



In Situ Graphene Oxide Reinforced Poly (Urea - Formaldehyde) Microencapsulation of Epoxy

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Abstract

In this study, graphene oxide (GO) reinforced epoxy loaded poly(urea-formaldehyde) microcapsules have produced by easy and cost-effective one step in-situ emulsion polymerization method without emulsifier agent. Low amounts of GO has incorporated into microcapsules without pre-treatment or ultra-speed agitation step. The effect of GO reinforcement on microcapsule size, shell structure, morphology and thermal behavior analyzed with Fourier transform infrared spectrometer (FTIR), scanning electronic microscope (SEM) and thermal gravimetric analysis (TGA), respectively. Results revealed that obtained microcapsules are resistant up to 225 °C. Besides, also, the addition of a certain amount of GO (0.5%, wt/wt) forms pretty small sized (3-4 µm) microcapsules with smooth surface, since GO nanoparticles act as a surfactant material. On the other hand, by increasing the amount of GO up to 1% (w / w), higher shell thickness was caused due to the coating of the GO layers into the shell. Produced GO-reinforced epoxy loaded microcapsules could be used in self-healing composites and also anticorrosion coatings.



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Introduction

Self-healing materials are very important due to increased service life and decreased maintenance costs. Since composites are composed of two or more different compounds, detection of damages and repair of the damages in the composites are very difficult.¹ So, especially, composites require self-healing property. Different methods are used to produce self-healing composites

such as vascular systems, microcapsules or introduction of reversible bondings to the material etc. Embedding of microencapsulated healing agents in the composites is one of the most effective and applicable method.² When damage occurs in the composite, microcapsules rupture and the healing agent releases then fills the damaged region then, solidifies by polymerization reaction.³

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In the literature, various self-healing agents have been used. Dicyclopentadiene (DCPD) have been used with Grubbs ring-opening metathesis polymerisation (ROMP) catalyst in the epoxy matrix composites.⁴ Epoxy compounds have been used with different curing agents in the matrix materials.⁵ Epoxy compounds have been used with solvents in the microcapsules to increase the healing effect by swelling of the matrix.^{6,7} Also, two microcapsules system have been used in composites; epoxy loaded microcapsules and hardener loaded microcapsules embedded in matrix.⁸ On the other hand, epoxy loaded microcapsules have been used in anticorrosion applications.⁹⁻¹¹ Urea - formaldehyde system is reactive, cost-effective and frequently used monomer system to obtain shell material in the microencapsulation process.¹² However, mechanical and thermal properties are not enough for harsh process conditions such as high temperature over 200 °C or high mixing rates.

Modification of microcapsule properties is possible by changing microencapsulation process conditions (stirring rate, emulsifier, core - shell ratio etc.) or surface modification with the addition of nanoparticles.² Fereidoon et al. have used carbon nanotubes (CNTs) and nano - alumina to improve morphology as well as thermal and water resistance of the poly(urea-formaldehyde) (PUF) shell walls of microcapsules filled with DCPD.¹³ Sarkar et al. used GO in the core epoxy and acetone solvent mixture to improve thermal properties and shelf life of epoxy-poly(urea-formaldehyde) microcapsules.^{3,14} Fan et. al. produced hexadecane loaded microcapsules with GO/ PUF hybrid shells with poly (ethylene-alt-maleic anhydride) (EMA) emulsifier agent. They reported that good emulsifying ability of GO sheets and improved thermal and barrier properties of microcapsules produced by ultrasonication.¹⁵

Although there are many studies on GO- reinforced microcapsules,¹⁶⁻¹⁹ studies on GO- reinforced epoxy - loaded PUF microcapsules without emulsification agent for self-healing applications are limited. In this study, GO nanoparticles were added to the microencapsulation process without any pre - treatment and microcapsules were produced in one step in situ-emulsion polymerization method without emulsification agent. Then, the effect of

GO on the chemical structure, morphology, and thermal behavior of the produced microcapsules were investigated.

