Composites Science and Technology 138 (2017) 80–90

Contents lists available at ScienceDirect

Composites Science and Technology

journal homepage: http://www.elsevier.com/locate/compscitech

Effect of solvent evaporation technique on the characteristics of curing agent microcapsules and the curing process

Jinsheng Fan [a], Yudong Zheng [a, *], Yajie Xie [a], Yi Sun [a], Yihao Luan [b], Wenge Jiang [b], Cai Wang [a], Shumin Liu [a], Xiaobing Liu [a]

[a] School of Material Science and Engineering, Beijing University of Science and Technology, Beijing 100083, China
[b] Institute of Aerospace Material and Technology Beijing, No. 1 South Dahongmen Road, Fengtai District, Beijing 100076, China

ARTICLE INFO

Article history:
Received 27 August 2016
Received in revised form
13 November 2016
Accepted 14 November 2016
Available online 17 November 2016

Keywords:
Functional composites
Curing
Statistics
Differential scanning calorimetry (DSC)
Powder processing

ABSTRACT

In this work, diuron (DCMU), which was encapsulated using polystyrene (PS) as the shell material via solvent evaporation method in an oil-in-water emulsion was used as an accelerator. Due to their temperature control release performance, these microcapsule-type latent curing agents have an excellent impact on prolonging the shelf life of prepreg in a one-component system. The structure and properties of microcapsules, such as size and coating rate, were influenced by dispersed phase/continuous phase ratio, mass ratio of core/shell, emulsifier concentration, and agitation rate. Orthogonal array design experiments were used to obtain optimum synthetic parameters. The temperature controlled release performance of microcapsules plays an important role during the curing reaction. Furthermore, the released amount of the curing agent throughout the heating process was evaluated. With the increase in the heating rate, the release rate of the core materials showed a growing trend. To explore the influence of the microcapsule-type curing agent by non-isothermal differential scanning calorimetry (DSC) technique at different heating rates, the heating flow of microcapsule-type and normal-type curing agents in the curing process were tested and data were compared., Compared to the normal ones, the microcapsule curing agents exhibited delayed kinetic behaviors throughout the curing process. The variations of activation energy over the course of the reaction were evaluated by using Iso-conversional methods. The results indicated that the activation energy of the microcapsule-type curing agent indicated a continuous decrease, proving that it is easier for the reaction to carry through to completion.

1. Introduction

A microcapsule-type latent curing agent can be used in a one-component system, where latent curing agents and accelerators are added ahead of time in epoxy resin to form prepreg [1–3]. If a curing accelerator is added, it is possible to lower the curing temperature; however, the accelerator will drastically damage the storage stability, consequently the resin cannot exhibit the latency of the high temperature-curable curing agent [4]. With the use of a microcapsule curing agent [5], the above-mentioned problems that are associated with the use of accelerators are eliminated. Moreover, the microcapsule latent curing agent has exceptional compatibility with epoxy resin; not only that, but it also renders the one-component system with low viscosity, a fast curing rate and excellent storage stability [6]. Additionally, it contributes to the remarkable properties of the final product [7,8].

Due to its excellent physical, chemical, and thermal properties, Epoxy resin can be regarded as one of the most extensively used engineering polymeric materials; nevertheless, there are also a series of drawbacks associated with its curing process and fragile features [9]. Within the last decade, the embedment of microcapsules containing healants has been the most popular approach to realize self healing in epoxy to overcome its brittleness [10–12]. Except for the use of microcapsules in self healing studies, the encapsulation is a feasible and economic method to prepare a latent curing agent to solve the problems mentioned above [13]. Until now, most studies on microcapsule-type latent curing agents have focused on preparing microcapsules of imidazole derivatives [14]. Ham et al. [15] and Lee et al. [11,16] synthesized the microcapsules of a 2-methylimidazole curing agent by the solvent evaporation (SE) method and spray-drying (SD) method,

* Corresponding author.
E-mail address: zhengyudong@mater.ustb.edu.cn (Y. Zheng).

http://dx.doi.org/10.1016/j.compscitech.2016.11.014
0266-3538/

respectively. By comparison, the shelf life of the microcapsules from the SD method was shorter compared to that from the SE method. Moreover, the microcapsules had a battered round shape if they were prepared by using the SD method, resulting in a shorter shelf life and a quicker initial release rate. Recently, Shin et al. [17] successfully solved this problem by using a water/oil (W/O) emulsion for a spray-drying method to prepare finer microcapsules. Additionally, through a simple emulsion/solvent evaporation method, Xing et al. [13] obtained the microcapsule of imidazole derivatives with polyetherimide (PEI) as the shell material. However, Xing et al. found that the curing agent cannot uniformly be released in the resin, which is attributable to the restriction of microcapsule shell during the process of curing. Although the shelf life was successfully prolonged with the use of the microcapsule imidazole curing agent, many intrinsic disadvantages of the imidazole curing agent still exist, such as the volatility that creates a handling problem and moisture absorbability, which significant impacts the curability and the compatibility with epoxy resin. The effect of these disadvantages would be avoided if the imidazole curing agent can be replaced by another variety of high performance curing agent.

