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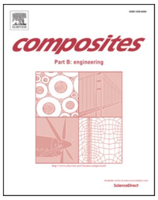

Solvent-free encapsulation of curing agents for high performing one-component epoxy adhesives

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ABSTRACT

One-component epoxy adhesives, in which the epoxy resin and curing agent are premixed, have many commercial advantages including reduced working time and stable performance. However, these adhesives suffer from a short shelf life even at room temperature. Here, core-shell structured curing agents were prepared via a dry particle coating (DPC) process that improved the storage stability of one-component epoxy adhesives. The DPC process is a simple, economic, and solvent-free method to fabricate core-shell structured materials using mechanical forces. Graphene nanoplatelets (GNPs) were used as encapsulating materials due to their high thermal conductivity and large surface areas. With the GNP-encapsulated curing agents, a one-component epoxy adhesive displayed significantly enhanced storage stability while maintaining its fast curing behavior. In particular, the pot life of the adhesive increased to 60 days, which is over two-times longer than that of a pristine epoxy adhesive. The curing temperature increased by up to 5.6 °C, which is a smaller increase than that observed when non-thermally conductive materials were used for encapsulation. Furthermore, the GNPs provided reinforcement in the cured epoxy adhesive, thereby improving the lap shear strength by 20–30%.

1. Introduction

Epoxy resins are widely used as adhesives due to their excellent adhesion to various materials, good chemical resistance, and high thermal stability [1–10]. Epoxy resin-based adhesives are composed of epoxy prepolymers and curing agents. When the curing reaction proceeds between the two components, a three-dimensional polymeric network is formed that has excellent chemical and mechanical properties [11]. Epoxy resin-based adhesives are classified into two types according to whether the epoxy resin is premixed with a curing agent or not. For commercial applications, one-component adhesives are often preferred because of their reduced working time and stable performance, as guaranteed by eliminating a mixing process. Since conventional curing agents rapidly react with epoxy resins even at room temperature, premixed epoxy resins have a relatively short shelf life [11–14]. To prevent curing at room temperature, latent curing agents have been developed that trigger the curing reaction only when an external stimulus is applied, such as heat, UV light, or humidity [1,11–14].

Encapsulation is one of the methods used to produce latent curing agents. The encapsulating layers protect the reactive functional groups of curing agents and thereby prevent reaction with epoxy prepolymers. Although the encapsulating process enhances the storage stability of one-component epoxy adhesives, it simultaneously increases the curing temperature of the adhesive [11,15–17]. For example, when polycaprolactone was used to encapsulate 2-phenylimidazole, the latent curing agent did not trigger the curing reaction with epoxy prepolymer at 20 °C for up to 30 days, but the curing temperature increased by 8–17.1 °C [11,15,16]. A dramatic increase in curing temperature prohibits efficient curing and can also thermally damage substrates. Thus, it is necessary to develop latent curing agents that exhibit improved storage stability at room temperature without losing their curing behaviors.

Typically, encapsulation processes use organic solvents, which increase the production cost and can lead to environmental pollution [18–20]. Recently, the dry particle coating (DPC) technique was

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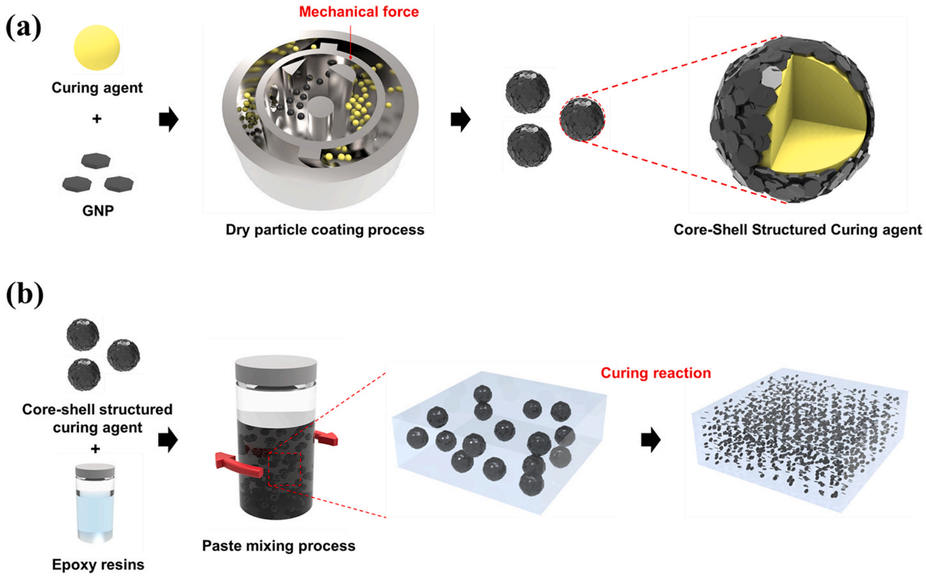