Experimental

Materials

Urea, formaldehyde (37% aqueous solution), ammonium chloride, resorcinol and graphite powder (ultra - thin grade) were analytical grade and purchased from Sigma - Aldrich Co, US. Epoxy (EP-100) resin was purchased from Hobbyart company, Turkey. All chemicals used without any purifications.

Experimental

Graphene oxide (GO) was produced according to modified Hummer's method²⁰ of our research group.²¹ Microcapsules were synthesized by in situ emulsion polymerization method without an emulsifier.⁹ Urea (0.04 mol), ammonium chloride (0.12 g) and resorcinol (0.12 g) dissolved in 40 ml deionized (DI) water. Resorcinol as a crosslinking agent and ammonium chloride were added to improve the shell formation and strength of microcapsules.^{3,22} Then a certain amount of GO added into 10 ml DI-water. GO suspension homogenized by 5 minutes sonication with ultrasonicator. The amounts of GO were determined according to the total weight of shell monomers 0.25%, 0.5% and 1% wt/wt shell material. GO-suspension was added into microcapsule solution. pH of the solution fixed to 3.5 with 1 M HCl aqueous solution. Then 10 mL epoxy resin was added dropwise into vigorous mixing microcapsule solution. The emulsion solution stabilized for 15 minutes mixing at 800 rpm with a mechanical stirrer. 0.076 mol formaldehyde solution was added into the reaction solution. The temperature of the reaction solution was slowly increased to 60 °C with 1 °C / min rate. The reaction was conducted for 4 hours with mixing at 800 rpm. The reaction solution was cooled to ambient temperature then filtrated through vacuum filtration. The obtained microcapsules were purified with excess acetone and DI - water and dried at room temperature.

Characterization

The chemical structure, thermal properties and morphology of GO reinforced microcapsules and unreinforced microcapsules were characterized with Fourier transform infrared (FTIR) spectrometer

(Thermo scientific Nicolet i550), thermal gravimetric analysis (Perkin - Elmer STA 6000) (TGA) and, scanning electron microscopy (SEM) (Carl Zeiss / Gemini 300), respectively. TGA analysis were done between 30 °C - 800 °C with 10 °C / min rate in N₂ atmosphere.

Results and Discussion

Chemical Structure of GO - reinforced PUF - Epoxy Microcapsules

FT - IR spectrums of GO-reinforced and unreinforced PUF-epoxy microcapsules were shown in Figure 1. Characteristic peaks of poly(urea-formaldehyde) shell were seen at 3327 cm⁻¹ (N-H stretching), 1615 cm⁻¹ (C=O bending of urea) and 1547 cm⁻¹ (N-H bending of urea). Epoxy as core compound is detected at 1031 cm⁻¹ (ether stretching of epoxy), 1235 cm⁻¹ (alkyl aryl ether stretching), 1500 cm⁻¹ (C-O-C stretching of phenyl ring) and 828 cm⁻¹, 914 cm⁻¹ (C-H and C=C bending of benzene, respectively), 2964 cm⁻¹ and 2926 cm⁻¹ (CH₃ symmetric and asymmetric stretching of methyl groups, respectively).¹² GO could not characterized due to peak overlapping²¹ and its very low concentration.

Thermal Behavior of GO - reinforced PUF - Epoxy Microcapsules

Thermal analysis results were shown in Figure 2. The first degradation temperature for all samples was 225 °C, so, this result shows that produced PUF - epoxy microcapsules are resistant up to 225 °C.⁹ Moreover, GO reinforced microcapsules show

two-step degradation behavior that proves the GO existence. This two-step degradation behavior could not be seen in 0.25 GO-MC samples since amount of GO is too low to effect the thermal behavior. Moreover, 2nd step degradation begins at 350 °C that indicates degradation of the GO and epoxy in the of GO-reinforced microcapsules.⁹ 1% GO-MC has more weight loss ratio at 2nd degradation step due to higher GO concentration.²³

