A Novel Method to Control UV Curable Microcapsule Release Behavior

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Abstract

A new family of core/shell microcapsules containing photopolymerizable tripropylene glycol diacrylate (TPGDA) was synthesized by using interfacial polymerization. The chemical structure and properties of microcapsule was characterized by using Fourier Transform Infrared spectroscopy. The particles size and morphology of the microcapsules were studied by using scanning electron microscope. The thermal properties of microcapsules with various UV curing time were investigated by using differential scanning calorimetry. The controlled releasing behavior of the microcapsules with various UV curing time in organic solvent was studied. Effects of core/shell ratio and agitation rate on average particle size, size distribution and shell thickness of microcapsules were investigated. The higher agitation rate results a smaller particle size with a narrow size distribution. The rate of polymerization of TPGDA in core of microcapsules increases with decreasing particle size and the shell thickness. A higher photoinitiator concentration also increases the photopolymerization rate of the core material. The experiments of controlled releasing behavior showed that the release rate of functional components such as dye in the core can be controlled by changing the crosslink density of network formed from TPGDA.

Introduction

Microcapsules composed of active or incipient core materials and polymer shell, have attracted interests and been extensively explored in the past few years[1-5]. Due to the special properties of microcapsules such as heat-sensitive, stress-sensitive, protective ability and especially the releasing property, they could be used in various areas, for example, liquid crystal display[6,7], textile industry[8], medical supplies[9-11], food additives[12,13], recording material[14,15] and biology technology[16-18]. In many applications, the characteristics of microcapsules required (i) the active core materials must be held in microcapsules stably until required condition was satisfied; (ii) the contents should release to the exterior of the microcapsule at a stretch or gradually as the occasion demands[19, 20]. Hence, the structure of microcapsule shell must respond to an external stimulus for a certain kind alternatively[21].

In this study, novel microcapsules were synthesized by using interfacial polymerization. The core material of the microcapsules includes tripropylene glycol diacrylate (TPGDA), which is photosensitive and could be crosslinked. The release behavior of encapsulated dye was controlled easily by changing the crosslink density of network formed from TPGDA. After microcapsules are synthesized, the release speed can be changed according to requirement by exposing microcapsules to UV light for minutes and this step is separate. Special devices are not necessary when microcapsules are applied in controlled delivery system. This is novel to the previous study. The microcapsules can be applied in drug carriers for a controlled delivery system and information recording materials.

Experimental

Materials

TPGDA, 4-Hydroxy-4'-isopropoxydiphenylsulfone (trade name: D-8) and a-HydroxyMethy1(trade name: Darocur 1173) used as core materials of the microcapsules were purchased from Sartomer Company, America, Zhejiang Longsheng Co. Ltd., China and Ciba Company, Switzerland, respectively; isophorone diisocyanate (IPDI) used to form shell material was purchased from Bayer Company, Germany; poly(vinyl alcohol) used as stabilizer in the continuous phase was purchased from Shanxi Sanwei Co., China; dibutyl tin dilaurate (DBTDL), Ethyl acetate and alcohol were purchased from Beijing Chemical Reagent Co., China. All the materials were used as received without any further purification. Figure 1 shows chemical structures of TPGDA, D-8, Darocur 1173 and IPDI.

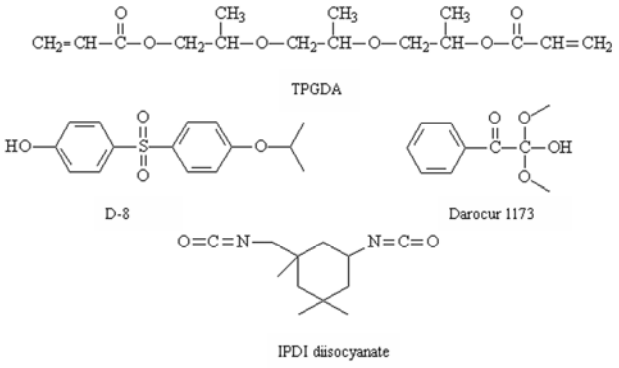

Figure 1 chemical structures of materials

Preparation of microcapsules

The microcapsules were prepared via interfacial polymerization by experimental condition as shown in Table 1. Given weight of D-8, TPGDA, IPDI were mixed in a beaker to get dispersed phase, increasing dissolving by heating. Then a given weight of Darocur 1173 was added to the oil phase to get UV curable property. The dispersed phase was poured into continuous water phase with 2 wt % of PVA1788 as protective colloid to form oil/water emulsion. Emulsification was carried for 1 min. by using homomixer (JSF-400, Shanghai Pushen Chem. Co., China) with emulsification rate of 2000 rpm. After emulsification, the oil/water emulsion was taken into a flask of 250 ml with three inlets. The emulsion was stirred with certain agitation rate by using two bladed stirring paddles at 40 °C. An hour later, DBTDL (0.05 mL) was added into the system and the reaction temperature was 50 °C for

another 4 hours. The suspension of microcapsules was separated by vacuum filtration and then washed with 30 % ethanol aqueous solution to remove unreacted IPDI and core materials on the surface. At last, the microcapsules were generated after being dried in a vacuum drier at 30 °C for 24 hours. Pure polyurea was also prepared at the same condition in order to characterize the chemical structure and crystallography of the shell materials.