Fig. 1. Schematic illustrations of the (a) dry particle coating (DPC) process and the (b) paste mixing and curing processes.

developed to coat submicron-sized shell materials onto larger, micron-sized core particles via mechanical forces [18,19,21–27]. Through this mechanofusion technique, strong mechanical forces can fuse shell and core materials to provide a coating layer [18]. Since this dry process does not require any solvents or binders, it is a simple, economic, and ecofriendly way to fabricate core-shell materials. Additionally, the chemical properties of the core materials are maintained because coating layers are formed without any chemical reaction.

Herein, we report the fabrication of core-shell structured latent curing agents using the DPC process with amine-based curing agents as core materials and graphene nanoplatelets (GNPs) as shell materials. There are two advantages when the curing agent is encapsulated with GNPs, which are two-dimensional, high-aspect-ratio carbon materials. First, the high thermal conductivity of GNPs enables efficient heat transfer to the curing agent so that the curing rate of the epoxy adhesive does not change significantly compared with other encapsulating materials. Second, GNPs can facilitate the encapsulation of core materials by increasing the frequency of collisions during the DPC process. This is due to the large surface areas of GNPs. A one-component epoxy adhesive was prepared with the core-shell structured latent curing agents and commercial epoxy resins. We found that this adhesive had significantly enhanced storage stability while maintaining its fast curing behavior. Furthermore, the lap shear strength of the epoxy adhesive was significantly increased due to the GNPs acting as reinforcement. The dispersion of GNPs in the epoxy adhesive was analyzed using transmission optical microscopy. Our dry coating strategy provides a simple, environmentally friendly, and cost-effective method to improve the overall properties of one-component epoxy adhesives.

2. Experimental section

2.1. Materials

Bisphenol A diglycidyl ether epoxy resin (EP; YD-128 grade) was obtained from Kukdo Chemical. It has a viscosity of 13,000 cPs at 25 °C. An amine/epoxy adduct (AJICURE PN-23; Ajinomoto Fine-Techno) was used as the curing agent for the EP. The latent curing agents had an average particle size of 10–12 µm. Graphene nanoplatelets (C500 grade) were purchased from XG Sciences and had an average surface area of 500 m^2/g. The GNPs had an average particle diameter of less than 2 µm.

Table 1
Compositions of the core-shell structured curing agents.

Sample	Curing agent	GNP	GNP coated curing agent
Pristine curing agent	1 g	–	–
DPCG-0.055	1 g	0.055 g	1.055 g
DPCG-0.111	1 g	0.111 g	1.111 g
DPCG-0.224	1 g	0.224 g	1.224 g
DPCG-0.340	1 g	0.340 g	1.340 g

2.2. Modification of GNPs by the tip-sonication process

The size of the GNPs was reduced using a tip-sonication process to ensure efficient coating on micron-sized curing agents. Graphene nanoplatelets (5 g) were dispersed in 100 mL of deionized (DI) water in an ultrasonic bath (Powersonic 410; Hwashin Technology) for 30 min. Subsequently, the well-dispersed GNP solution was treated with a tip sonicator (VCX-750; Sonics & Materials), operating at 80% amplitude for 1 h, while cooled in an ice bath to prevent overheating of the sonication probe. After the treatment, the GNP solution was frozen in liquid nitrogen and freeze-dried for 72 h. The average lateral size of the treated GNPs was 500 nm.

2.3. Preparation of the core-shell structured curing agent

The core-shell structured curing agent was prepared via the Mechanofusion® AMS system (Hosokawa Micron), which simultaneously applied mechanical forces (compressive, shear, and frictional forces) to the core and shell particles. A photograph of the equipment is provided in the Supplementary Information (Fig. S1). The equipment consisted of a circular rotating chamber, a fixed scraper, and a fixed rounded press-head. The distance between the inner wall of the rotating chamber and the head was 1 mm. Fig. 1a illustrates the DPC process used to prepare the core-shell structured curing agent. First, curing agents and GNPs were placed in the chamber at GNP:curing agent weight ratios of 0.055, 0.111, 0.224, or 0.340. The DPC process was performed for 2 h at 5000 rpm. During this process, DI water (25 °C) was circulated through a cooling jacket to maintain a constant operating temperature. Hereafter, the curing agents coated with GNPs using the DPC process are referred to as DPCG-X (where X refers to the amount of GNPs); each composition is detailed in Table 1. For comparison purposes, fumed silica (Sigma–Aldrich; average particle size: 7 nm) and GNPs with larger

Table 2
Compositions of the one-component epoxy adhesives.

