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Fabrication of SiO_2 wrapped polystyrene microcapsules by Pickering polymerization for self-lubricating coatings

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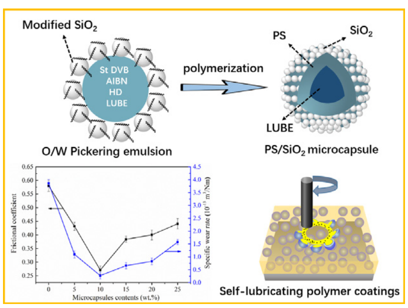
GRAPHICAL ABSTRACT



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ABSTRACT

The facile and efficient encapsulation of a lubricant oil in SiO_2 wrapped polystyrene microcapsules is accomplished using a Pickering polymerization technique. Triton X-100-IPTS fumed SiO_2 nanoparticles are used as emulsifiers for the formation of O/W Pickering emulsions and the stability factor of the Pickering emulsions was investigated. The as-obtained microcapsules are characterized by scanning electron microscope, thermogravimetric analysis, Fourier transform infrared spectra and dynamic laser scattering. These results suggest that the microcapsules display a spherical shape with a core content of ~38.3%, an average diameter of 3.3 μm, a shell thickness is ~900 nm and outstanding thermal stability for lubricant oil with a decomposition temperature of 250 °C. Moreover, the microcapsules are embedded into an epoxy resin for self-lubricating coatings. On the basis of frictional coefficient measurements and wear testing, the self-lubricating microcapsules-incorporated epoxy coatings on an aluminum plate indicate the excellent dispersibility of the microcapsules in coatings and the favorable antifriction effects.

1. Introduction

Organic/inorganic hybrid shell microcapsules have attracted increasing attention in a variety of academic and industrial areas [1–4]. These hybrid microcapsules combine the advantageous properties of inorganic nanoparticles and polymers. Organic materials offer structural flexibility, whereas, inorganic materials are well known for their good thermal stability, higher structural strength and higher thermal conductivity [5]. Meanwhile, the microcapsules can alter the surface properties with different particle loadings in the shell of the microcapsules. Organic/inorganic hybrid shell microcapsules can be synthesized by many methods, as summarized as follows: (1) adsorption of inorganic materials onto the shell surfaces (e.g. biomimetic adhesion [6], etc.), (2) in situ polymerization of the adsorbed inorganic materials

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(e.g. miniemulsion polymerization, etc.) and (3) the removal of the sacrificial templates [7–9]. Pickering emulsions have been confirmed to be ideal systems for fabricating organic–inorganic hybrid microcapsules, owing to their low toxicity, surfactant-free nature, low emulsifier content and adjustable droplet size. Solid particles are permanently immobilized at the oil–water interface to suppress the coalescence of the emulsion, which is highly thermodynamically stable. Recently, the encapsulation of different functional chemicals in microcapsules has been reported widely by nanoparticles stabilization of Pickering emulsion [10–13]. For example, Gao et al prepared a poly(urea-formaldehyde)/TiO_2 hybrid shell microcapsule- loaded photoinitiator by a Pickering stabilized emulsion for a photo-responsive self-healing polymer coating [14]; Cong et al. reported encapsulation dodecafluoroheptyl-propyl-trimethoxysilane via Pickering polymerization with SiO_2 and TiO_2 nanoparticles [12]. However, Lubricant oil–loaded micro/nanocapsules synthesized by Pickering emulsion templates for Self-lubricating polymer coatings have seldom been reported.

Single polymer wall microcapsules, as a method for improving tribological properties, have been widely reported [15–17]. However, these microcapsules have average sizes from dozens of micrometers to hundreds of micrometers, which limit their application in the fields of coatings. In addition, larger microcapsule size lead to a more significant reduction in the mechanical strength of polymeric composites. To achieve these breakthroughs, microcapsules fabricated by O/W Pickering emulsion polymerization are applied and the size of the microcapsules is controlled, depending on the mass ratio of the nanoparticles to oil phase. The small particle size of the microcapsules facilitates their dispersion into the polymer matrix. In addition, organic/inorganic hybrid wall microcapsules not only possess a well-defined structure and excellent thermal resistance, but also combine the advantageous properties of solid lubricant [18–20] and liquid lubrication [21,22] , compared to traditional single wall microcapsules.

In this study, we successfully fabricated SiO_2 wrapped polystyrene (PS) microcapsules using lubricant oil as a core material based on Pickering emulsification polymerization. SiO_2 particles were applied as emulsion stabilizer to protect emulsion droplets from demulsification. After polymerization, PS/SiO_2 microcapsules were formed. The synthesized microcapsules were incorporated in an epoxy matrix to form a self-lubricating composite coating. This coating is demonstrated to be effectively wear-resistant using tribological tests.

