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Analysis of graphene-encapsulated polymer microcapsules with superior thermal and storage stability behavior

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ABSTRACT

A new series of urea-formaldehyde polymer microcapsules with two-component cores have been synthesized by an in-situ polymerization procedure. Graphene was used as one of the components in the core material along with a bisphenol-A epoxy resin. Preparation of graphene oxide was carried out by the Staudenmaier oxidation process, followed by further thermal treatment in a controlled environment to produce thermally treated graphene (TTG). The thermal and physical properties of the microcapsules were investigated by TGA (Thermogravimetric analysis) and, SEM (Scanning electron microscopy) among other methods. The chemical composition of the microcapsules was ascertained by FTIR (Fourier-transform infrared) spectroscopy. The resultant graphene-encapsulated microcapsules have shown an increasing degree of thermal stability in the range from 250 °C to over 400 °C, depending on the TTG wt%. They also exhibited good storage stability (>90%) over different periods of time. It was determined that the thermal and physical properties of the microcapsules are closely linked to the core materials and the processing conditions. The processing conditions, in turn, can be varied to synthesize different types of microcapsules with different sizes, thermal stability and yield percentage values. The improved sway over the thermal degradation provided better control over the release rate of the core material under various conditions. Also, the unusually high thermal stability behavior of the polymer microcapsules' shell wall demonstrates better survivability of these microcapsules under harsh external conditions which can be exploited in their use as highly stable self-healing agent carrier in high-performance polymer materials.

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1. Introduction

Polymer microcapsules and microcapsule-based self-healing constitute the most prominent research branch in the autonomous self-healing approach in high-performance polymers. Microcapsule-based healing has been applied a number of times in different polymers, in which the microcapsules primarily work as containers to safely carry the self-healing agents inside the polymer matrix [1–5]. Generally, microcapsules are small particles with an active core surrounded by a shell material. This active core can be a variety of chemicals based on the end application, such as drugs, enzymes, dyes, water, or any type of self-healing agents. The mechanism of self-healing is dependent on the progression of micro cracks and their interaction with the healing agent containing microcapsules embedded in the polymer matrix. The microcapsules release the self-healing agents after getting ruptured by the sharp edges of the micro cracks during crack propagation in the polymer matrix. The subsequent polymerization of the healing agents triggered by interaction with either an embedded catalyst or curing agents from the polymer matrix helps to close the micro crack, thus repairing the polymer matrix internally and preventing further damage. This self-healing technique has the potential to significantly increase the life of polymer materials with minimal cost and human involvement.

Survivability under harsh external environments along with long shelf life are some of the primary and essential characteristics needed before employing a certain type of microcapsules as self-healing delivery agents in a specific polymer matrix. Generally, an elevated curing temperature (100 °C-175 °C) is used during the curing process for high-performance polymers, which has proven detrimental to the survivability of most polymer microcapsules.

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Thus, increasing the thermal stability of polymer microcapsules that can survive under high curing temperatures is the most logical way forward. Apart from high thermal stability, microcapsules must also show adhesion with the polymer matrix to facilitate the release of healing agents after composite rupture.

As high-performance polymer materials, various types of epoxy resins have been developed for a wide range of applications. These include, but are not limited to, uses as adhesives, coatings, and composite materials due to their impressive chemical-resistant properties as well as mechanical attributes such as high strength and modulus [6–9]. There have been many instances where epoxy resins have been used as a standard core material, i.e., self-healing agents in microcapsules, which can polymerize upon release [10]. The basic purpose of this work was to synthesize a special class of microcapsules that can withstand the harsh fabrication procedure of high-performance polymers. Kang et al. demonstrated in 2015 that the overall thermal stability of polymer microcapsules can be increased to as high as 180 °C by a protective PDA (polydopamine) coating [11]. We believe the thermal stability threshold can further be stretched well beyond this point. Toward this goal, we selected thermally treated graphene (TTG) as a nano-filler to be used along with epoxy resin to increase the thermal stability threshold of microcapsules. It has already been reported that core materials can have a very crucial role in shaping the thermal behavior of microcapsules [12]. Graphene is well known for its excellent thermal properties resulting from its unique sp^2 bonded honeycomb surface and has been observed to increase the thermal stability of epoxy resin-based composite materials [13,14].

