by SEM and DSC investigations. Thus, considering the experiences, it can be stated that the interfacial tension measurements and spreading coefficient analysis can be utilized to presage whether the forming capsules possess real core-shell structure. Both theoretically and in the experiments, composites prepared with PMAA showed the most desirable properties regarding the size and the latent heat storage capacity, furthermore, there was no significant temperature and enthalpy change observed after thermal cycling. Due to its simple preparation method, good thermal energy storage capacity and thermal reliability, this microcomposite can be considered as suitable encapsulated PCM for thermal energy storage applications.

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Table 1. Yield (%) and PCM content (%) of ethyl cellulose-n-hexadecane microcapsules prepared by PVA, Tween 80 and PMAA surfactants.

Emulsifier	Yield (%)	PCM content (%)
PVA	84.7	66.0
Tween 80	82.8	40.8
PMAA	95.5	71.7

Table 2: Measured surface tension (mN/m) and contact angle (degrees) data, as well as calculated interfacial tension and spreading coefficients

			Surfactant solution L-V	HD L-V	Surfactant soln-HD L-L	Surfactant solution-EC film S-L, HD-EC film S-L				S3	S2	S1
						contact angle,		interfacial tension				
Tween, 2%	EC, 5%	HD	43.21	26.94	9.78	71.83	22.22	18.53	7.06	-15.81	-21.25	1.69
PVA, 2%	EC, 5%	HD	46.82	26.94	16.29	73.12	22.22	18.40	7.06	-9.17	-27.64	-4.94
PVA, 2%	EC, 4%	HD	46.82	26.94	16.29	72.00	21.48	17.53	6.93	-8.17	-26.89	-5.69
PMAA, 1%	EC, 5%	HD	73.34	26.94	32.51	67.33	22.22	3.73	7.06	21.72	-29.18	-35.84

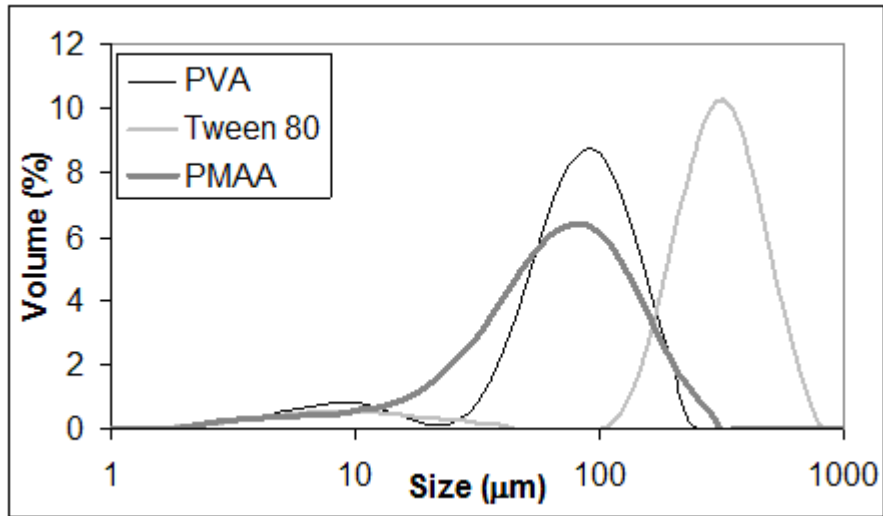
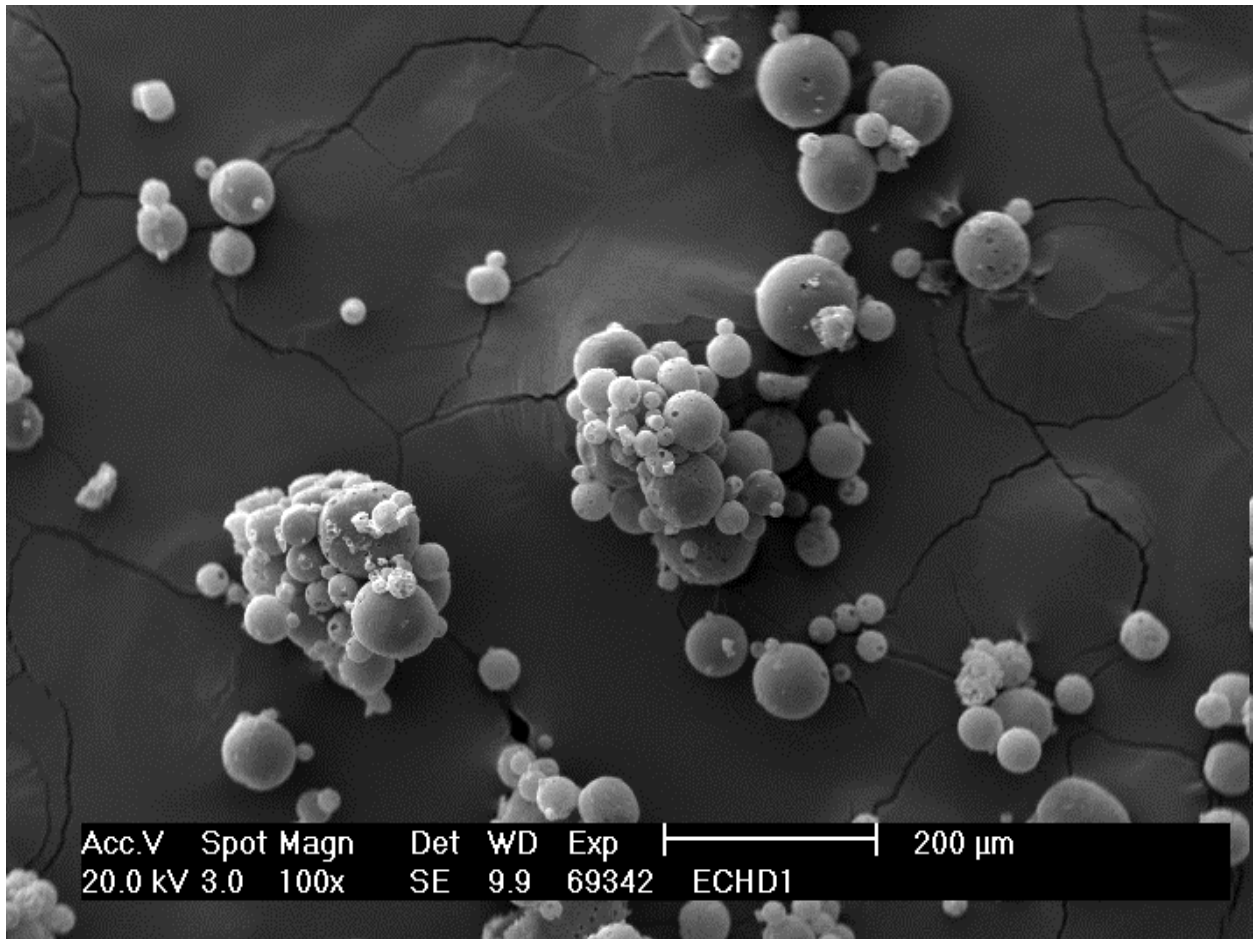
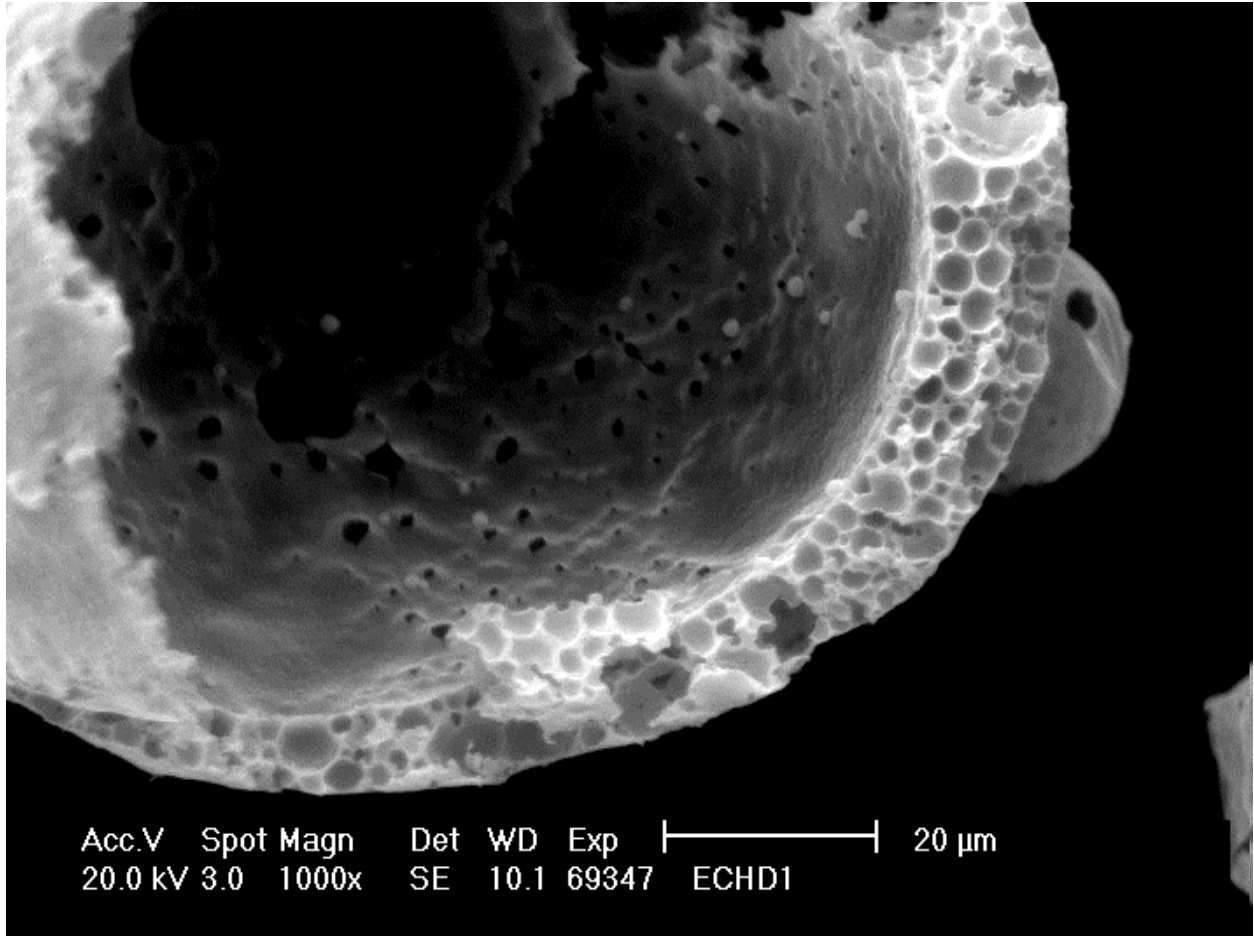