Sample	EP	Curing agent (10 phr)	GNP	GNP coated curing agent	Weight ratio
EP-P (Epoxy + pristine curing agent)	10 g	1 g	–	–	–
EP-DPCG-0.055	10 g	1 g	0.055 g	1.055 g	GNP 0.5 wt%
EP-DPCG-0.111	10 g	1 g	0.111 g	1.111 g	GNP 1.0 wt%
EP-DPCG-0.224	10 g	1 g	0.224 g	1.224 g	GNP 2.0 wt%
EP-DPCG-0.340	10 g	1 g	0.340 g	1.340 g	GNP 3.0 wt%

lateral size (M5; XG Sciences; average laterial size: 5 μm as-received but 2 μm after the modification described in Section 2.2) were used as shell materials. DPCM5-X and DPCS-X refer to the curing agent coated with M5 and fumed silica, respectively (X indicates the amount of the shell materials).

2.4. *Fabrication of the epoxy/core-shell structured curing agents*

After the DPC process, a paste-mixing process was used to disperse the core-shell structured curing agents into the EP (Fig. 1b). The resin was mixed with 10 phr (parts per hundred resin by weight) of the curing agents using a high-speed paste mixer (ARE-310; Thinky) at room temperature for 10 min at 2000 rpm, and for 5 min at 2200 rpm. Subsequently, the samples were degassed in a vacuum oven for 2 h. The one-component epoxy adhesives containing DPCG-X are referred to herein as EP-DPCG-X; their compositions are summarized in Table 2. Additionally, EP-G samples were prepared by mixing various ratios of EP with curing agents and GNPs to investigate the effect of the DPC process on the thermal and mechanical properties of the epoxy adhesives.

2.5. *Analysis*

The surface morphology of the core-shell structured curing agent was characterized by scanning electron microscopy (SEM; Sigma 300; Zeiss). The average viscosity value of epoxy adhesive was obtained using a viscometer (HBDV-II+; Brookfield) from five measurements. The standard deviation of each measurement ranged up to 7% (Fig. S2). The pot life was defined as the amount of time required for an initial viscosity of the epoxy adhesive to double [28–30]. All of the samples were maintained in a convection oven at 40 °C and viscosity tests were conducted every 24 h at 23 °C until the viscosity doubled. The curing behaviors of the one-component epoxy adhesives were investigated using differential scanning calorimetry (DSC; DSC7; PerkinElmer) under a nitrogen atmosphere. A specimen (10 mg) was placed in an aluminum DSC pan. Dynamic DSC analysis was performed from 30 °C to 300 °C at cooling and heating rates of 10 °C min^{-1}. Isothermal DSC analysis was carried out at 130 °C. The contact angles of epoxy resin were measured by a contact angle measuring equipment (GSS, SurfaceTech Co, Ltd, Korea) and the values were averaged out from at least two specimens. Lap shear tests were performed using a universal testing machine (model 5567; Instron) at 1.3 mm (0.05 in)/min according to the standard ASTM D1002. An aluminum plate was used as the substrate, onto which was applied a 0.2-mm-thick coating of epoxy adhesive over a $25.4 \times 10\ \text{mm}^2$ area. Samples were cured at 120 °C for 2 h. Lap shear strength is reported as the average value of five specimens for each composition; error bars in the figures represent one standard deviation. The morphology and dispersion of the GNPs in the compositions were observed using an optical microscope (OM; Optiphot 2 POL; Nikon). All OM images were obtained using transmitted light with a 200–400 × lens and a hot-stage (FP82HT; Mettler). Measurements were taken in situ from 30 °C to 150 °C at a heating rate of 10 °C min^{-1}. The GNP dispersion state was determined by analyzing the gray-scale intensity histograms of the OM images.

