



Synthesis of novel multilayer composite microcapsules and their application in self-lubricating polymer composites

Haiyan Li^a, Yingjie Ma^a, Zhike Li^a, Yexiang Cui^a, Huaiyuan Wang^{a,b,*}

^a Provincial Key Laboratory of Oil & Gas Chemical Technology, College of Chemistry & Chemical Engineering, Northeast Petroleum University, Daqing 163318, PR China

^b School of Chemical Engineering and Technology, State Key Laboratory of Chemical Engineering, Tianjin University, Tianjin 300072, PR China

ARTICLE INFO

Keywords:

Carbon nanotubes
Polymer-matrix composites
Interface
Friction/wear

ABSTRACT

Novel lubricant oil-loaded multilayer composite microcapsules with poly(urea-formaldehyde) (PUF) shells assembled with polydopamine-functionalized oxidized carbon nanotubes (CNTs-o-PDA) are fabricated. Results indicate that the PUF microcapsules show spherical shape structure with a mean diameter of 110 μm and an encapsulation capacity of 83.5%. CNTs are successfully assembled on the surface of lubricant oil-containing PUF microcapsules (LPMs). Thermal stability tests reveal the initial decomposition temperature of microcapsules elevated by 75 °C. Furthermore, the microcapsules are embedded into epoxy to prepare self-lubricating composites. The coefficient friction and wear rate of self-lubricating composites incorporating 20 wt% CNTs-o-PDA assembled LPMs are 33.79% and 74.28% lower than that of composites incorporating LPMs, and which are 64.07% and 99.54% lower than that of the pure epoxy resin, respectively. Further studies confirm that the interface bonding strength between epoxy and microcapsules is effectively improved by the introduction of CNTs-o-PDA on the surface of PUF microcapsules. The synergistic effect between microcapsules containing lubricant oil and CNT layer played an important role in improving the tribological properties of polymer composites.

1. Introduction

The development of new polymer composites for tribological application has attracted more interest in materials scientific fields. The improvement of friction and wear properties of polymer composites was carried out by the addition of solid additives [1,2], ionic liquid lubricant [3–6] or nano/microcapsules [7–11] into polymer matrix. Nano/microcapsule-based self-lubricating composites have attracted widespread attention in recent years due to the ability to lubricate materials automatically whenever and wherever friction occurs and had been extensively investigated. Since the first report on the microcapsule-based self-lubricating composites [7], many research groups have focused their attention in this aspect. Lubricant oil-loaded Poly(melamine-formaldehyde) (PMF) microcapsules and wax-loaded poly(urea-formaldehyde) (PUF) microcapsules were synthesized by an *in situ* polymerization method, and self-lubricating epoxy composites were prepared by incorporating these microcapsules into polymer matrix, the self-lubricating properties were studied, respectively [8,9]. Yang et al. synthesized SiO₂ microcapsules containing the ionic liquid [BMIm][PF₆] by sol-gel process and investigated the frictional behaviors of the

polyurethane composite coatings filled with microcapsules [10]. Li et al. prepared two kinds of microcapsules, lubricating oil or another ionic liquid [EMIm][NTf₂] was encapsulated in a polysulfone (PSF) wall respectively by a solvent evaporation method, and self-lubricating composites were prepared by filling them in epoxy resin [11,12]. The results of these studies show that the PSF and SiO₂ microcapsules have high thermal stability, but the encapsulation capacity is relatively lower compared with PMF and PUF microcapsules. Despite the large encapsulation capacity, PMF and PUF microcapsules are brittle and susceptible to rupture. Moreover, the temperature resistance of these wall materials is in the range of 200–260 °C, which prohibits high temperature applications. In general, the tribological properties of polymer composites are greatly improved due to the incorporation of microcapsules, however, the mechanical properties, such as tensile properties, hardness and Young's Modulus, are greatly reduced as a result of the microcapsule structure. Additionally, the weak interfacial bonding strength between the microcapsules and polymer matrix also has a significant effect on the mechanical properties of polymer composites.