Fig. 1 Size distribution of the EC-HD composites manufactured by PVA, Tween 80 and PMAA emulsifiers.

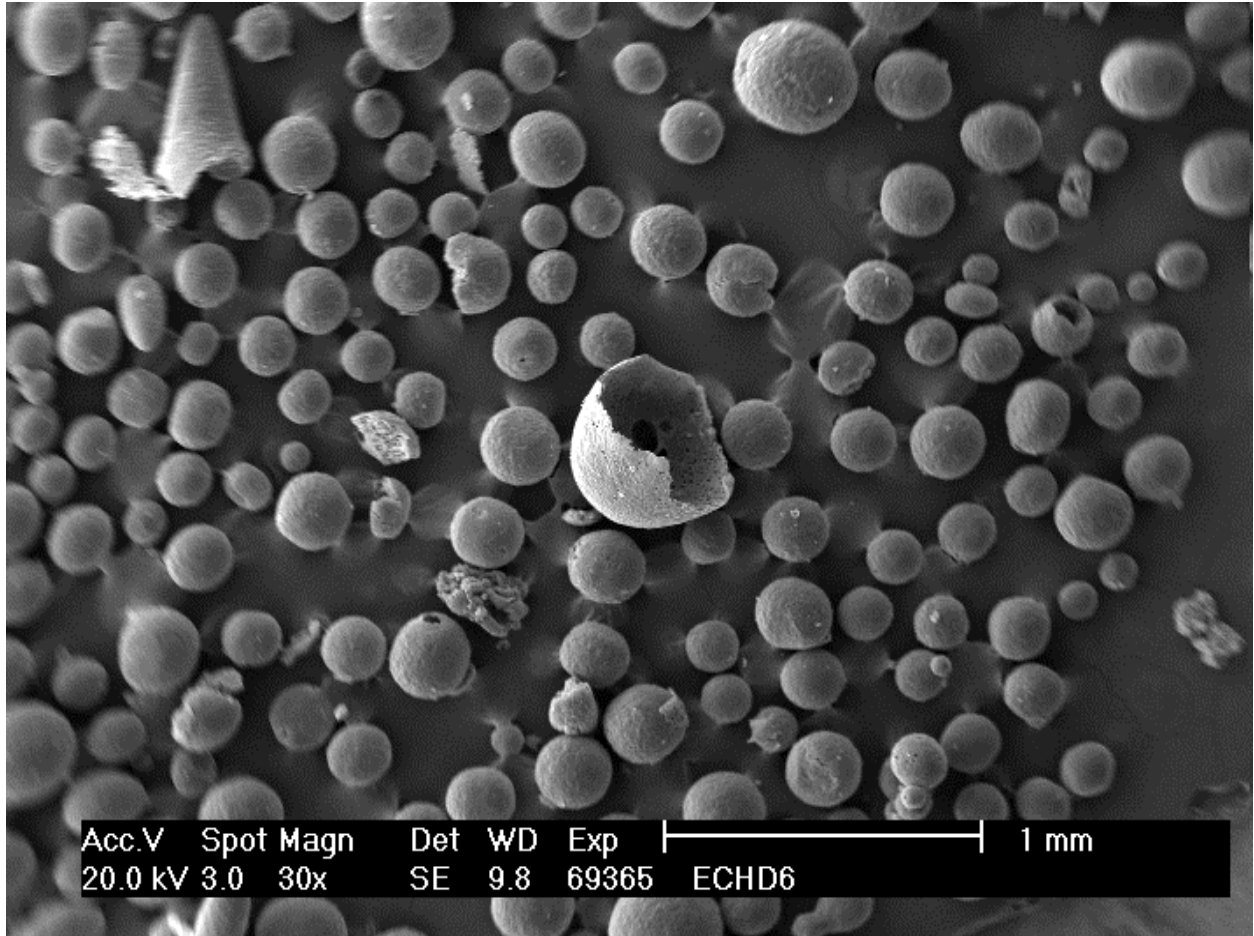
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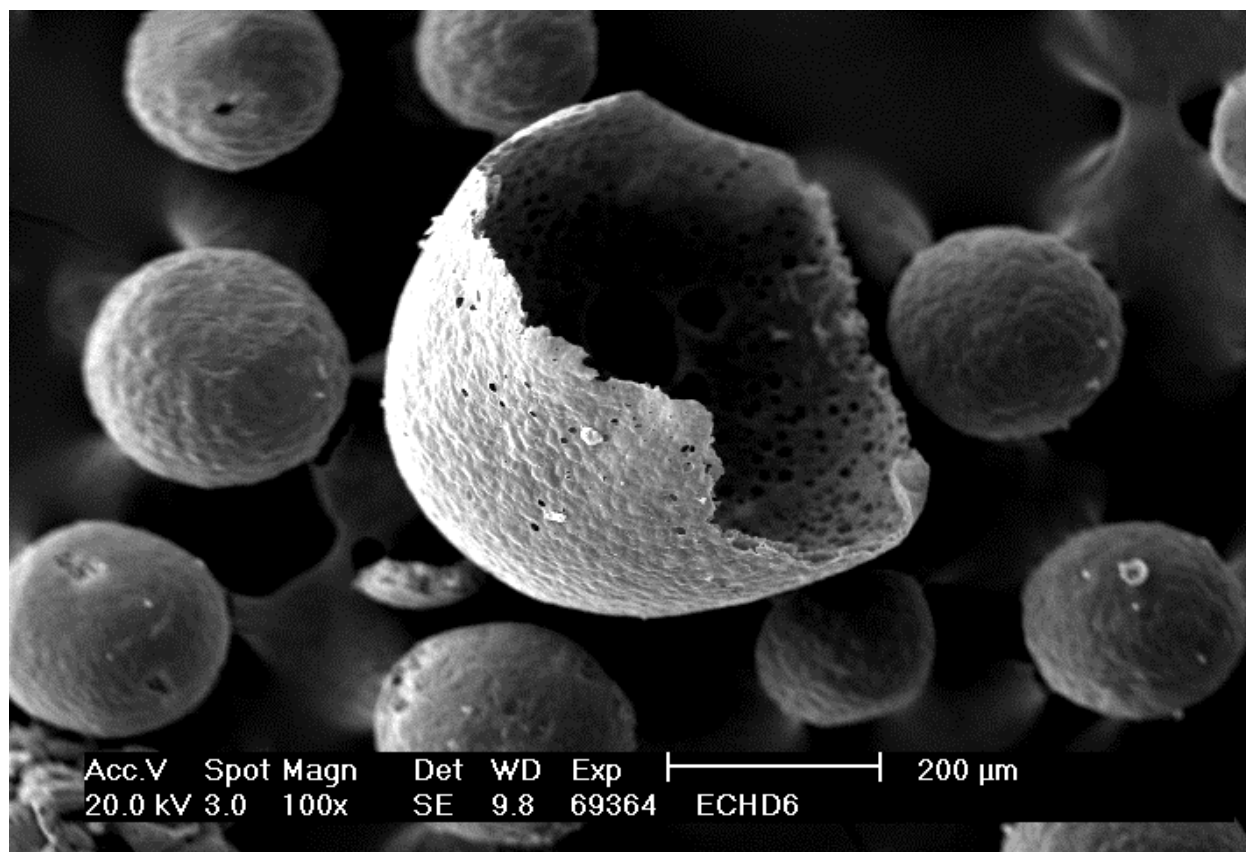
