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Mesoporous silica as amine immobiliser for endowing healing functionality to epoxy resin

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ABSTRACT

Feasibility of physical entrapment approach towards the immobilisation of amine hardener in mesoporous silica has been demonstrated for potential applications in the perspective of self-healing. A representative mesoporous silica (SBA-15) was synthesised using polymer-templated technique and employed as a substrate for immobilizing triethylene tetramine, a conventional epoxy hardener. Polymeric composites containing microencapsulated epoxy microcapsules and amine loaded SBA-15 were prepared by room temperature curing. The autocatalytic nature associated with the curing of epoxy remained unaltered due to introduction of either SBA-15 or epoxy loaded microcapsules, as confirmed by calorimetric studies. Healing efficiency, as quantified in terms of the ratio of impact strength before and after healing, was found to increase proportionally with increasing loading of healing additives in the formulation, with complete healing (100%) being exhibited at 20% microcapsule loading.

1. Introduction

Self-healing materials are an emerging class of smart responsive materials, which are finding increasing applications in varied fields, e.g anti-corrosive, scratch resistant coatings, structural fiber-reinforced composites to name a few [1]. As is suggestive, these materials possess an innate ability to regain their structural integrity in the event of damage, which can be initiated by any external stimulus e.g. light, mechanical force, surrounding pH-variations etc. Extrinsic self-healing functionality can be bestowed to any composite by the inclusion of healant loaded microcapsules in the formulation. In a conventional self-healing organization, an encapsulated liquid healing agent and a solid phase hardener or catalyst is dispersed homogenously throughout the polymeric matrix. Crack propagation leads to the rupture of microcapsules lying within the crack plane, which result in the release of the healant to subsequently undergo polymerization and restrict the crack growth.

The first generation self-healing systems were based on monomeric healants capable of undergoing ring opening polymerization, e.g. endodicyclopentadiene, 5-ethylidene-2-norbornene [2]. Lately, this elementary theme has been extended to encompass diverse healing chemistries, e.g. unsaturated polyester [3], siloxane [4], epoxy-amine system [5,6] with the latter being most extensively studied in view of the associated economic factors. It is imperative to mention here that though there exist a number of successful methodologies for encapsulation of liquid epoxy, but encapsulation of the liquid hardener still remains a major challenge in view of its hydrophilic nature. To address this issue, several strategies have been adopted including encapsulation of amine in polyurea shells using reverse emulsion technique [7] and interfacial polymerization [8]. Alternatively, hollow microballoons of poly(urea-formaldehyde) and silica have also been explored as amine containment structures [9,10]. However, these microcapsules usually exhibit low core contents, which has led researchers to explore other alternatives.

Surprisingly, porous siliceous substrates e.g. SBA-15, MCM 41, which are routinely employed towards enzyme immobilization [11–13] have not yet been explored for immobilizing amines. In view of their extremely high surface areas, and suitable pore sizes, these materials apparently possess excellent candidature as amine containments. In this paper, we adopt a “physical” entrapment technique for immobilisation of triethylene tetramine hardener for potential application in self-healing applications. Here, the liquid amine remains immobilized within the extended interconnected channels of SBA-15, and is made available to the flowing epoxy in the event of crack propagation. The feasibility of such a system has also been experimentally demonstrated.

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2. Materials and methods

Urea, formalin (37% formaldehyde in water), sodium hydroxide, conc. HCl, ammonium chloride and resorcinol were obtained from CDH and poly(ethylene-alt-maleic anhydride) (EMA), P-123 amphiphilic block-copolymer poly (ethylene oxide)-poly (propylene oxide)-poly (ethylene oxide) ($EO_{20}PO_{70}EO_{20}$), tetraethyl orthosilicate (TEOS) were purchased from Sigma-Aldrich. Epoxy monomer, (Araldite CY 230; epoxy equivalent 200 eq/g) and triethylene tetramine (TETA) based curing agent (HY 951; amine content 32 eq/kg) were obtained from Ciba Geigy. Distilled water was used throughout the course of this work.

3. Amine Immobilization in mesoporous silica (SBA-15)

The detailed procedure for preparation of mesoporous silica (SBA-15) has been discussed in our previous paper [14]. N_2 adsorption-desorption profile, PXRD pattern and SEM image of SBA-15 is presented in the Supplementary section (Figs S1 and S2). Liquid hardener was entrapped within the pores of SBA-15 by vacuum infiltration technique [9,10]. For this purpose, an accurately weighed amount of SBA-15, thermally activated at 200 °C for 12 h, was placed in excess triethylene tetramine under vacuum at 25 °C. The hardener infiltrated into the pores of SBA-15, which led to its settling to the bottom of the vessel. After 24 h, the sample was centrifuged at 600 rpm for 5 min, filtered and washed with ethanol to remove excess amine adhering to the surface. The ratio of entrapped amine to the initial mass of SBA-15 was estimated to quantify the extent of loading (Supplementary section).

