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POLYMERIC CAPSULE PREPARATION TAILORED FOR FOOD PACKAGING APPLICATION

Key words: modified Polyetheretherketone (PEEKWC), polymeric porous PE film, capsule preparation, phase inversion technique.

SUMMARY

Polymeric droplets formed, using themono-porous membrane, were converted in polymeric capsules by phase inversion technique. Capsules of modified PEEKWC were prepared employing this technique. The polymeric droplets were prepared using a mono-pore polyethylene (PE) film with pore diameter ranging from 300 to 800 µm. The capsule morphology, porosity, shell thickness and size were modified changing some process and ingredient parameters such as the polymeric concentration, oil phase and pore film diameter. Active carbon was loaded into the capsules during their production. The interaction of the loaded active carbon and the polymeric capsule matrix was also investigated.

INTRODUCTION

Capsules of different polymeric material are largely employed in industrial applications such as cosmetic, pharmaceutical, chemical and food packaging. Therefore, the preparation of loaded capsules by means of a reliable procedure is an important challenge.

In this work, macro-capsules using the membrane process concept combined with phase inversion technique have been developed. This technique can be considered as an integration between the traditional chemical capsule preparation (coacervation or phase inversion) and the mechanical capsule technique (pressure extrusion) [Figoli *et al.* (2007)].

The polymer employed was the modified polyetheretherekene (PEEWC) which has excellent chemical, thermal and mechanical properties; moreover it has the advantage, compared to traditional PEEK, to be soluble in several common organic solvents which facilitates the membrane preparation [Liu *et al.* (1987), Zhang *et al.* (1987), Drioli and Zhang (1989)] and capsules. In a previous work, the suitability of PEEKWC as potential food packaging was verified by means of overall migration tests, using different food simulants [Torchia *et al.* (2004)]. Therefore, its excellent thermal and chemical properties combined with its food suitability makes PEEKWC an interesting matrix for preparing capsules in food packaging application. The preparation of PEEKWC membranes by phase inversion has been widely studied and different membrane morphologies have been obtained [Jansen *et al.* (2006), Buonomenna *et al.*(2003)].

The objective of this work was

to prepare polyetheretherketone (PEEKWC) capsules of different morphology, porosity, size and shell thickness changing the ingredient and process parameters such as polymer concentration, oil and pore dimension of the PE film.
The morphology and dimension of the prepared capsules are the fundamental parameters to control the release of different active compounds loaded and their adsorbent properties.
The active carbon was loaded into the capsules during their production. The interaction of the loaded active carbon and the polymeric capsule matrix was hence investigated.
Active carbon finds its application in food packaging as ethylene scavengers. Ethylene (C_2H_4) acts as plant hormone which accelerates the respiration rate causing the ripening of many kinds of fruits and vegetables. A reduction of the ethylene level in the packaging extends the ripening stage of the fruit, the storage time of ripe and ready-to-eat fruits. Charcoal, containing PdCl as a metal catalyst, was effective at 20°C in preventing the accumulation of ethylene, in reducing the rate of softening in minimal processed kiwifruits and bananas and in reducing chlorophyll loss in spinach leaves [Abe *et al.*(1991), Vermeiren *et al.*(1999)].
Most of the scavengers are supplied as sachets or integrated into films. C_2H_4-scavengers are not yet very successful, probably due of insufficient adsorbing capacity or of the low adsorbent quantity loaded in the film. This could be overcome by encapsulation of the adsorbents.

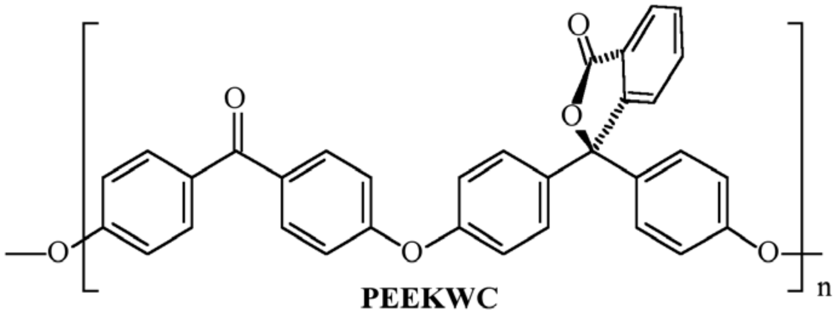

Fig. 1 - Chemical structure of PEEKWC.