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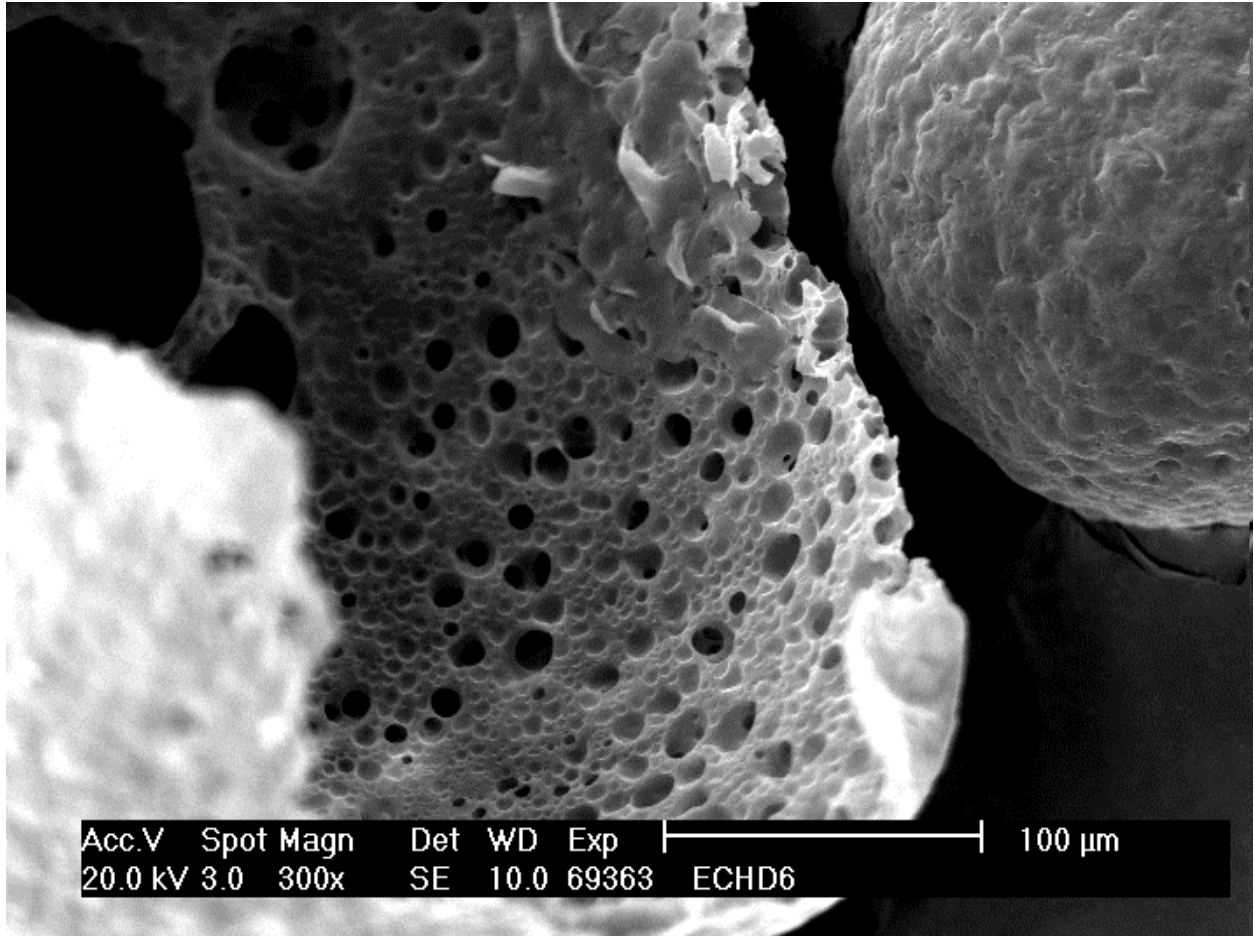
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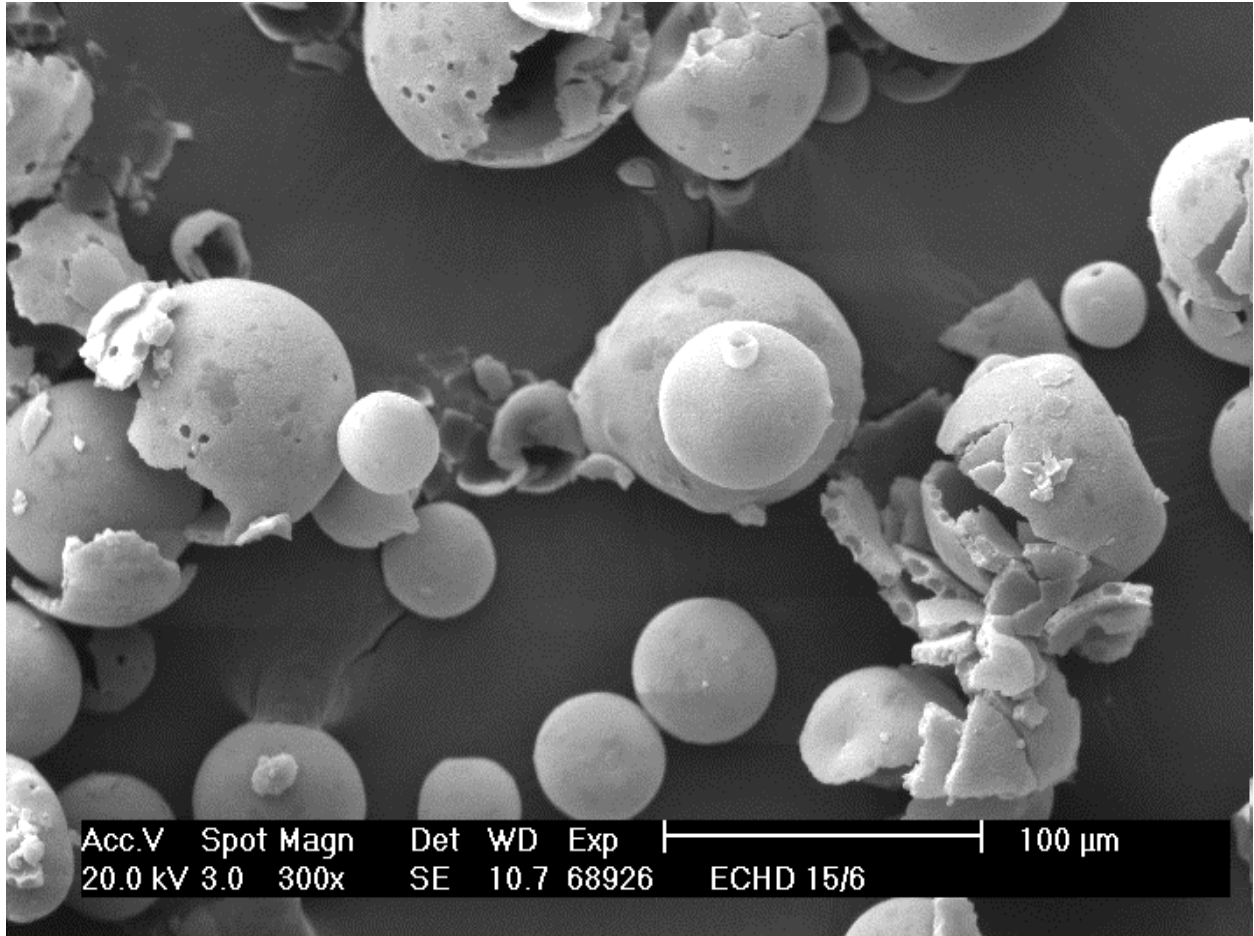
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G