To address these mechanical challenges, many researchers have dispersed nanofillers into a pure polymer matrix to act as a

* Corresponding author. Provincial Key Laboratory of Oil & Gas Chemical Technology, College of Chemistry & Chemical Engineering, Northeast Petroleum University, Daqing 163318, PR China.

E-mail address: wanghyjiji@163.com (H. Wang).

<https://doi.org/10.1016/j.compscitech.2018.05.042>

Received 21 February 2018; Received in revised form 10 May 2018; Accepted 21 May 2018

Available online 24 May 2018

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reinforcement phase that enhances the mechanical properties. The materials used as nanofillers include glass fibers [13], carbon nanotubes (CNTs) [14,15], short carbon nanofibers [2,8,16], nanosilica [17], nanoclays [18] and carbon black [19]. Although the mechanical properties of the polymer composites are improved by simply adding the nanofillers, the tribological properties of the nanofillers/polymer composites are inferior to that of the microcapsules/polymer composites. Therefore, strategies to prepare self-lubricating polymer composites by adding microcapsules and nanofillers in polymer at the same time have been explored [20–22]. Nanofillers have their own difficulties; they are difficult to disperse and easily to form clusters in the matrix because of the electrostatic effects. Moreover, nanofillers do not address the main factor affecting the mechanical and tribological properties of composites, which is weak interfacial bonding strength between microcapsules and the matrix.

Another approach to improve the mechanical properties and temperature resistance of the microcapsules is the preparation of double-walled and multi-walled microcapsules. For example, Caruso et al. prepared double-walled polyurethane/poly(urea-formaldehyde) microcapsules with improved thermal stability and mechanical properties [23]. Yang et al. synthesized polyurea/poly (melamine-formaldehyde) double-wall microcapsules that show high thermal stability and compactness [24]. Huang et al. developed multi-walled (melamine formaldehyde resin/carbon nanotubes (CNTs)-poly (4-styrenesulfonic acid) sodium) phase-change microcapsules via a combined strategy of *in situ* polymerization and layer-by-layer self-assembly method, and these microcapsules revealed the excellent thermal stability with a higher hardness and Young's modulus than the microcapsules without grafting CNTs [25]. Our group has also prepared high temperature resistant organic/inorganic hybrid double-wall microcapsules with PSF and silica as the encapsulating materials [26,27]. Although much of the literatures reports on how to improve the temperature resistance and the mechanical properties of microcapsules, there are few reports on how to improve the interfacial properties between microcapsules and the polymer matrix. Methods to improve the tribological properties of self-lubricating polymer composites by the surface modification of microcapsules are also lacking in the literature.

In this work, multilayer composite microcapsules with PUF shells assembled with CNTs were synthesized. The mechanical strength and thermal stability of microcapsules were improved compared to microcapsules without CNTs. Meanwhile, the CNTs assembled onto the surface of the microcapsules contained more hydroxyl groups due to modification by dopamine, which allowed the microcapsules to form covalent bonds with the epoxy and curing agent in their interface. Therefore, the interfacial bonding strength between microcapsules and epoxy was effectively enhanced. Additionally, the synergistic effect between microcapsules containing lubricant oil and a CNT layer played an important role in improving the tribological properties of the polymer composites. This study encompasses a thorough investigation of interfaces, nanocomposites, and functional coatings.

2. Experimental

2.1. Materials

Lubricant oil (70SN, density $\approx 0.82 \text{ g cm}^{-3}$) was supplied by Daqing

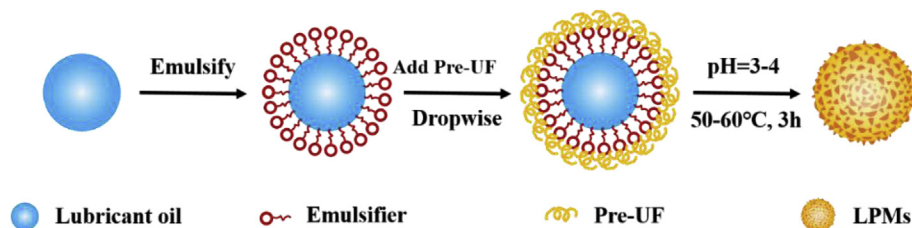


Fig. 1. Synthetic mechanism scheme of LPMs via *in situ* polymerization.

