Materials Letters 94 (2013) 79–82

Contents lists available at SciVerse ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

Statistical analysis of the self-healing epoxy-loaded microcapsules across their synthesis

V.V. Zuev [a], J. Lee [b,*], S.V. Kostromin [a], S.V. Bronnikov [a], D. Bhattacharyya [b]

[a] Institute of Macromolecular Compounds of the Russian Academy of Sciences, Bolshoi pr.31, 199004 Sankt Petersburg, Russian Federation
[b] Centre for Advanced Composite Materials, Department of Mechanical Engineering, The University of Auckland, Auckland 1142, New Zealand

ARTICLE INFO

Article history:
Received 10 August 2012
Accepted 7 December 2012
Available online 20 December 2012

Keywords:
Encapsulation
Self-healing
Epoxy resins
Statistical analysis
Mean size
Microcapsules

ABSTRACT

Statistical analysis of the microcapsule size has been successfully applied for the characterization of epoxy-loaded polymer microcapsules useful for self-healing process. Melamine-formaldehyde polymer was chosen as a capsule shell material. The mean droplet size of microcapsules increases with the reaction duration. In addition, they had tendency to form clusters. However, it was shown that the mean diameter of microcapsules is predetermined by the size of epoxy droplets in water emulsion. The droplets form through diffusion and coalescence. The duration of microencapsulation process increases the stability of the final microcapsules.

1. Introduction

Appearance of microcracks is a fatal problem for polymers and polymer composites utilized as structural components. Development and coalescence of microcracks cause catastrophic failure of polymer structures. Therefore, imparting self-healing function to the materials is an ideal way for prolonging their lifetimes.

Self-repairing polymers have attracted increasing research interest [1–3]. Substantial achievements have been made in this field recently, which are based on two strategies: (i) intrinsic self-healing — polymers are able to heal cracks by themselves without the aid of any healing agents, and (ii) extrinsic self-healing — healing agent is pre-embedded in polymer matrix [2]. To produce the materials of later type, healing agent should be stored by fragile containers in advance. Upon cracking they can release healing agent into the damaged areas. As a result of polymerization of the released healant, the cracks are autonomously re-bonded. Therefore, the feature of the chemical reaction of the healing agent and the compatibility between the healant and cracked planes are critical for the degree of restoration of the materials. In this context epoxy is a very preferable healing agent [4]. Epoxy resins are used in many thermoset coatings and also are an obvious material of choice for healing chemistry.

The microencapsulation is by far the most studied self-healing concept [1]. In this work, melamine-formaldehyde polymer has been chosen as the capsule shell material. As has been demonstrated in several reports [5], cross-linked polymers can form capsules of insoluble shell. Furthermore, those polymers are inexpensive and reasonably safe to work with. These characteristics of cross-linked polymers make them potentially suitable for utilization in high-performance coatings and subsequent potential scale-up of production.

Polymerization of melamine-formaldehyde can be both acid- and base-catalyzed, and, conventionally, is carried out in two stages, where the first one is basic and the second one is acidic. Under basic conditions, series of addition reactions between formaldehyde and amine groups of melamine lead to the formation of pre-polymers with one to six methylol groups [6]. Process duration, amine to formaldehyde ratio, and alkalinity of medium determine the chemical composition and structure of formed pre-polymers and hence are crucial factors for their stability.

The aim of this work was to estimate the influence of encapsulation process duration on the formation, structure and size of capsules that are very important for different types of applications [7]. The size distribution of microcapsules can be described with the aid of kinetic model of reversible aggregation which goes back to formulations used in the description of living polymerization or aggregation of polymer in solution [8]. Universality of the model has been shown by its application to statistical ensembles of carbon-black particles [8], spherulites in isotactic poly(methylmethacrylate) [8,9], microdomains of polyamic acids in the course of their transformation to polyimides [10], defects of metallographic samples at tensile loading [9], bacteria and yeast in the course of their growth [8], and the ordered phase

* Corresponding author.
E-mail address: jl11018@gmail.com (J. Lee).

0167-577X/$ - see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.matlet.2012.12.026

droplets in liquid crystalline systems [11,12]. This has given us hope for successfully describing the microcapsules size distribution during the encapsulation process.

2. Experimental work

Materials and methods: The diglycidyl tetrahydro-o-phthalate (DTHP) purchased from Jindong Chemical Plant, Tianjin, China was used as the polymerizable component of the healing agent in the microcapsules. Melamine, formaldehyde and poly (4-styrenesulfonic acid-co-maleic acid) sodium salt (Na-PSAM) were purchased from Aldrich (Saint Louis, Missouri).

To make the epoxy microspheres, DTHP (400.0 g) was added to a 2 wt% aqueous solution of Na-PSAM (1200 ml). The mixture was vigorously stirred at 1500 rpm for 5 min and then a few drops of 1-octanol were added to eliminate surface bubbles of the epoxy emulsion. After that, the temperature of the solution was raised to 50 °C, and melamine-formaldehyde precondensate (62.5 g of melamine and 135.5 g of 37% water solution of formaldehyde) was added. The formed aqueous phase was agitated for about 2 h at 500 rpm. The pH value of the solution was adjusted to about 3 by adding citric acid. Finally, the solution was cooled to room temperature; the formed microcapsules were separated by filtration, washed with deionised water, and dried in vacuum.