We have applied an in-situ polymerization procedure to synthesize microcapsules with urea-formaldehyde (UF) polymer as a shell along with TTG attached to epoxy resin as active core materials. TTG was prepared by a thermal reduction technique with graphene oxide (GO) prepared by the Staudenmaier oxidation procedure from raw graphite. The 'as prepared' graphene-encapsulated microcapsules have shown incredible thermal stability to over 400 °C in TGA. The chemical functional groups present in the microcapsules were evaluated using FTIR spectroscopy. It was deduced, after analyzing the experimental data, that the thermal, chemical and physical properties of microcapsules are closely dependent on various process parameters. All the relevant data concerning the close relationship between the process parameters and the prepared microcapsules have been established and presented in this article along with the most probable explanations. In this work, we were able to demonstrate for the first time that thermally treated graphene can be encapsulated inside the UF microcapsules under certain conditions, and the properties of those microcapsules can be controlled according to various requirements. In one of our previously reported study, GO had been encapsulated inside the UF microcapsules, rendering them more thermally stable than other types of microcapsules [15]. This work has utilized the superior thermal stability of graphene by adding it to the core material when synthesizing UF microcapsules with much higher thermal stability. TTG was one of the key components of the prepared microcapsules, contrary to previous works in which graphene had been added to the shell after microcapsules preparation by layer by layer assembly [16,17] The unusual high thermal stability of the microcapsules makes them ideal for application in high-performance polymers.

2. Materials and methods

Raw graphite (Code No. 230U, Size - 44 μm) was supplied by Asbury Carbons. Nitric acid (HNO_3, Reagent grade, fuming >90%) and potassium chlorate ($KClO_3$, 99+%, ACS Reagent) and sulfuric acid (H_2SO_4, ACS, 95%–99%) were purchased from Sigma Aldrich for graphene oxide (GO) preparation by the Staudenmaier oxidation procedure. EPON 828 was used as the standard epoxy resin and was purchased from Alfa Aesar. Acetone was bought from Sigma Aldrich and used as the solvent for attaching of the TTG with epoxy resin. For microcapsule preparation, urea (ACS, 99.0–100.5%) and ethylene maleic anhydride (EMA) were purchased from Sigma Aldrich. Resorcinol (ACS, 99.0–100.5% crystalline), ammonium chloride (NH_4Cl, 98%+) and formaldehyde (HCHO, 37% w/w aq. Solution, stabilized with 7–8% methanol) were bought from Alfa Aesar. Sodium hydroxide (NaOH, 50% w/w aq. Solution), hydrochloric acid (HCl, ACS, 36.5–38% liquid) were bought from Alfa Aesar and were used to control the pH of the reaction.

2.1. Preparation of thermally treated graphene (TTG)

We used the Staudenmaier oxidation procedure to prepare GO from raw graphite in the presence of acid mixtures of HNO_3 (nitric acid), H_2SO_4 (sulfuric acid) (mixing ratio 1:2) and $KClO_3$ (potassium chlorate). The reaction continued under magnetic stirring for 96 h at a stirring rate of 900 rpm before being stopped. Graphite oxide was formed when the reaction mixture changed color from black to green. The graphite oxide was then ultrasonicated to obtain few-layer graphene oxide (GO). GO was washed first with 5% HCl, followed by multiple distilled water washes until the pH value approached neutrality. The heavily oxygenated GO was then thermally treated using a simple hotplate procedure to obtain thermally treated graphene (TTG) [18].

2.2. Attachment of TTG with epoxy resin

A measured amount of TTG was dispersed in acetone by an ultrasonicator for 30 min. The dispersed TTG in acetone was then added to epoxy resin (EPON 828) in a shear mixer for 15 min under 2000 rpm. Acetone was chosen because of its low boiling point and high volatility. Additionally, the presence of the >C=O group in its structure made it ideal to form a stable dispersion of TTG by stable bonding interactions with the active groups of TTG.

2.3. Emulsification process

Ethylene maleic anhydride (EMA) was chosen to be applied as an emulsifier in the encapsulation process. 2.5 wt % of EMA solution was prepared by adding it to deionized water. The solution was stirred with a mechanical stirrer for 20 h at 30 °C so that the emulsifier fully dissolved.

2.4. In-situ polymerization process

The emulsifier solution was then added to distilled water and stored in a glass beaker. Urea, resorcinol and ammonium chloride were added to the aqueous medium under stirring. For detailed analysis, different batches of samples involving different amounts of core and shell materials accompanied by a varied degree of mechanical stirring rates were prepared. In the preparation process, the shell material of the resultant microcapsules was composed of urea and formaldehyde. Experimental data described in the discussion section also revealed the presence of water molecules in the capsule shell walls. Resorcinol was used as a cross-linking agent, while ammonium chloride reacted with the formaldehyde to facilitate the shell forming process of the microcapsules [19]. The pH of the solution was maintained at 3.5 by the addition of adequate amounts of NaOH (sodium hydroxide) and HCl (hydrochloric acid). The overall synthetic process of the in-situ polymerization procedure followed the pathway reported in our earlier work involving the encapsulation of GO [15]. After 4 h of

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