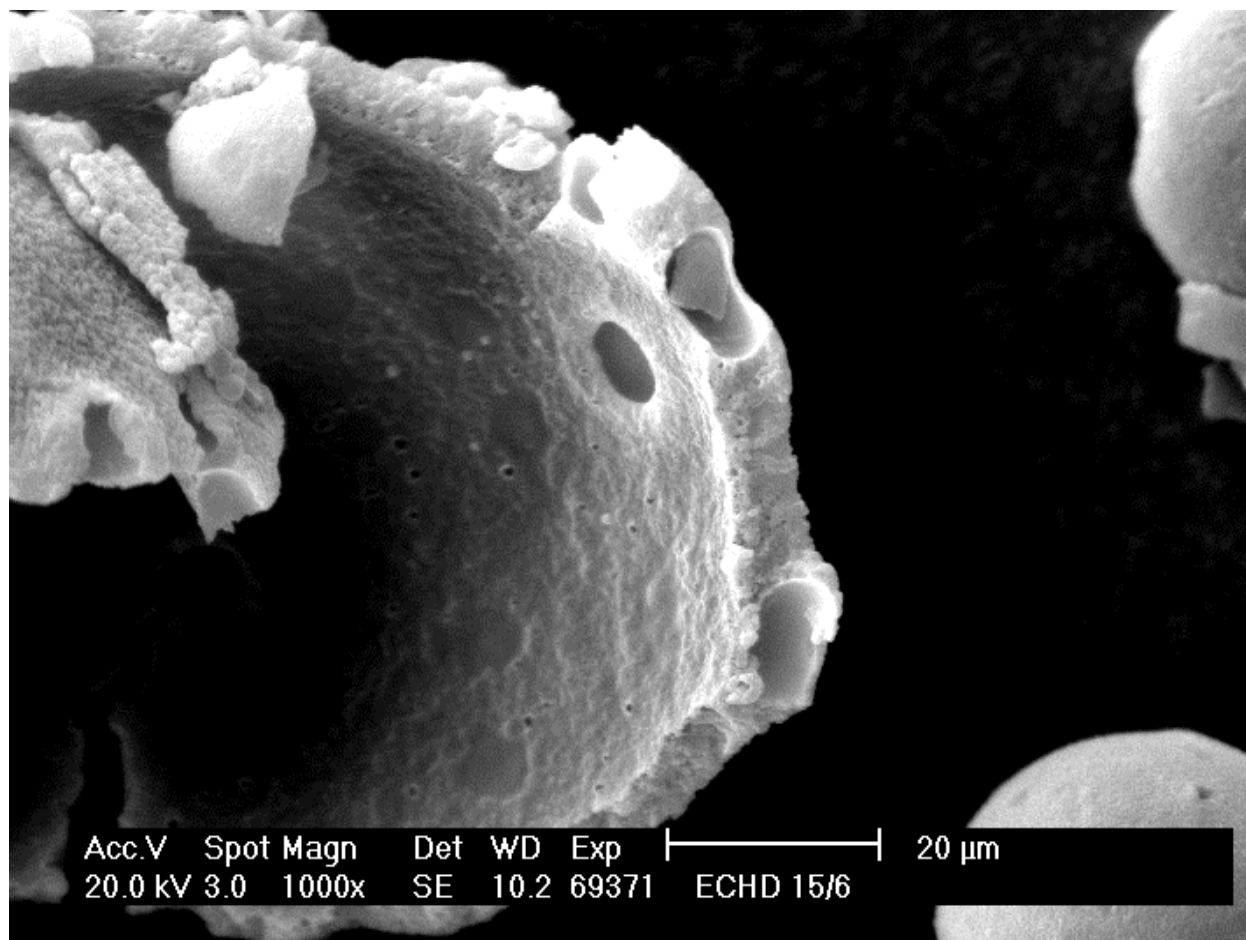
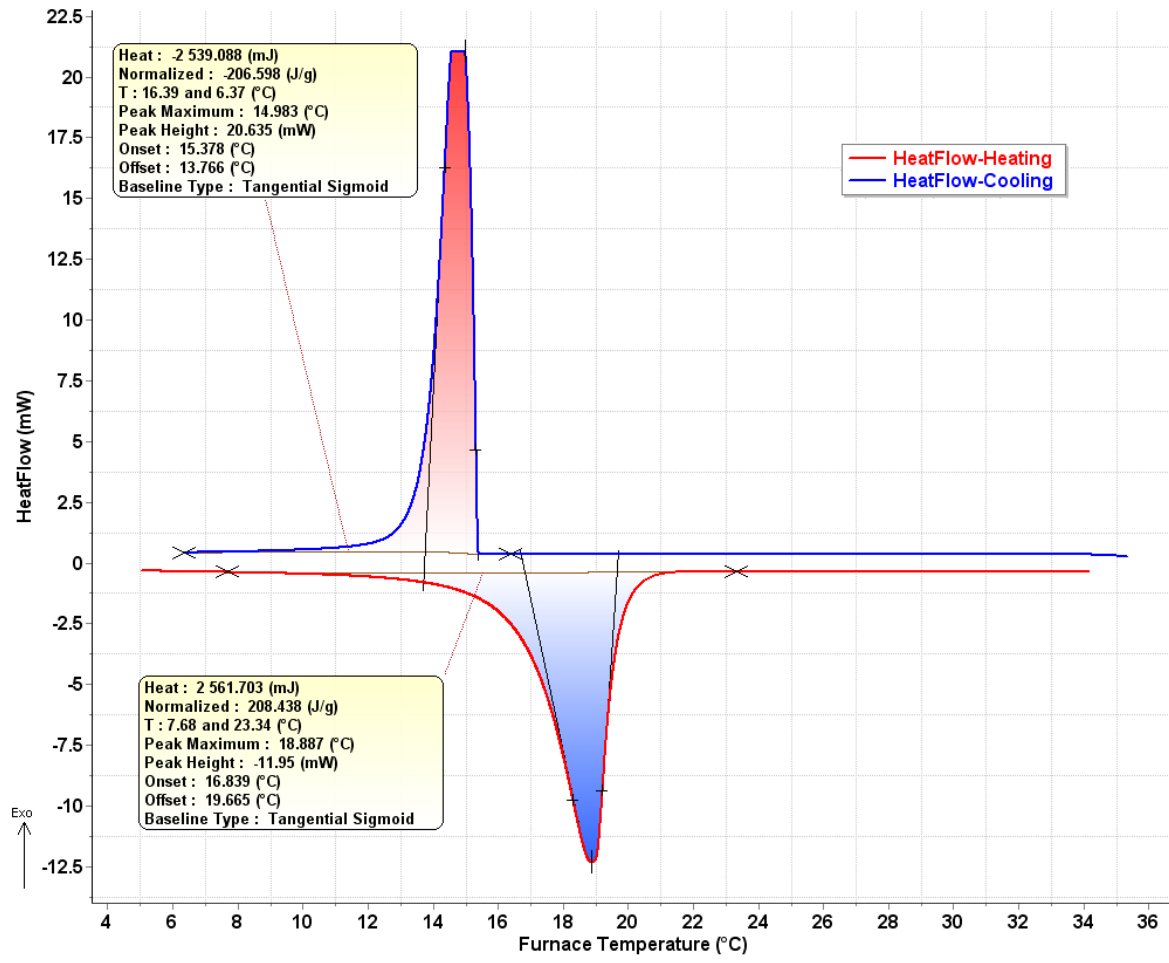