MATERIALS AND METHODS

PEEKWC was supplied by the Chan Chung Institute of Applied Chemistry, Academia Sinica. N,N-dimethylformamide (DMF) was purchased from Merck and used as polymer solvent without further purifications. The active agent used was the active carbon, purchased by Norit BV with average particle dimension of 5 μm.
The solvents used (dodecane, iso-octane and iso-propanol) were purchased from Sigma-Aldrich and used as oil phase and as polymer non-solvent, respectively. The repeating unit of the polymer is shown in **fig. 1**.

A model system with a single micro-pore was used. Since the capsule preparation is a new pocess, the use of membranes (multiple pores, high porosity, pore morphology not well defined) get to misleading interpretation of the data at this stage of the research.

Capsule preparation and characterisation
The polymer, PEEKWC (8, 10 and 12 wt.%), with and without active agents was dissolved in DMF at room temperature. The solution was magnetically stirred for at least 1 day to allow a complete dissolution of the polymer.
The polymer solution (phase

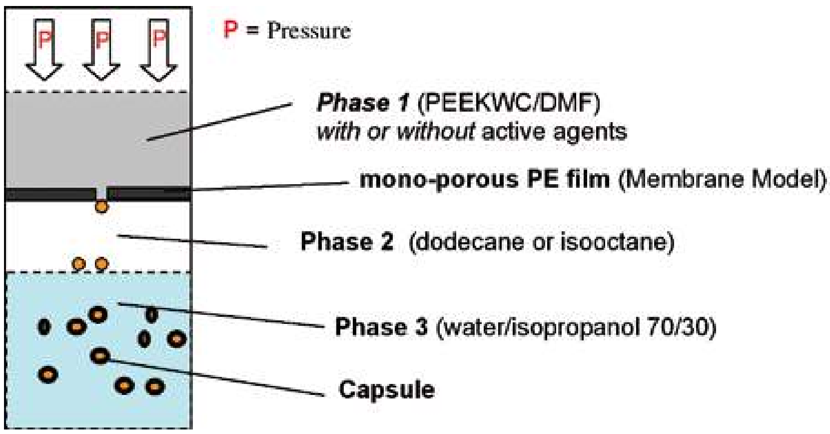

Fig. 2 - Scheme of capsule formation unit.

Table 2
Summary of the ingredients involved in the capsules preparation.

Phase 1	Phase 2	Phase 3
PEEKWC/DMF 8 wt.%	Dodecane	Water:isopropanol (70:30)
PEEKWC/DMF 10 wt.%	Dodecane, Iso-octane	Water:isopropanol (70:30)
PEEKWC/DMF 15 wt.%	Dodecane	Water:isopropanol (70:30)
PEEKWC/DMF 10 wt.%+active carbon 5 wt.%	Dodecane	Water:isopropanol (70:30)

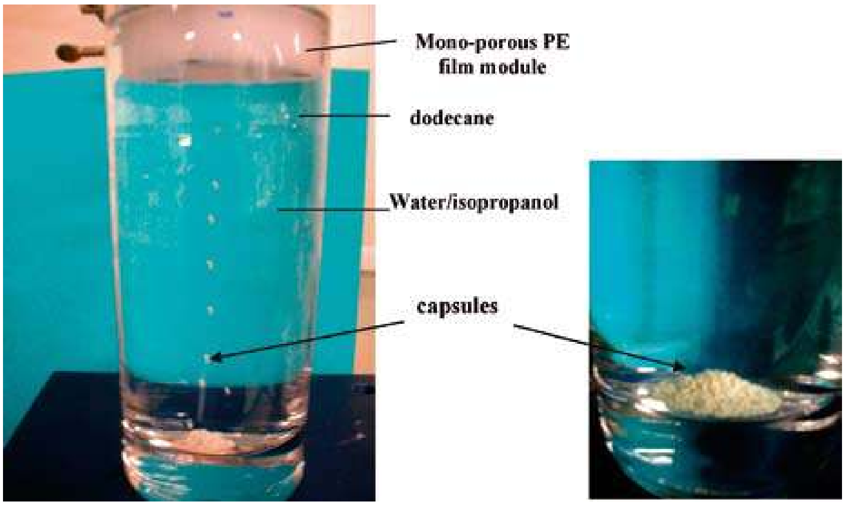

Fig. 3 - Picture of the lab device for polymeric capsule preparation.