Morphology of GO - reinforced PUF - Epoxy Microcapsules

The reinforcing effect of GO on microcapsule were analysed in terms of size, morphology and shell thickness by using SEM analysis. Un-reinforced microcapsules (MC) were also shown in Figure 3. The surfaces of MC samples are rough and the shapes of microcapsules are straight. Yuan *et. al.* obtained similar microcapsules with two-step polymerization method by using sodium dodecyl benzene sulfonate (SDBS) as emulsifying agent.²⁴ On the other hand, two different microcapsules exist in the 0.25 GO - MC sample (Figure 4); one of them is rougher with bigger size, the other one is smooth with small size. Moreover, 0.5 GO-MC samples (Figure 5) have just one type of microcapsules which is smooth with small size. This situation shows that GO addition significantly affects the microcapsule formation process.

GO acts as a surfactant in the microcapsule production process due to its high surface energy. GO addition to the microencapsulation process

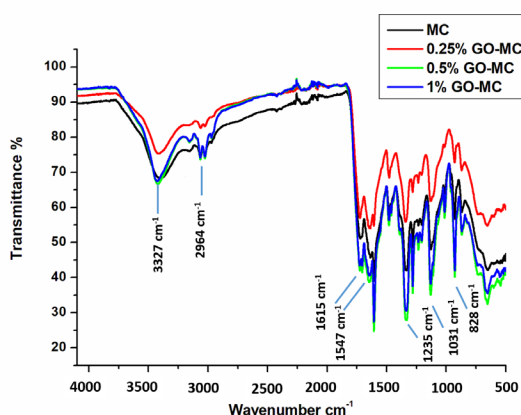


Fig. 1: FT-IR spectrums of GO-reinforced and unreinforced PUF-epoxy microcapsules

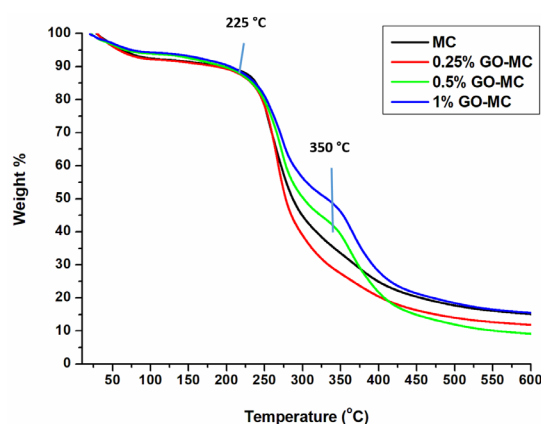


Fig. 2: TGA thermograms of GO-reinforced and unreinforced PUF-epoxy microcapsules

decreases the interfacial tension between epoxy and aqueous shell reaction solution and results in smaller epoxy droplets in the emulsion solution.¹⁵ Therefore, it alters the microcapsules' shell morphology from rough to smooth and decreases the size of

microcapsules and narrows the size distribution. While the average size of MC is approximately 140 μm , in 0.25% GO - MC and 0.5% GO - MC samples, size decreases to 3 - 3.5 μm . In the literature, the microcapsules in that size (1-5 μm) produced with