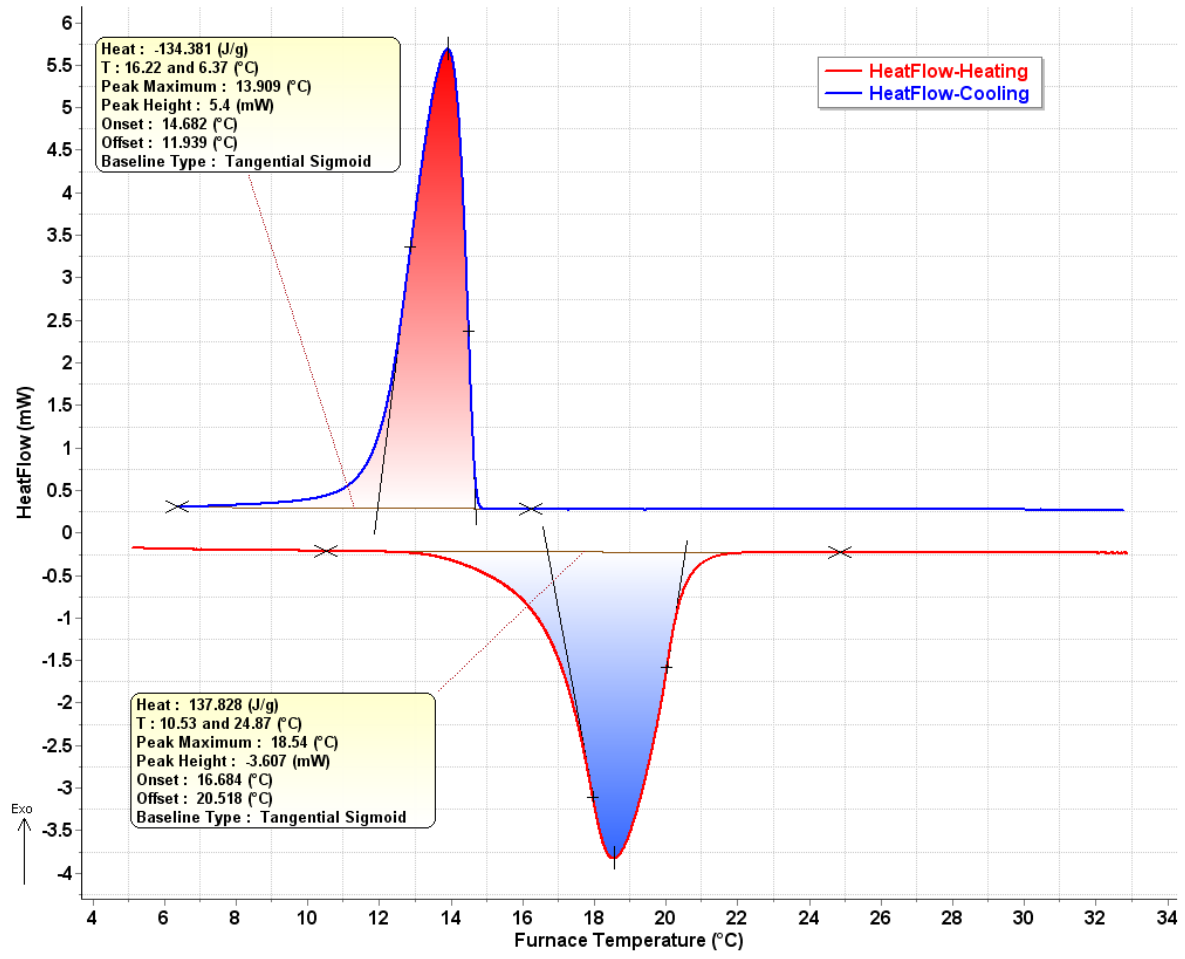