1) was add to the feed tank of the module used in the capsules preparation (**fig. 2**). Then, it was pressed through the mono-pore film of polyethylene (PE) which has a pore diameter ranging from 300 to 800 μm. The droplets formed at PE hole border move through the dodecane (phase 2), which should give a spherical shape to the droplets, and immediately polymerised by phase inversion when in contact with the non-solvent phase, water/isopropanol 70/30 (phase 3). The capsules were then recovered using a filter paper. The capsules were left to evaporate over night at room temperature and set in an oven under vacuum for 24h to remove completely the solvent.
In **tab. 1**, the summary of the main ingredients and process parameters involved in the capsules preparation is reported.
The morphology and the shell thickness of the dried capsules were determined using a Scanning Electron Microscopy (SEM), Cambridge, Stereoscan 360, at 20kV. The capsules were freeze-fractured in liquid nitrogen for cross-section analysis. All samples were evacuated and then sputter-coated with gold under argon atmosphere before SEM analysis.
The capsules size was measured by a digital micrometer (Carl Mahr D 7300 Esslingen a.N.).

RESULTS AND DISCUSSION

The capsule formation lab set-up is shown in **fig. 3**.
The SEM pictures of the capsules, obtained with PEEKWC/DMF 8 wt.%, are shown in **fig. 4**. These

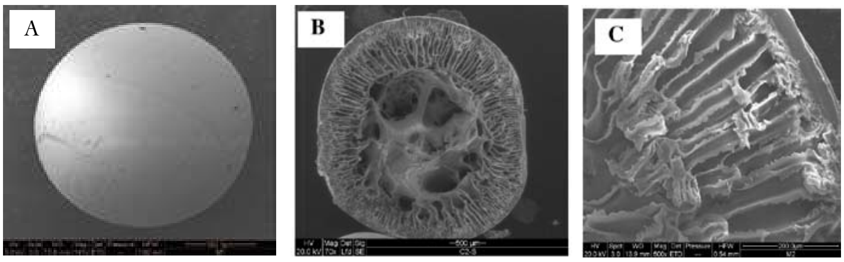

Fig. 4 - SEM pictures of the a) Surface and b,c) Cross-section of the capsules prepared using a film with the pore size of about 500 μm and PEEKWC/DMF 8 wt.%, phase 1, dodecane, phase 2, and water:isopropanol, phase 3.

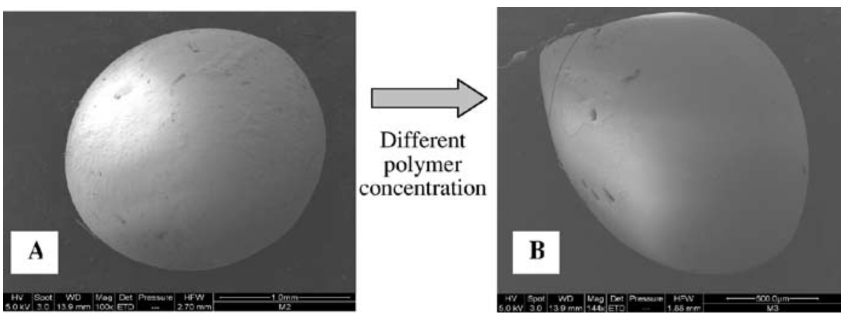

Fig. 5 - SEM picture of the capsules surface prepared using a film with the pore size of about 500 μm and as phase 3, water:isopropanol, phase 2, dodecane and phase 1, PEEKWC/DMF: a) 10 wt.% and b) 15 wt.%.

capsules were made by a pore diameter of about 500 μm, dodecane as oil phase 2 and water: isopropanol as non-solvent (phase 3). The capsules were spherical and with a smooth surface (fig. 4a). Moreover, in fig. 4b and c, the capsule cross-section shows a central cavity and a asymmetric (finger type) structure with a dense skin layer at the shell side.

Fig. 5 shows the surface of the capsules obtained using the same previous conditions but increasing the polymer concentration from 10 to 15 wt.%.

The increase of the polymer concentration determined a deformation of the spherical symmetry, probably, due to a decrease of the droplet interfacial tension.

In **fig. 6**, the influence of phase 2, which strongly modify the morphology of the made capsule is reported. In fact, the variation of phase 2 (from dodecane to iso-octane) changed the capsule morphology from a dense to porous surface. The higher affinity of iso-octane caused a starting of the droplet demixing before coagulating at the non-solvent phase.

The diameter of the prepared capsules varied, from 500 to about 2,100 μm, depending on the pore film diameter. However, the change of pore size did not influence the morphology of the capsules.