Analysis of microcapsule size: The morphology and size of microcapsules was characterized by scanning electron microscopy (XL30 ESEM-FEG, Philips). The SEM images obtained (Fig. 1) were subsequently segmented and subjected to digital analysis using the Image Tool 3.0 software elaborated at the Health Science Center, the University of Texas, San Antonio, USA, to elucidate the statistical size distributions of the dispersed phase droplets. To analyze the resulting histograms, we used the model of reversible aggregation.

Model: The model of reversible aggregation [8–10] was inspired by application of irreversible equilibrium thermodynamics. It gives a generalized characterization of micro-structure in different liquids. According to the model, a stationary micro-structure is developed by linking the energy-equivalent units in metastable clusters called aggregates. The aggregates are perpetually composed and decomposed under thermal fluctuations (condition of their reversibility).

According to the model, the stationary statistical distribution $h(s)$ of the projected diameter s of the micro-structural entities reads as follows [8–10]

$$h(s) = as^2 \exp\left(-\frac{s\Delta u_0}{kT}\right) \tag{1}$$

where a is the normalizing factor, Δu_0 is the energy of aggregation, k is the Boltzmann constant, T is the absolute temperature and kT is the energy of thermal fluctuation. Eq. (2) allows the determination of the mean entity area $< s_i >$ related to the i-th statistical ensemble as a normalized mathematical expectation:

$$\langle s_i \rangle = \frac{\int_{s_i = s_{0i}}^{\infty} s_i^3 \exp\left(-\frac{s_i \Delta u_{0i}}{kT}\right) ds_i}{\int_{s_i = s_{0i}}^{\infty} s_i^2 \exp\left(-\frac{s_i \Delta u_{0i}}{kT}\right) ds_i} = \frac{3kT}{\Delta u_{0i}} \tag{2}$$

Taking into account a circular form of the capsules, their mean diameter can be found as

$$< d > = 2\sqrt{\frac{< s >}{\pi}} \tag{3}$$

3. Results and discussion

In the development of self-healing materials though microencapsulation, a proper control of capsule diameter is a key issue because the diameter greatly influences the self-healing performance [7]. The investigations [7] of the relationship between microcapsule size, healing agent delivery and healing performance have shown that specimens with larger capsules perform better than those with smaller capsules at the same weight fraction. In some conditions, only the capsules with a given range of diameters are suitable.

The microcapsule diameter is influenced by a combination of several factors including the geometry of the mixing device, viscosity of the reaction media, surfactant concentration, agitation rate, temperature, etc. However, from the thermodynamics point of view, all these factors act as parameters to influence free energy of the systems that determine the size of compact aggregates in liquid [8]. It is well known that the mean diameter of microcapsules is primarily controlled by the agitation rate because it determines the starting dispersion of capsulation medium [13]. It stimulated us to investigate the influence of parameters such as the time of microencapsulation on the mean diameter of microcapsules. As a method for analysis of the evolution of the microcapsule size distribution, the statistical analysis of microcapsule size was chosen. Our analysis is based on the model of reversible aggregation proposed by Kilian et al. [8–10] which has been successfully applied for the description of stationary size distribution of the micro-structural entities in various systems.

Two opposite processes determine the mean droplet size of insoluble liquid during an agitation in a liquid medium: break-up at diffusion (small droplets) and coalescence controls (big droplets). However, the breakage of droplets is the main mechanism in the emulsification stage. It is well known that higher agitation speed should generate smaller droplets in the emulsification stage, which led to smaller microcapsules [13]. The average diameter of microcapsules depends on the type of agitator used, the physical properties of the two phases and their interfacial tension. Hence,

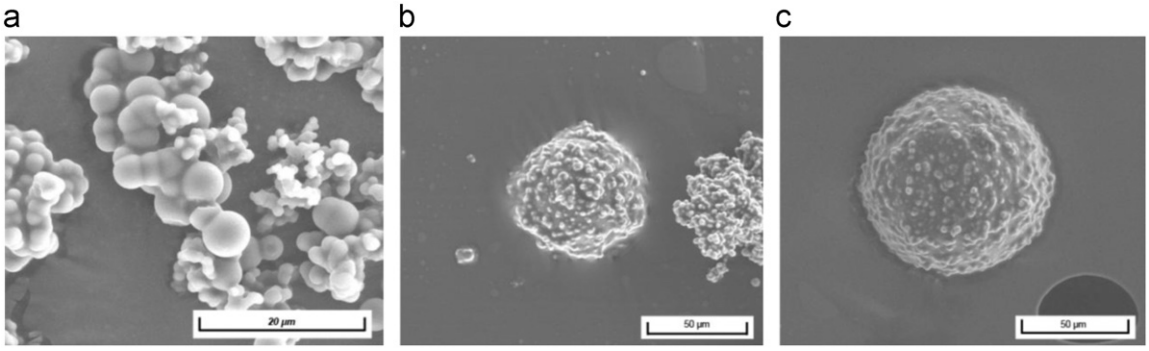

Fig. 1. SEM images of epoxy-loaded microcapsules obtained across encapsulation for (a) 25 min; (b) 38 min; (c) 210 min.