Fig. 2 SEM images of fractured EC-HD microcapsules prepared by PVA (A,B), Tween 80 (C,D,E) and PMAA (F,G).

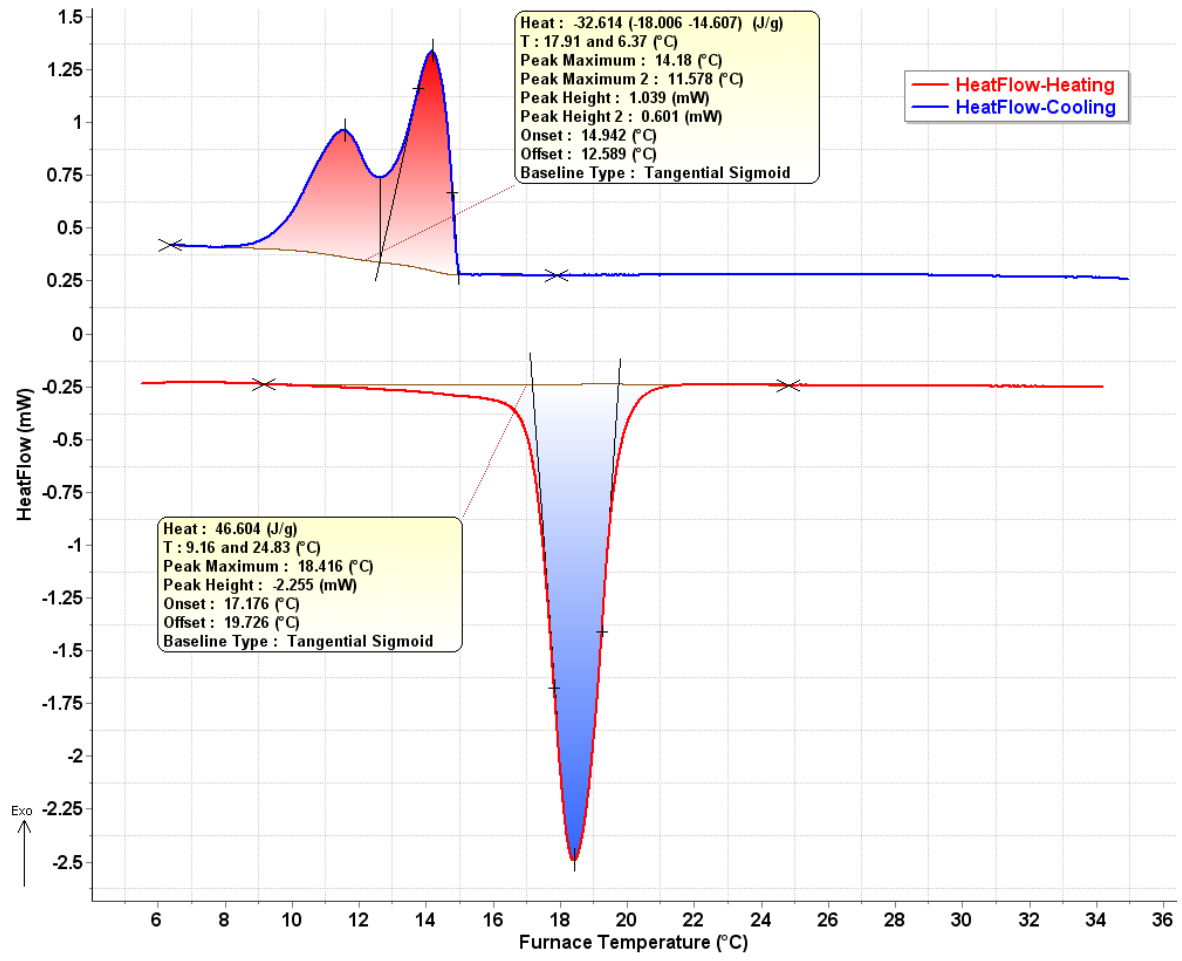