3. Results and discussion

3.1. *Encapsulation of curing agents*

The amine/epoxy curing agents were encapsulated with GNPs via a DPC process using the Mechanofusion® AMS system. The curing agents and GNPs passed between the arm head and chamber wall, which applied strong shear and compressive forces to the core and shell materials. SEM images of the pristine curing agent and GNP-coated curing agents with different GNP contents are shown in Fig. 2. The pristine curing agent had an angular shape (sharp-edged irregular shape) with a diameter of 10–12 μm. For the core-shell structured curing agents, several layers of GNPs were embedded on the surface of the curing agents but the original shape of the pristine agent was retained. Coverage of the GNP coating layer increased with increasing weight

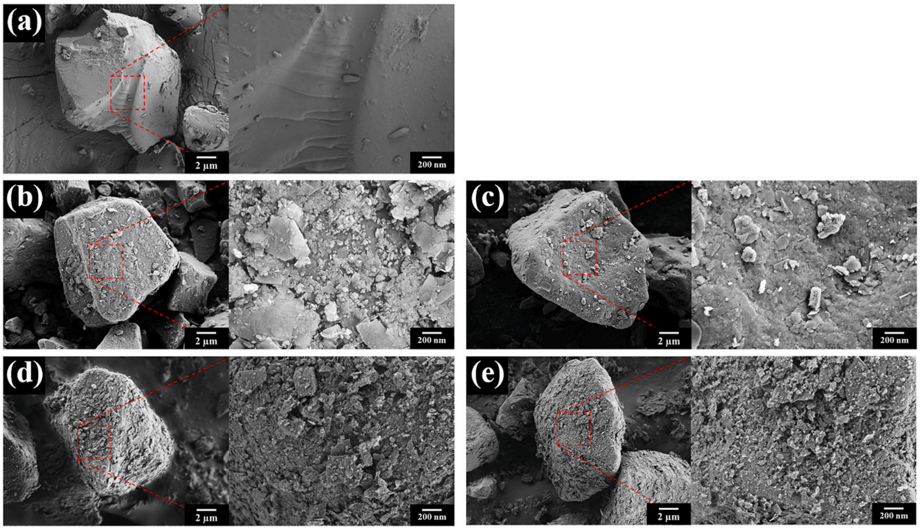

Fig. 2. SEM images of (a) a pristine curing agent particle and (b–e) core-shell structured curing agent particles: (b) DPCG-0.055, (c) DPCG-0.111, (d) DPCG-0.224, and (e) DPCG-0.340.

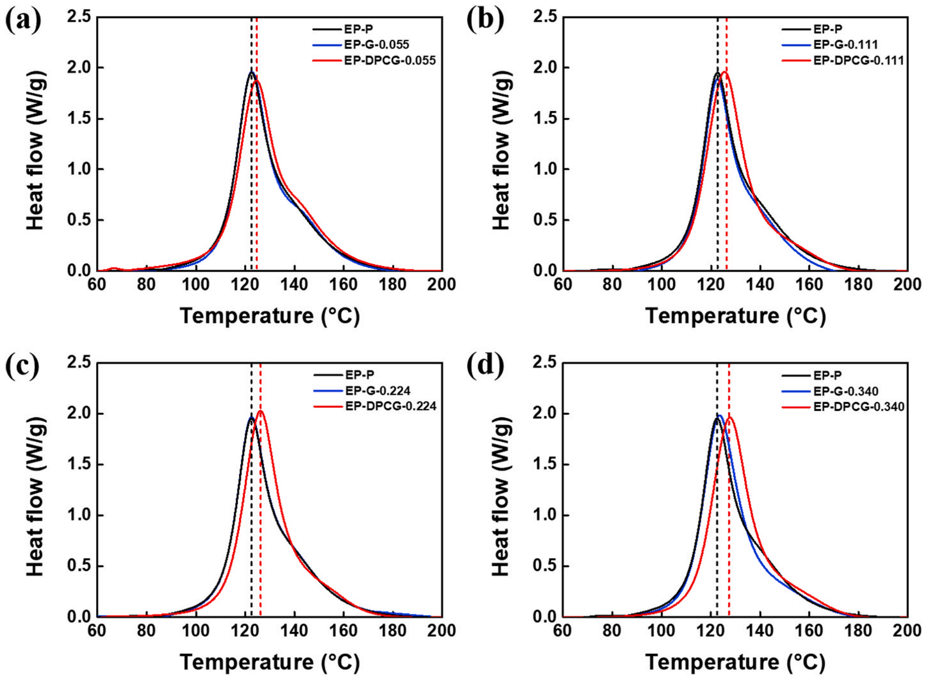

Fig. 3. Dynamic DSC curing behaviors of EP-P, EP-G, and EP-DPCG for different GNP contents: (a) 0.5, (b) 1.0, (c) 2.0, and (d) 3.0 wt%. The dotted lines indicate the curing temperatures.