Oil Field Co. Ltd. Urea, 37 wt% formaldehyde aqueous solution, hydrochloric acid (HCl), triethanolamine (TEA) and anhydrous ethanol were purchased from Tianjin Damao Chemical Reagent Co. Ltd. Lignosulfonate (Reax 88A) was bought from MeadWestvaco Corporation. Resorcinol and ammonium chloride were supplied from Shanghai Macklin Biochemical Co. Ltd. CNTs (diameter: 15–30 nm) was bought from Beijing Boyu High-tech New Materials Tech Co. Ltd. Dopamine and tris (hydroxymethyl) aminomethane hydrochloride (Tris-HCl) were provided from Suzhou Tianke Trade Co. Ltd. E-51 epoxy resin (EP) and harder tetraethylenepentamine (TEPA) were obtained from Heilongjiang chemical Engineering Institute Co. Ltd. Distilled water was used throughout the study. All materials were used as received without any further purification.

2.2. Synthesis of lubricant oil-containing PUF microcapsules

Lubricant oil-containing PUF microcapsules (LPMs) were prepared by *in situ* polymerization. Urea was dissolved in a 37 wt% aqueous formaldehyde solution, with a 1:2 weight ratio of urea to formaldehyde solution. The pH of the mixture was adjusted between 8 and 9 by adding the TEA, gradually heated to 70 °C, and further reacted for 1 h to form the PUF prepolymer. Lubricant oil (5 g), resorcinol (0.5 g), ammonium chloride (0.5 g), and 0.1 wt% Reax-88A solution (130 mL) were added in a 250 mL three-neck flask. A stable O/W emulsion was made by mechanical stirring at an agitation rate of 500–600 rpm for 30 min at 40 °C. Then, the PUF prepolymer solution was added dropwise into the emulsion. After all the prepolymer was added and stirring for about 5 min, two to three drops of *n*-octanol were added to eliminate the foam generated in the system and the pH of the solution was adjusted to 3–4 using HCl (2 mol/L). The system temperature was then kept between 50 °C and 60 °C for 3 h. The resultant microcapsules were washed with distilled water and ethanol for three times. The precipitate was dried in a vacuum oven at 60 °C for 12 h. Fig. 1 schematically shows the synthesis mechanism of the LPMs.

2.3. Fabrication of polydopamine modified oxidized carbon nanotubes

Firstly, polydopamine modified oxidized carbon nanotubes (CNTs-o-PDA) were prepared according to Wang and Fei's reports [28,29]. CNTs (0.1 g) was magnetically stirred in a 50 mL mixture of H₂SO₄ and HNO₃ (the volume ratio was 3:1) at 80 °C for 1 h. The obtained CNTs slurry were rinsed and filtered with deionized water until the solution was neutral. After drying at 60 °C for 12 h, the oxidized CNTs were obtained. To functionalize the oxidized CNTs, dopamine (200 mg) and Tris-HCl (120 mg) were added to distilled water (100 mL) resulting in a mixture with a pH value of ~ 8.5 . As-oxidized CNTs (100 mg) were then transferred to the solution and ultrasonically dispersed for 20 min. The self-polymerization reaction of dopamine occurred on the surface of CNTs under mechanical stirring at room temperature for 24 h. The products were filtered and washed three times with distilled water and the anhydrous ethanol, and finally dried at 60 °C for 3 h. Fig. 2 outlines the preparation progress of CNTs-o-PDA. Fig. 2a displays the reaction mechanism of dopamine self-polymerization, in the self-polymerization process, the oxidation of dopamine to quinone, the generation of the dihydroxyindole by intramolecular cyclization and the formation of 5, 6-indolequinone by further oxidizing dihydroxyindole would be

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