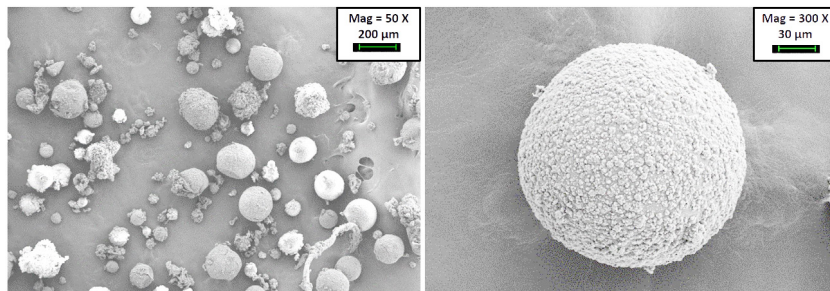


Fig. 3: SEM images of MC sample

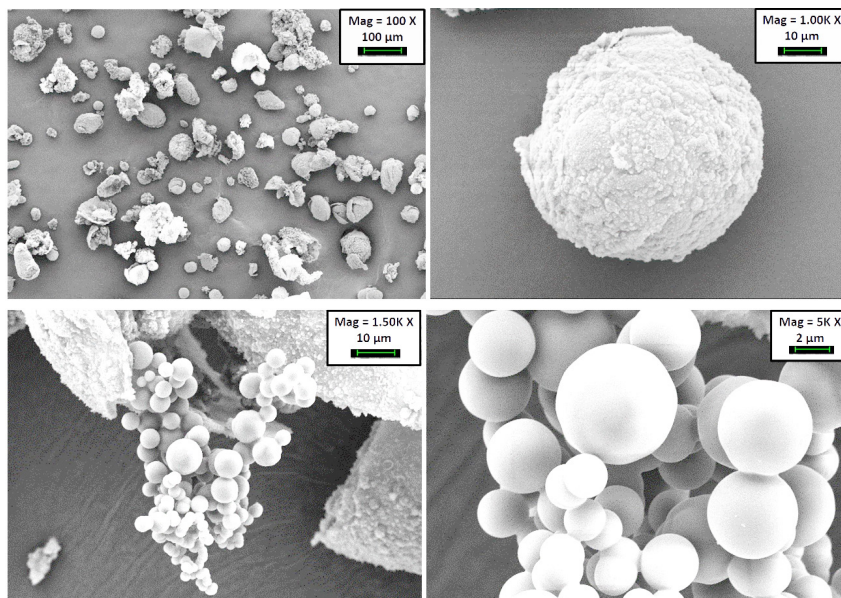


Fig. 4: SEM images of 0.025 GO-MC sample

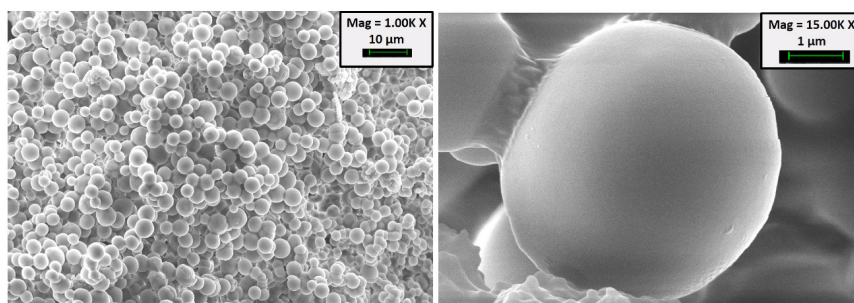


Fig. 5: SEM images of 0.05 GO-MC sample

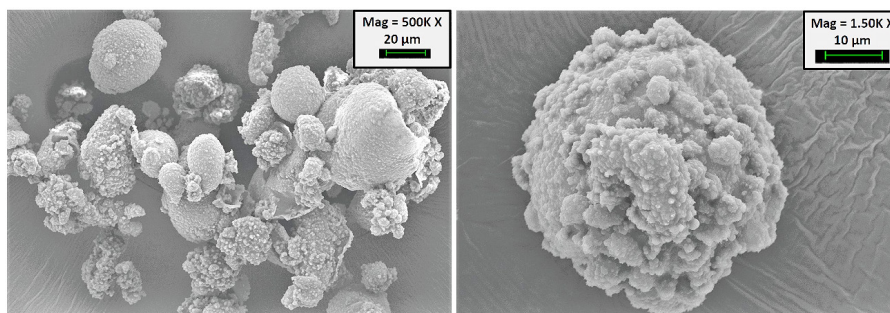


Fig. 6: SEM images of 0.05 GO-MC sample

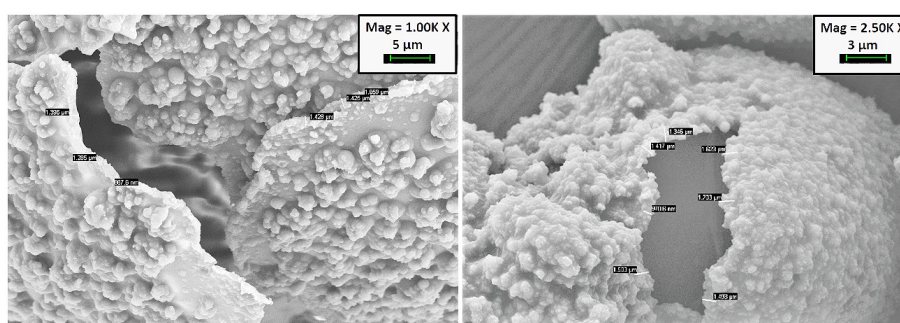


Fig. 7: Shell thicknesses of MC (1.47 µm) and 0.1% GO-MC (1.52 µm)

very high mixing rates (1500- 2000 rpm) or ultrasonic homogenization and also by the help of emulsifiers [10, 25]. Sarkar *et al.* have produced microcapsules with urea–formaldehyde (UF) and GO - epoxy resin by using EMA as an emulsifier. They investigated the microcapsule production parameters such as stirring rate, core-shell content etc.³ However, in our study, we showed that the emulsification effect of GO addition to the microencapsulation process and the small sized microcapsules can be obtained by a very low amount of GO addition without the need of high rate agitation or surfactant.

On the other hand, in the 1% GO-MC samples (Figure 6), the smooth and small microcapsules disappeared and very rough and layered microcapsules were seen. This situation shows us the surfactant effect of GO has an optimum concentration. When GO amount was increased, the morphology of microcapsules has changed and GO layers deposited onto the shell of the microcapsules. Also, the shell thickness of microcapsules increased from 1.47 to 1.52 by addition of 1% GO to the microcapsules (Figure 7). While, the shell thickness of the microcapsules indicated GO existence on the

