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Healant release from microcapsules with varied internal microstructure

Manorama Tripathi[a,b], Devendra Kumar[b], Prasun Kumar Roy[a,*]

[a] Centre for Fire, Explosive and Environment Safety, DRDO, Timarpur, Delhi 110054, India
[b] Department of Applied Chemistry and Polymer Technology, Delhi Technological University, Delhi 110042, India

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ABSTRACT

One of the most common methodologies of introducing extrinsic healing property to a polymer composite involves inclusion of healant-loaded microcapsules in the formulation prior to curing. In this paper,we discuss an analytical model for predicting the amount of healant released due to microcapsule rupture. Of particular interest is to understand the role of internal microstructure in the context of extrinsic healing. In microcapsules possessing "reservoir" type microstructure, the healant exists as a single droplet, and the entire contents are released upon rupture. On the other hand, in monolithic microcapsules, the healant is dispersed in the form of discrete micro-droplets, and depending upon the micro-droplet dimensions, significantly lower amount of healant is released in comparison to reservoir microcapsules. For the purpose of validation, composites were prepared using epoxy encapsulated microcapsules with varied internal structures. In line with our predictions, the extent of healing was much lower in the case of samples containing monolithic microcapsules. At 20% w/w microcapsule loadings, healing efficiencies close to 60% was observed upon introduction of reservoir type microcapsules, while under similar loadings, only 10% healing could be evidenced in the presence of monolithic microcapsules.

1. Introduction

One of the most common methodologies towards introduction of self-healing functionality to any polymer involves inclusion of healant-loaded microcapsules in the formulation prior to curing [1]. Upon rupture of these microcapsules, the encapsulated healant flows into the crack plane and undergo crosslinking, forming a polymer which bridges the gap thereby arresting the crack growth. Conventionally, the healant is encapsulated in a fragile shell by adopting a dispersion polymerization route, which leads to formation of microcapsules with "reservoir" type microstructure. Typically, during the polymerization process, the shell wall constituents within the aqueous phase form a low molecular weight pre-polymer, which deposit preferentially over the hydrophobic healant at the oil-water interface. Eventually, a spherical solid shell is formed around a droplet of liquid healant forming a microcapsule with healant "reservoir".

Another relatively less complex methodology is that of "solvent evaporation", which is routinely employed for drug encapsulation [2]. The same is lately been explored for encapsulation of healants too [3–6]. The adoption of this route leads to the formation of microcapsules with monolithic structure, where the healant is dispersed as micro-droplets within the polymeric shell. It is obvious that the self-healing efficiency is strongly dependent on the internal morphology of the microcapsule. Numerical models for healant delivery exist for rupture of "reservoir" type microcapsules [7], however, to the best of our knowledge, such models for a monolithic type geometry have not yet been developed, which prompted us to take up this study.

In the present paper, we propose and discuss an analytical model for estimating the amount of healant released in the event of rupture of microcapsule with monolithic morphology and compared with "reservoir" type microcapsules. The predictions have been validated with experimental studies, where epoxy encapsulated microcapsules with varied microstructure were included in the formulation to obtain mendable compositions. The healing efficiency was quantified in terms of the ratio of impact strength and the effect of internal microstructure was evidenced.

2. Experimental

2.1. Materials

Aliphatic Epoxy resin (Ciba Geigy, Araldite CY 230; epoxy equivalent 200eq g^{-1}) and TETA based hardener (HY 951; amine content 24 eq kg^{-1}) was used as received. Urea, formalin (37% formaldehyde in water), sodium hydroxide, resorcinol, ammonium chloride, dichloromethane and polyvinyl alcohol (PVA) (Mw ~14,000) was obtained from

* Corresponding author.
E-mail addresses: pk_roy2000@yahoo.com, pkroy@cfees.drdo.in (P.K. Roy).

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CDH. EMA (Sigma Aldrich) and ethyl acetate (E.Merck) was used without any further purification. Polystyrene used for the preparation of monolithic microcapsules was obtained by emulsion polymerization, the procedure of which is presented in the Supplementary section. Double distilled water was used throughout the course of this work.

2.2. Epoxy microencapsulation

Epoxy encapsulating microcapsules with monolithic structure were prepared by solvent evaporation technique [8] for which a solution of epoxy(4 g) and polystyrene (1 g) in dichloromethane (30 ml), was added to 50 ml of aqueous PVA solution (2.5% w/w) followed by agitation. The same was poured into 150 ml aqueous PVA solution, while maintaining a stirring speed of 550 rpm at a temperature of 35 °C. Post-solvent evaporation, epoxy encapsulated PS microcapsules were filtered, washed and dried under vacuum.

The procedure employed for encapsulation of epoxy in Urea-formaldehyde shells to form microcapsules with "reservoir" microstructure has been detailed in our previous paper [9]. In brief, 100 mL distilled water was mixed with 25 ml EMA solution (2.5% w/v) by stirring at room temperature (~ 350 rpm). To this solution, 2.5 g urea, 0.25 g ammonium chloride and 0.25 g resorcinol was added. After complete dissolution, the pH was adjusted to 3.2 ± 0.2. Subsequently, ~ 60 ml of the healing agent solution (epoxy: ethyl acetate: 1:1 w/w) was slowly added over a period of 20 min while maintaining a stirring speed of ~350 rpm. Thereafter, requisite amount (6.33 g) of formalin was introduced and the temperature was increased to 50–55 °C, while maintaining a constant stirring speed of ~350 rpm. The reaction was allowed to proceed for 4 h, followed by filtration of the microcapsules and air drying for 24 h, which resulted in free-flowing powder.