The vaporization of the entrapped amine from SBA-15 was assessed through isothermal thermogravimetric analysis. For this purpose, amine loaded silica was subjected to isothermal conditions (40, 70 and 100 ° C) for extended time periods and the mass loss profile as a function of time is presented in Fig. 1. Interestingly, even at temperature as high as 100 °C, complete loss of the amine could not be effected, with ~40% amine entrapped within the pores of the substrate.

4. Epoxy microencapsulation

The procedure for encapsulation of epoxy in poly(urea-formaldehyde) microcapsules has been discussed previously [15,16]. In brief, urea and formaldehyde were allowed to undergo dispersion polymerization over the surface of stabilized dispersed epoxy droplets. Microcapsules with an average diameter of 190 ± 49 μm with a core content of 56 ± 2% were used for demonstrating self-healing in composites.

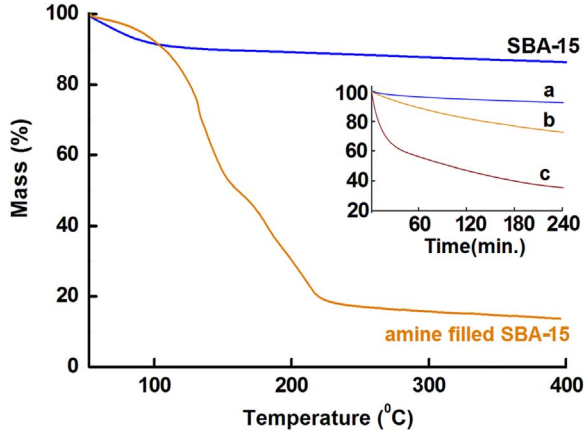

Fig. 1. TG traces of SBA-15 and amine immobilized SBA-15. Isothermal TG traces at different temperatures a) 40 °C, b) 70 °C and c) 100 °C.

5. Results and discussion

We have demonstrated the potential of mesoporous silica (SBA-15) as an immobiliser for TETA for potential in self healing application. Studies reveal that the dimensions of TETA (0.307 nm × 0.294 nm × 1.173 nm) are sufficiently small so as to permit its diffusion within the pores of SBA-15 (pore size 5.4 nm, Supplementary section, Fig. S3). Vacuum infiltration of TETA led to its entrapment within the porous structure of SBA-15 (Loading ~5 g/g). Such high loadings could be attributed to the presence of surface hydroxyl functionalities, which led to strong chemical interactions between the siliceous substrate and the amine, particularly hydrogen bonding and acid–base interactions. TG traces of SBA-15, both before and after amine entrapment is presented in Fig. 1, which clearly reveal the high loadings. In the TG trace of the neat SBA-15, ~3% w/w mass loss was observed initially (T < 150 °C), which could be attributed to the removal of condensed water present within its pores.

6. Healant delivery

The amount of healant delivered in the event of rupture is proportional to the diameter of the microcapsule as well as microcapsule loading [17]. A plot of the healant delivery (on crack plane) as a function of microcapsule loading is presented in Fig. 2. It has been reported that ~4.5 mg/cm^2 healant delivery is required for complete healing purposes. SEM image of a representative batch of microcapsule and the reservoir type internal morphology is also included in the inset. The rough external appearance of the microcapsules can be attributed to the deposition of small poly(urea-formaldehyde) particles formed during the encapsulation process [2].

7. Curing studies

Curing of epoxy with triethylene tetramine, being an exothermic reaction (Supplementary section, Fig. S4), was followed by non-isothermal DSC studies. For this purpose, epoxy and amine, in stoichiometric ratio were transferred to a DSC pan and subjected to a controlled heating program at 10 °C/min. A single exothermic peak was observed (Fig. 3a), with an onset temperature of ~70 °C. DSC studies were also performed, where the amine was derived from TETA entrapped in SBA-15 (Fig. 3b). A third set of experiment was performed in the presence of crushed microcapsules, which served as the epoxy source and TETA loaded SBA-15 which served as the amine source (Fig. 3c). In all the cases, similar profile was observed, with the only difference being the amount of heat liberated.

In view of the envisaged application of the developed additives (microcapsules and SBA-15) in the field of self healing, it was

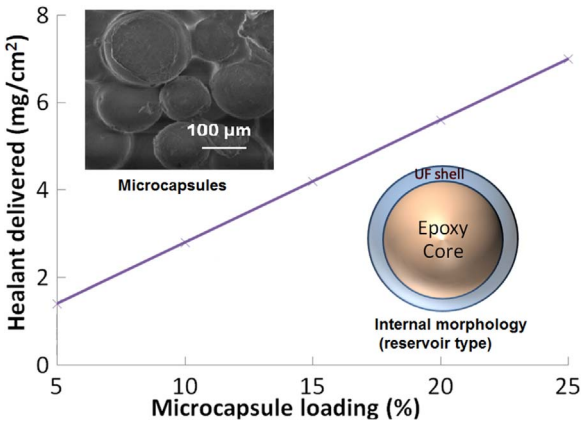

Fig. 2. Epoxy delivery into a crack plane as a function of microcapsule loading (diameter = 200 μm). SEM image and reservoir type internal morphology of the microcapsule.