shell structure, moreover, the size of microcapsules decreased from 140 µm (MC) to 35 µm (1% GO-MC). Fereidoon *et al.* obtained similar results showing microcapsule size reduction with CNT addition in PUF-DCPD microcapsules.¹³ While GO - reinforced microcapsules were produced via grafting GO to the shell with expensive compounds (CTAB)¹⁷ in this study, GO-reinforced PUF / epoxy microcapsules were produced via an easy (one step) and cost - effective (without emulsifier) method.

Conclusion

Graphene oxide reinforced epoxy loaded poly(urea-formaldehyde) microcapsules were produced by one step in-situ emulsion polymerization method without emulsifier agent. GO was incorporated into microcapsules without pre - treatment or ultra-speed agitation step. By using this easy and cost-effective method, application microcapsule-based self-healing property to various material can be facilitated. Analysis results revealed that obtained microcapsules are resistant up to 225 °C and also, second degradation step exists in GO reinforced microcapsules that indicates GO existence and thermal resistance of microcapsules. Addition of a

certain amount of GO (0.5 % wt/wt), results in acting of GO nanoparticles as a surfactant. Therefore, pretty small (3 - 4 μm) microcapsules were produced with low size distribution and smooth surface morphology. On the other hand, increasing amount of GO to 1% results in higher shell thickness due to GO layers

acting as a coating layer on microcapsule shell. Moreover, 1% GO addition decreased the size of the microcapsules from ~140 μm to ~34 μm . Produced GO-reinforced epoxy loaded microcapsules have potential to be used in self-healing composites and anticorrosion coatings.

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