A



B



C



D

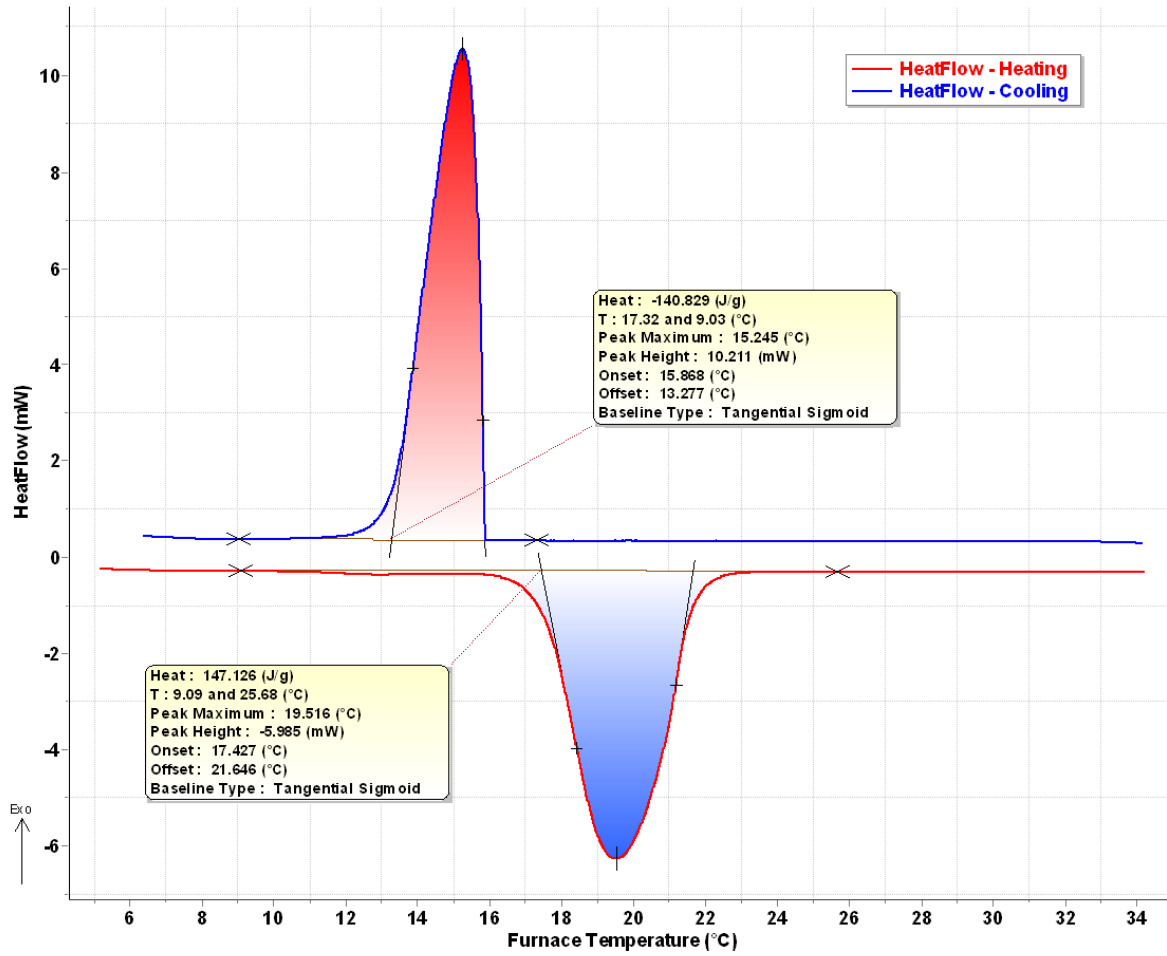
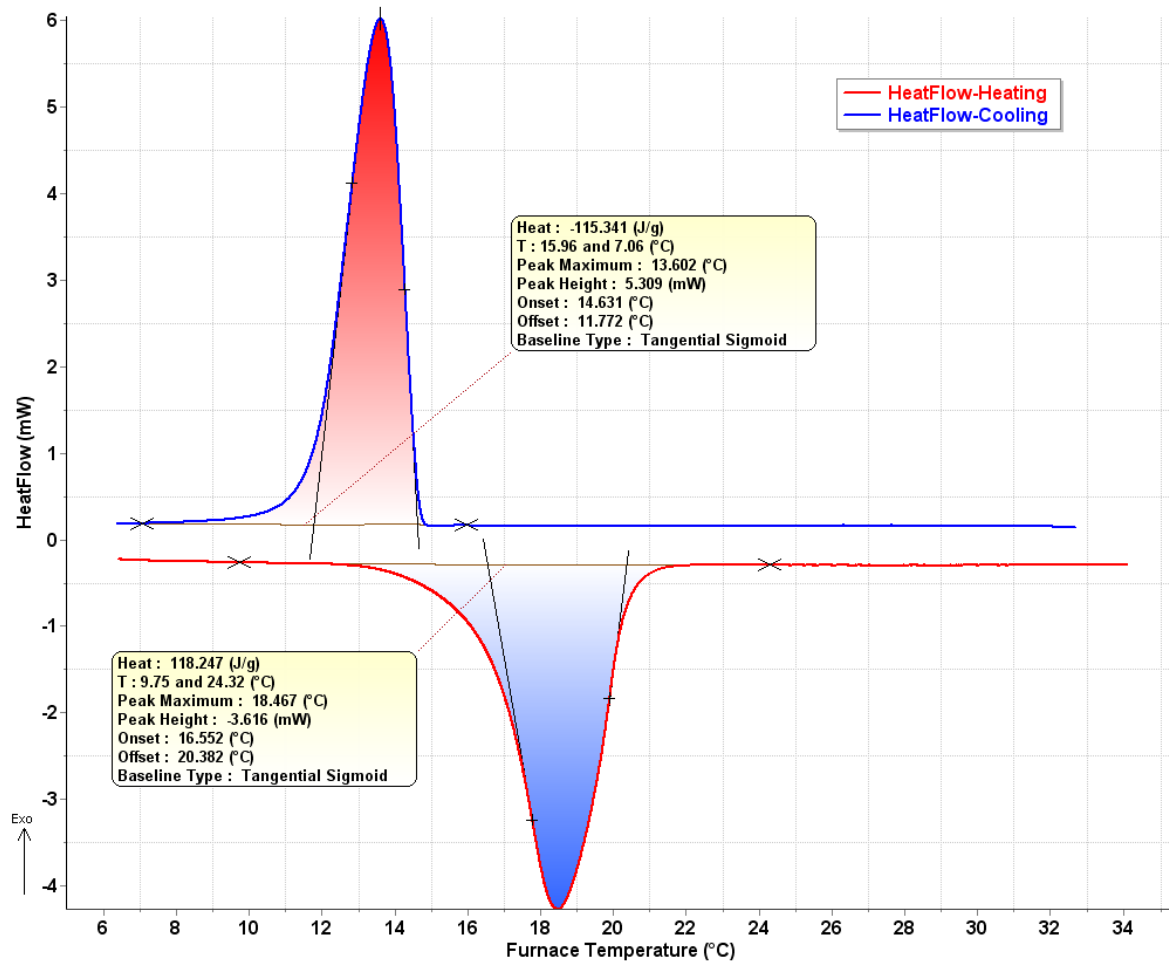
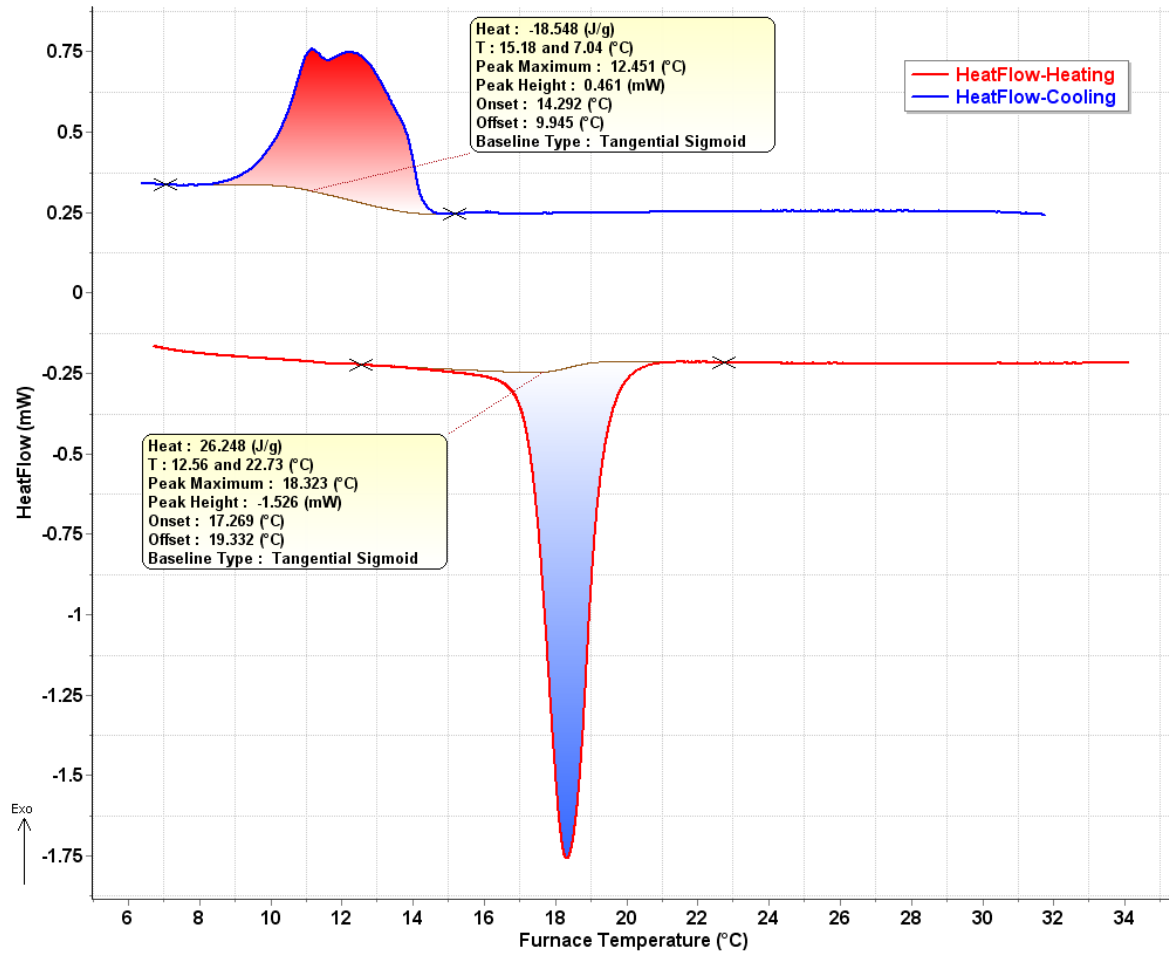