2.3. Preparation of self-healing composites

Self-healing epoxy composites containing varying amounts of microcapsules (5–25% w/w) were prepared by room temperature curing of epoxy with TETA as per the procedure reported previously [10]. Copper imidazolate (1% w/w microcapsule) was included in the formulation to act as the latent hardener, and all the healing studies were performed at 150 °C.Healing efficiency was quantified in terms of the ratio of impact strength both before and after healing [11].

3. Results and discussion

The cross-sectional view of the plane formed as a result of rupture of microcapsules with different internal microstructure is presented in Fig. 1. It is clear that rupturing of microcapsules with "reservoir" type morphology lead to the release of the entire amount of healant into the crack place. Also, if all the microdroplets present within the monolithic microcapsule rupture, the healing efficiency of reservoir and monolithic microcapsules would not vary. However, only the healant released from microdroplets present on the crack plane due to rupture of monolithic microcapsules is available for healing purposes. In view of the same, the healing efficiency for monolithic microcapsules will be lesser than that obtained using reservoir microcapsules.

3.1. Release of healant from microcapsules with "monolithic" microstructure

For the sake of calculation, it is assumed that the healant is homogeneously dispersed inside the microsphere, with each micro-droplet separated from the other by the matrix. A single microcapsule is assumed to be composed of cubic spaces each of length (L) containing a single microdroplet (Fig. 2a) [2]. The micro-droplets are assumed to be perfectly spherical (diameter, D_d) with the distance between each droplet being L_{drop}. The core content ($core_{mic}$%, v/v), is related to the droplet diameter (D_d) and cubic edge length (L) as:

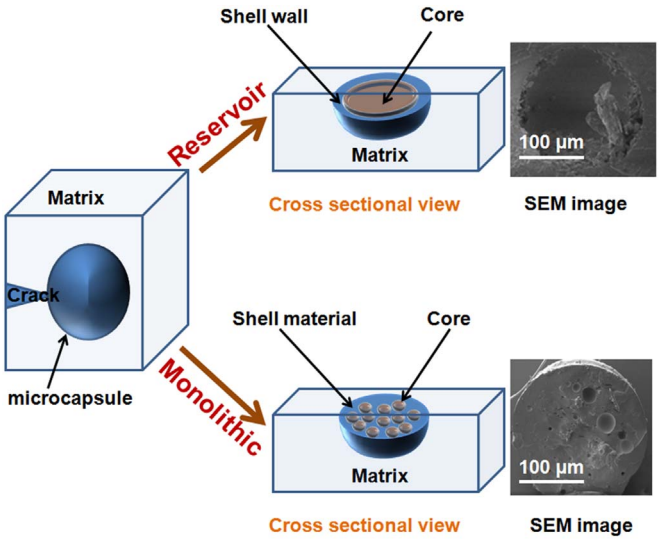

Fig. 1. Pictorial representation of reservoir type and monolith type microcapsule. SEM image of the fractured microcapsules is also included.

$$\text{core}_{\text{mic}} = \frac{(\frac{\pi}{6})D_d^3}{L^3} \quad (1)$$

The distance between two microdroplets($L - D_d$) can hence be expressed as

$$L_{drop} = D_d\left[\left(\frac{\pi}{6\times core_{mic}}\right)^{1/3} - 1\right] \quad (2)$$

The effect of increasing microdroplet dimensions on the distance between drops (L_{drop}) is also presented in Fig. 2b. It can be seen that with increasing droplet size, the distance between two adjacent drops increases. The effect of increasing core content on the distance between two adjacent droplets is also presented in Fig. 2c. As can be seen from the figure, at core content≥ ~50%, irrespective of the dimensions of the dispersed microdroplets, the microcapsules essentially exhibit "reservoir" type morphology, as the distance between two adjacent droplets reduces to zero.

For the purpose of determining the amount of healant released in the event of rupture of microcapsule, a 2D cross-section of both monolithic and reservoir type microcapsule is considered, as shown in Fig. 3.

The number of micro-droplets in a single microcapsule (N) can be estimated as $\frac{\pi r^2}{(L_{drop}+D_d)^2}$.The volume of liquid entrapped in a single micro-droplet (V_d) is $\frac{4}{3}\pi r_d^3$. The total volume of liquid released in the event of rupture of monolithic microcapsule, $V_{monolith}$ is $N \times \frac{4}{3}\pi r_d^3$. For a representative scenario (D = 150 μm) the detailed calculations are presented in supplementary section (Table S1).

In comparison, the total volume of liquid released in the event of rupture of microcapsule with comparable core contents, but possessing "reservoir" type microstructure, is $V_{reservoir} = \frac{4}{3}\pi r_{reservoir}^3$, where the radius of the healant reservoir ($r_{reservoir}$) is related to the diameter of the microcapsule (D) by $r_{reservoir} = \frac{D}{2}(core\ content)^{1/3}$. It is obvious that for lower core contents, $V_{monolith}$ is much lesser than $V_{reservoir}$.

3.2. Healant delivery into the crack plane

Rule et al. [7] has proposed an analytical model for predicting the extent of healant delivery, where it is assumed that the entire amount of healant flows into the crack plane and undergoes curing to aid the healing phenomenon. A pictorial of the model as well as the involved calculations are presented in the supplementary section (Fig. S2). It is obvious that these predictions are restricted to that of microcapsule