2. Experimental

2.1. Materials

Styrene (St, ≥99%), divinylbenzene (DVB, ≥80%), 2,2′-azobis(2-methylpropionitrile) (AIBN, ≥99%), *t*-octylphenoxypolyethoxyethanol (Triton X-100, biochemistry grade), 3-isocyana-topropyl triethoxysilane (IPTS, ≥95%), *n*-hexadecane (HD, >98%), ammonia solution ($NH_3{\cdot}H_2O$, 25 wt%), ethanol (EtOH, >99.7%), dibutyltin dilaurate (DBTDL, ≥95%) were purchased from Sinopharm Chemical Reagent Co. (China). Lubricant oil (trade name: 70SN, density = 0.8175 g cm^{-3}) was kindly donated from Daqing Oil Field Co. Ltd (Daqing, China). EP (Exopy-51) and tetraethylenepentamine (TEPA) curing agent were obtained from Nanjing Huntsman Advanced Materials Company (China). Nano silica (SiO_2, diameter: 15 nm) was provided by Nanjing hydratight nanomaterials Co. Ltd.(China). St and DVB were distilled under vacuum before use and the other reagents were used as received.

2.2. Synthesis of PS/SiO_2 hybrid shell microcapsules containing lubricant oil

The modified SiO_2 particles were prepared according to our previously reported method [23]. First, the modifier of Triton X-100-IPTS (T-IPTS) was synthesized with IPTS and Triton X-100 under the catalysis of DBTDL. Then, the SiO_2 was treated with T-IPTS to obtain the modified SiO_2 [24]. The PS/SiO_2 hybrid microcapsules were synthesized by Pickering templates with different SiO_2 contents. A schematic of the fabrication process of the PS/SiO_2 hybrid microcapsules is shown in Fig. 1. A quantity of 0.5 g of as-treated SiO_2 was dispersed in 50 mL of distilled water using ultrasonic agitation for 10 min. Subsequently, the SiO_2 dispersion was mixed with the oil phase (7 g of St, 0.2 g of DVB, 7 g of Lubricant oil, 0.2 g of HD and 0.276 g of AIBN) in a 100 mL glass beaker. The Pickering emulsion was prepared using a FLUKO homogenizer at 11,000 rpm for 5 min, and then transferred into a 100 mL three necked flask and deoxygenated by nitrogen gas for 30 min. Then, the emulsion was magnetically stirred for 24 h in 70 °C to produce microcapsules with PS shells. The products were centrifuged at 8000 rpm and the collected microcapsules were rinsed by dispersion into ethanol or water, and centrifugation three times. Finally, PS/SiO_2 hybrid microcapsules were dried at 60 °C or freeze-drying. For the sake of comparison, we also prepared microcapsules without the addition of lubricant oil.

2.3. Preparation of the epoxy/microcapsules composite coatings

In order to verify the self-lubricating properties, PS/SiO_2 microcapsules were embedded into epoxy coatings. First, the raw aluminum plate (1100 grade, 80 mm × 80 mm × 1 mm) was preprocessed by polishing with 600 mesh sandpapers in one direction, ultrasonically washing in absolute alcohol and drying under a nitrogen flow. Afterwards, the pre-weighed microcapsules (0, 5, 10, 15, 20, 25, and 30 wt%) were added into the epoxy at 60 °C with stirring for 10 min. Subsequently, the 12 wt% TEPA curing agent based on epoxy was added to the microcapsules/epoxy mixtures and ultrasonication was used to remove bubbles in an ice bath. Finally, the microcapsule/epoxy mixtures were deposited on the aluminum plate and cured at room temperature for 4 h and then 80 °C for 5 h.

2.4. Characterization

2.4.1 Optical microscopy (OM)

Pickering emulsions with different SiO_2 contents and oil-water ratios were recorded by a Reversed Biological Microscope (Shanghai Yiyuan Optical Instrument Co., Ltd) equipped with a camera.

2.4.2 Scanning electron microscopy (SEM)

The morphology of microcapsules, shell wall thickness and wear surfaces of the epoxy/microcapsules composite coatings were analyzed with a scanning electron microscope (SEM ZEISS, Germany) operating at 10 kV.

2.4.3 Energy dispersive spectrometer X-ray analyzer (EDS)

Elemental analysis was conducted by energy dispersive spectroscope (EDS) equipped to SEM.

2.4.4 Microcapsule size analysis

The average diameter and size distribution of microcapsules were measured in data sets of about 200 measurements from SEM images.