Dicyandiamide (DICY), a type of amine-based latent epoxy resin curing agent, is not as toxic compared to most of the other amines [18]. Therefore, its use can eliminate the disadvantages associated with the imidazole curing agent. When using these high temperature-curable curing agents, it is generally recognized that it is best to use them with a curing accelerator such as diuron. The encapsulation of diuron can eliminate the weaknesses mentioned above. To the best of our knowledge, there have been no reports of a diuron-filled microcapsules curing agent yet. From a practical standpoint, the polymers used to encapsulate the curing accelerator of an epoxy resin microelectronic packaging material should possess a controllable softening-point or a suitable decomposition temperature [14]. Dowding et al. [19] used PS as the shell-forming polymer, while the experimental factors governing microcapsule formation were investigated accordingly. In this paper, PS, which can be employed as the shell materials for the preparation of the microcapsules, was selected based on the consideration of the properties of the accelerator (diuron). PS has a stable chemical structure, and it has a low melting point. Moreover, it is compatible with the epoxy resin, which makes it easy to cure in a molten state. It is with high curing reactivity in a smallest possible amount of addition. When the temperature increases to a desired point, the capsules are broken and the curing agents are released to cure the epoxy resin [20]. Suitable shell materials and core curing agents have been reported in a patent [21]. At the same time, the selection of the preparation method largely depends on the properties of core/shell material [10,22]. The formation of PS shelled microcapsules using solvent evaporation methods involves numerous extrinsic variables. In previous studies [13,23,24], factors such as size distribution and coating rate were found to influence the structure of the microcapsules. Moreover, the structure of the microcapsules has an impact on the amount of core material released over time when heated, which has a close relationship with the cure kinetics of curing reaction. Therefore, it is necessary to further investigate the synthesis and structure control of the microcapsules.

In this paper, a diuron (DCMU)-filled microcapsule-type latent curing agent was fabricated using PS as the shell material via solvent evaporation method [25] in an oil-in-water emulsion. We examined the influence of the volume ratio of dispersed phase/continuous phase (DP/CP), the mass ratio of core/shell, the concentration of emulsifiers, as well as the agitation rate on the formation and morphology of the microcapsules during the preparation process. In order to determine the main parameters of preparation, the core fraction of the microcapsules was measured through orthogonal array experiments. The released amount of the core material from microcapsules and the effect of melting behaviors on the variation of size distribution during the heating process with different heating rates, were both studied on a heated stage under a microscope. To explore the influence of the microcapsule-type latent curing agent on the curing process, the heating flow of microcapsule-type and normal type curing agents in the curing process were tested and compared.

2. Experimental methods

2.1. Materials

The curing agent dicyandiamide (DICY) and diuron (DCMU) were provided by the Institute of Aerospace Materials and Technology Beijing. The diglycidyl ether of bisphenol A (DGEBA) epoxy resin was a commercial product obtained from the Baling Petrochemical Company (China) with an epoxy equivalent weight of 160 g. The sodium dodecyl benzene sulfonate neopelex (SDBS), which was used as a dispersant, was obtained from the Aoli Chemical Company (China). Methylene dichloride used in the oil phase was purchased from the WeiSi Chemical Company (China). Polystyrene (PS, Mw 6500) used as shell material was purchased from the Beijing Red Star Chemistry factory (China). The chemical structures for all of the chemicals mentioned above are given in Scheme 1. All commercial chemicals in this study were used without further purification unless otherwise specified.

2.2. Synthesis of microcapsules containing curing agent

Since it can be used for mass production, the solvent evaporation method was selected among all of the possible encapsulation methods for this study [26]. The preparation of microcapsules was based on the solvent evaporation method in an oil-in-water emulsion system [19,23,27], The manufacturing process of the microcapsule-type latent curing agent is shown in Scheme 2. DCMU-filled microcapsules were prepared according to the following procedures. First, 400 mL of 2 wt% SDBS aqueous solution was prepared as the surfactant in a 1000 mL beaker at room temperature. The beaker was then placed in a temperature-controlled water bath located on a programmable hot plate with an external temperature probe. The solution was stirred with a digital mixer driving a two-bladed propeller at a rate of 500 rpm and heated to 35 °C with a heating rate of 2 °C/min. Methylene dichloride was used as an oil phase. The encapsulated material and polymeric wall material were dissolved in the oil phase. In order to form the encapsulated product, drop increments were then added into the aqueous solution. The emulsion system was stirred for 180 min, the suspension of microcapsule slurry was then obtained. The acquired slurry was filtered and washed with distilled water 3–4 times. Finally, the produced microcapsules were air-dried for 24 h and then sieved to remove debris for further analysis.

2.3. Characterization of curing agent filled microcapsules

Using a scanning electron microscopy (SEM), the size and morphology of the microcapsules were observed. The size distribution of the microcapsules was measured from the optical images of at least 100 individuals [28]. The thermal properties and compositions of the microcapsules were characterized by thermogravimetric analysis (TGA) [29]. During the TGA test, 10 mg powder samples were placed in a platinum pan and heated in a nitrogen atmosphere at a heating rate of 10 °C/min. To calculate the core fraction of the synthesized microcapsules, powder samples were heated to 500 °C for complete thermal decomposition. The