UV cure of microcapsules

The samples were prepared by placing the microcapsules under a high pressure UV lamp (100 W/cm) equipped with a parabolic reflector (RW-UVAOP301-10, Run Wing, China). The distance between the samples and the lamp was 20 cm.

Characterization

The chemical structure of the microcapsules was characterized by Fourier transform infrared spectroscopy (FTIR) (Nicolet 5700, America). Samples were thoroughly mixed with KBr and pressed into pellet form. For each sample, 32 scans at 2 cm^{-1} resolution were collected in the adsorption mode.

The surface morphology of microcapsules was observed using electron scanning electron microscope (SEM) (S-4700, Hitachi, Japan). The microcapsules were dispersed in water, a drop of the microcapsule dispersion was placed on a stainless steel stub and allowed to air-dry, and then the samples were sputtered with a thin layer (about 10 nm) of gold. The microcapsule size distribution was observed from SEM images and the size distribution analysis was performed based on at least 500 particles. The morphology of microcapsules was also observed by an optical microscope (OM) (MM6-LS22, Olympus, Japan).

Wide Angle X-ray diffraction (WAXD) patterns of samples were obtained at room temperature on X-ray diffraction (XRD) (RU-200, Ragaku, Japan) diffractometer with a CuKa radiation source (wavelength 0.154 nm). Samples were exposed at a scan rate of 2θ = 10 °/min between 2θ = 5 ° - 60 °.

The releasing behaviors of different UV-cured microcapsules were characterized by UV/visible spectrophotometer (U-3010, Hitachi, Japan). The release of microcapsule was carried out in ethyl acetate, which has a perfect solubility to D-8. The release assay was reproduced twice to obtain the average value. An accurate weight (0.1500 g) of microcapsules was added in dissolution medium while the solution was agitated using a two bladed paddle at stirring rate of 200 rpm. 1 mL of sample was collected and replaced with fresh medium at appropriate intervals. The sample was added into volumetric flask to dilute into 25 mL solution. An absorbance of collected sample was measured by UV/visible spectrophotometer at 258 nm. The D-8 release amounts were plotted as the cumulative amount and percentage content in the dissolution medium against the release time.

Results and Discussion

Chemical structure of microcapsules

Figure 2 shows FTIR spectra of core materials, IPDI and microcapsule D. The spectrum of core materials shows two peaks from TPGDA due to unsaturated -C=C-H group at 1650 cm^{-1} (stretching) and 810 cm^{-1} (bending) (Figure 2a). A strong characteristic peak of N=C=O can be observed at 2260 cm^{-1}(stretching) in spectrum of IPDI. However, this peak completely disappeared in spectrum of microcapsule D, indicating that the reaction of IPDI and water was complete. The appearance of other absorption peaks such as 3340 cm^{-1}, 1640 cm^{-1}(stretching), 1560 cm^{-1}(bending), and 1262 cm^{-1}(amide III, urea C-N, N-H, C=O) as the characteristic of polyurea further confirmed the reaction. The peak at 1650 cm^{-1} (stretching) of unsaturated -C=C-H groups in core of microcapsule D is shielding by the C=O stretching peak while peak at 810cm^{-1} (bending vibration) still can be clearly observed in Figure 2 (c). From these results, we can conclude that polyurea microcapsules have been prepared without destroying the functional groups of TPGDA and therefore microcapsules are UV curable.

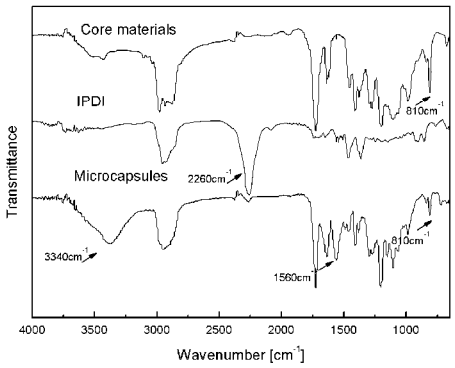

Figure 2 FTIR spectra of core materials, IPDI and microcapsule D

Morphology of microcapsules

As discussed above, the microcapsules are produced via emulsification of followed by interfacial polymerization of the wall-formers. Therefore, all the factors that determine size and size distribution of colloid particles should affect the size of the microcapsules. In this section, the variation in morphology of microcapsules is investigated by changing agitation rate and core/shell weight ratio. From Figure 3, it can be seen that increasing the agitation rate reduces the microcapsules' size and narrows the size distribution. The SEM micrographs further show that a higher agitation rate leads to smaller microcapsules, which is shown in Figure 4.