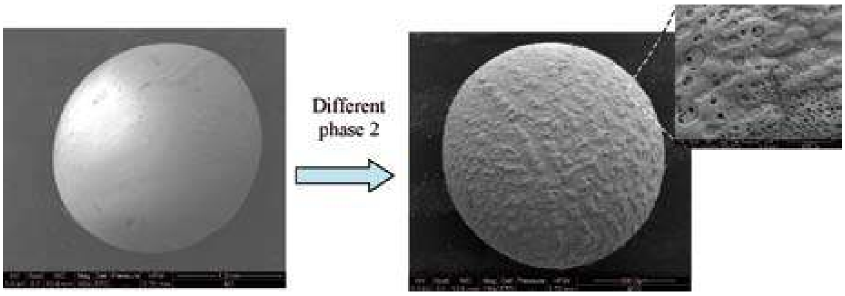

Fig. 6 - SEM pictures of different capsules using: pore size (800 μm), PEEKWC/DMF 10 wt.%, dodecane (a) and isooctane (b) as phase 2.

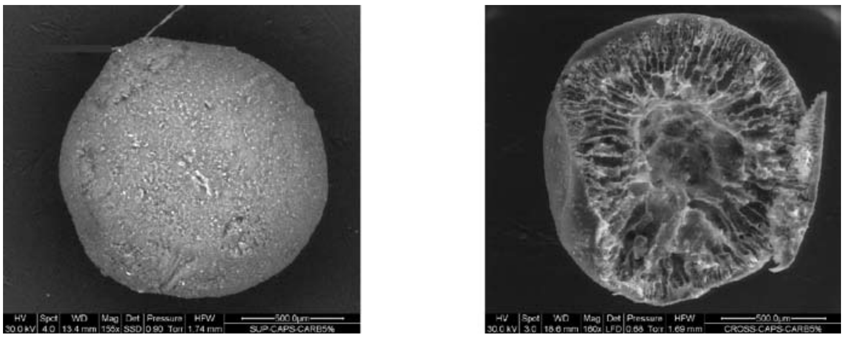

Fig. 7 - SEM pictures of the capsule loaded with active carbon using as phase 1, PEEKWC/DMF 10 wt%, phase 2, dodecane and phase 3, water:isopropanol (70:30).

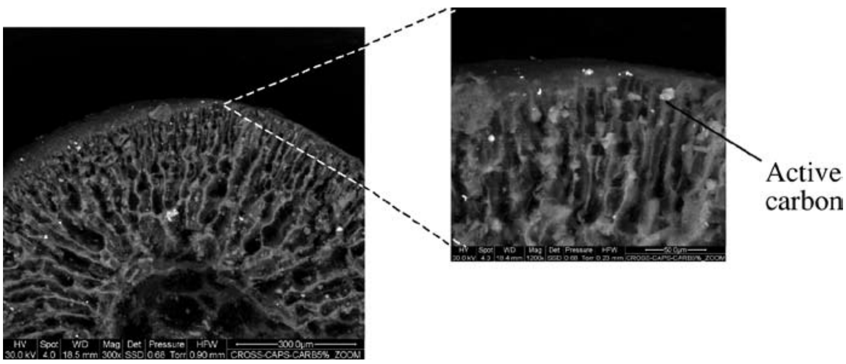

Fig. 8 - Cross-section of the capsule loaded with active carbon (at higher magnification, detail of the skin layer).

After the study of the influence of the main variables on the capsule morphology, PEEKWC capsules loaded with active agents were prepared.

In **fig. 7**, capsules formed using PEEKWC solution containing 5 wt.% of active carbon and pore size of about 500 μm are shown. The addition of the active carbon to the polymer solution did not affect the final morphology and shape of capsules which resulted to have the same asymmetric morphology and the central cavity of the capsules prepared without adding any active agent. On the other hand, the surface of the loaded capsules showed a pronounced roughness, compared with the capsules prepared with the same solvent, probably due to the presence of the inorganic specie also on the outside of the capsules itself.

The active carbon was randomly distributed in the asymmetric part of the capsule, as shown in the cross-section reported in **fig. 8**.

CONCLUSIONS

The formation of mono-dispersed PEEKWC capsules with different morphologies has been carried out. The capsule morphology and dimension could be adjusted changing some process and ingredients parameters, such as the polymer concentration, oil phase and the PE film pore diameter.

These tests showed that the capsules sizes depend on film pore diameter. Furthermore, the PEEKWC capsules were successfully loaded with active carbon for potential applications in food packaging, in which the removal of volatile compounds (e.g. ethylene) or off-flavours is needed.

It is worth nothing that this research has to be considered a preliminary work. In fact, the further developments will focus on the use of commercial membranes and on the optimisation of the procedure for converting the droplets in the solid tailored capsules. These last aspects are crucial for the scale-up of the whole process.

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