Fig. 3 DSC curves of n-hexadecane (A) and ethyl cellulose-n-hexadecane composites manufactured using PVA (B), Tween 80 (C) and PMAA (D) surfactants.

A



B



C

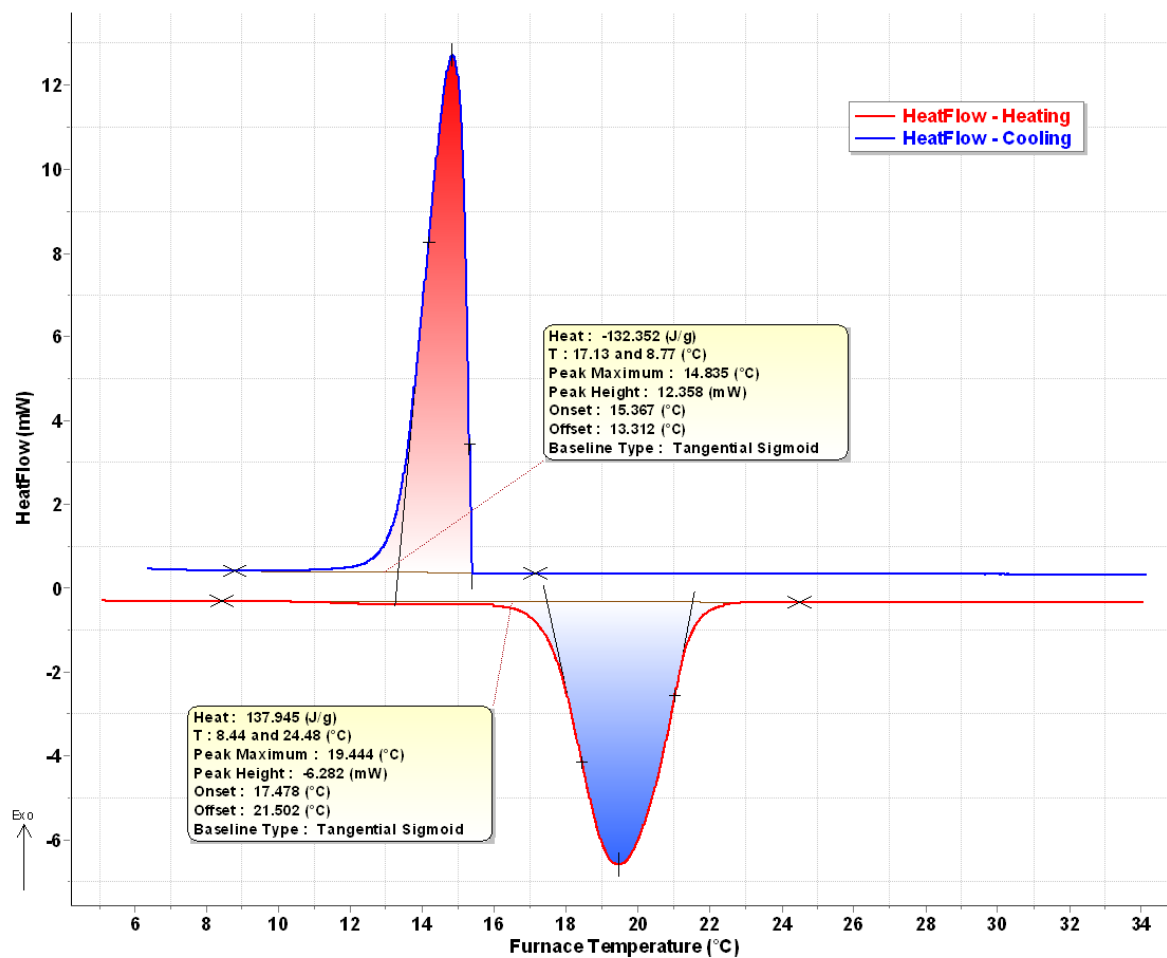


Fig. 4 DSC curves of ethyl cellulose–n-hexadecane composites manufactured by PVA (A), Tween 80 (B) and PMAA (C) surfactants after 1000 thermal cycles.