WAXD analysis of microcapsules

Figure 5 shows 1D WAXD intensity profiles of D-8, polyurea, mixture of D-8 and polyurea, microcapsule D. The two strong peaks at 16 °, 24 ° corresponds to the characteristic diffraction peaks of D-8 crystal. Only a wide amorphous peak exists in the intensity curves of polyurea. This is because it is amorphous materials. Mixture of D-8 and polyurea show the addition of the diffraction peaks of the two materials. All the diffraction peaks of D-8 disappeared, revealing that the D-8 was entirely encapsulated in the microcapsules[22], and therefore it could not form any crystal.

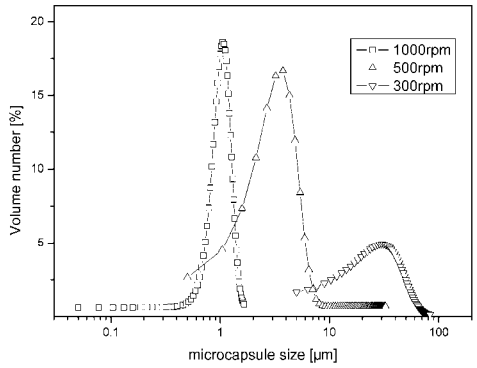

Figure 3 The microcapsules' size and their distribution vis agitation rate

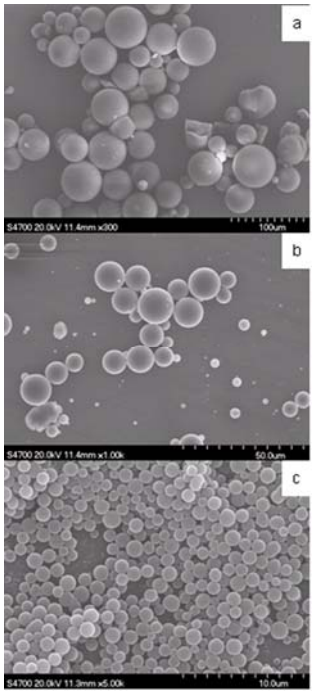

Figure 4 SEM micrographs of the microcapsules vis agitation rate

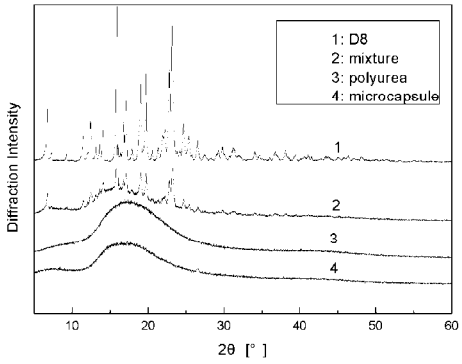

Figure 5 WAXD analysis of microcapsules

UV curing property of microcapsules

The encapsulated TPGDA in microcapsules could polymerize, when it is exposed to UV light, the polymerization is induced by Darocur 1173, which forms radicals by absorbing UV-light. Thus, the crosslinked network is formed. From FTIR spectrum shown in Figure 2, TPGDA has an characteristic absorption peak at 810 cm^{-1}, which is related to the –C=CH out of plane deformation vibration, so the degree of reaction can be monitored by IR-spectroscopy as the decreases of the intensity of the absorption of double bond due to the polymerization. Figure 9 shows the decrease in IR absorption of the C=C-H bond at 810 cm^{-1} as radiationure time increased. The reduction in the intensity of 810 cm^{-1} peak corresponds to the disappearance of C=C-H. At this investigation the absorption of -CH stretching vibration at 2950 cm^{-1} which remained constant during the polymerization is used as internal standard. The ratio of absorption area at 810 cm^{-1} to the absorption area at 2950 cm^{-1} is defined as the degree of conversion[23]. The degree of conversion is calculated as:

$$C(\%) = \frac{(A_{810}/A_{2950})_0 - (A_{810}/A_{2950})_t}{(A_{810}/A_{2950})_0} \times 100\%$$

where $(A_{810}/A_{2950})_0$ and $(A_{810}/A_{2950})_t$ are relative absorbances of C=C-H bond before curing and at given curing time t, respectively.

Figure 6 shows the decrease in IR absorption of the C=C-H bond at 810 cm as radiation time increased. The reduction in the intensity of 810 cm peak corresponds to the disappearance of C=C-H. The reaction rate and final conversion are dependent on the size of microcapsule, shell thickness and the photoinitiator content. Because the shell material can absorb the UV light, it is more difficult for Darocur 1173 inside the shell to absorb UV light when the shell becomes thicker[24].

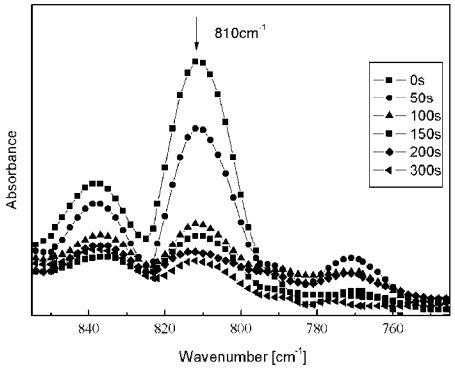

Figure 6 UV curing property of microcapsules

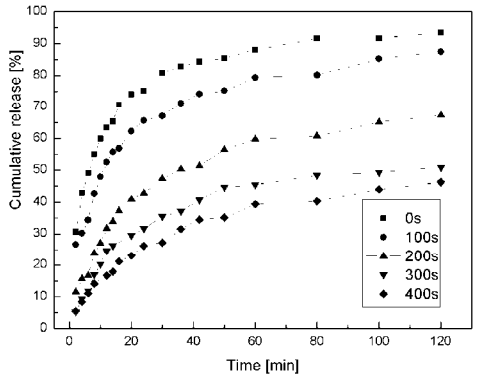

Figure 7 Releasing behaviors of UV cured microcapsules

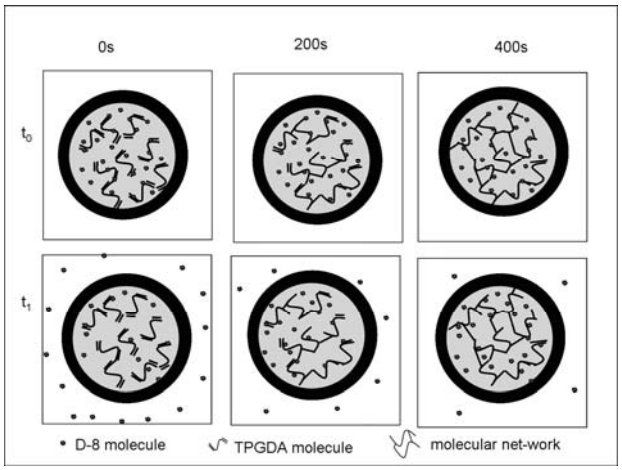

Figure 8 Relation between crosslink density network and releasing behaviors of UV cured microcapsules

Releasing behaviors of UV cured microcapsules

It is difficult to control the releasing behavior of polyurea microcapsules without reactive core materials. The controlled release behavior can be achieved by introducing polymerizable TPGDA into the core. Figure 7 shows the effects of typical UV radiation time on release behavior in terms of percent release of microcapsules in oil solvent. The release profiles of all samples are found to occur in a biphasic manner, with an initial fast release phase followed by a slower release phase.

The releasing behavior of D-8 could be controlled by the crosslink reaction or double bond conversion ratio of the TPGDA in the core. As shown in Figure 8, with the higher C=C double bond conversion ratio, a higher crosslink density network could be formed, and therefore slows down the release of D-8 in core. UV radiation time is one of the most effective factors to change the C=C double bond conversion ratio. Therefore, it is applied in this study. However, we should also be noted that other factors such as UV light intensity, type and concentration of initiators, wall thickness and chemical structure of the wall materials, temperature and type of solvents will also play an important role on controlling releasing behavior of the microcapsules, and those could be some interesting topic for future study in this area.

Conclusion

In this study, microcapsules with UV curable material in core were successfully synthesized via interfacial polymerization. It demonstrates that agitation rate and core/shell ratio significantly affect the structure and morphology of the microcapsules. A smaller average size can be obtained by using a higher agitation rate. The surface of microcapsules is smoother with a lower core/shell ratio. In addition, UV curing property of TPGDA in core of microcapsules is affected by UV radiation time, concentration of photoinitiator and the structure of the microcapsules. The release behavior of encapsulated dye in core can be controlled by changing UV radiation time, the results show that the releasing speed of encapsulated D-8 could be significantly reduced by increasing the UV curing time. The present results suggest that microcapsules with UV curable materials in core can be applied in controlled drug delivery system.

Acknowledgement

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