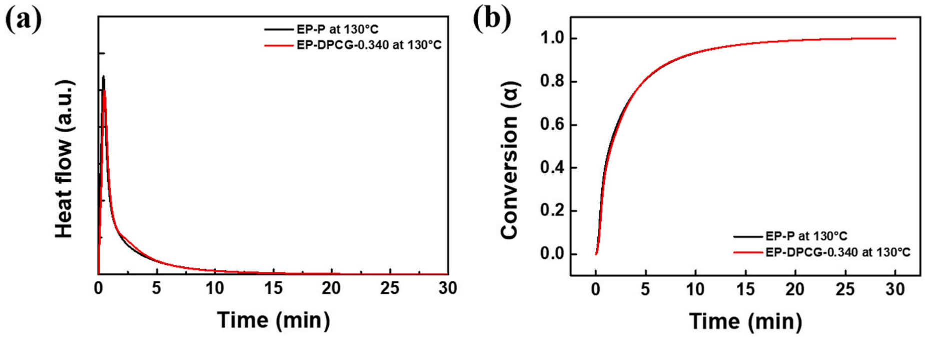

Fig. 4. Curing behaviors of EP-P and EP-DPCG-0.340 (GNP 3.0 wt%). (a) Isothermal DSC curves and (b) conversion (α) as a function of time at 130 °C.

ratio of GNPs. Specifically, DPCG-0.055 and DPCG-0.111 exhibited uncovered areas even after the DPC process, whereas DPCG-0.224 and DPCG-0.340 displayed dense GNP coating layers across the entire surface of the curing agents.

3.2. *Curing behaviors of epoxy/core-shell structured curing agents*

DSC was used to characterize the curing behavior of the epoxy adhesives. Fig. 3 presents the exothermic heat-flow diagrams for the curing reaction. All of the EP-DPCG samples showed slightly higher curing temperatures than the EP-P (122.5 °C). The curing temperature increased with increasing GNP content: 124.7 °C for EP-DPCG-0.055

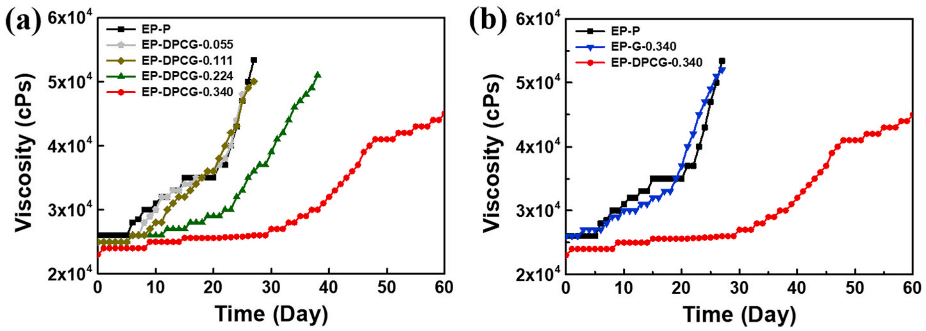

Fig. 5. Change in viscosity of the one-component epoxy adhesives prepared from (a) the pristine curing agent (EP-P) and core-shell structured curing agents (EP-DPCG) for different amounts of GNPs, and (b) EP-P, EP-G-0.340, and EP-DPCG-0.340.

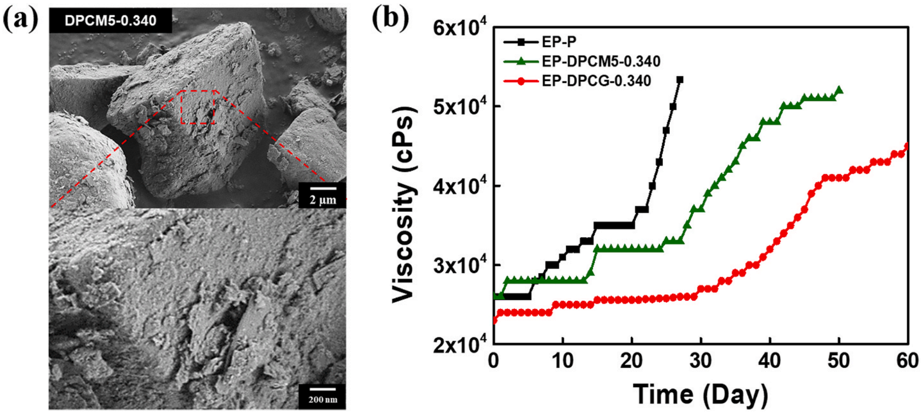

Fig. 6. (a) Surface morphology of core-shell structured curing agents coated with M5 GNPs (DPCM5-0.340) and (b) comparative pot lives of one-component epoxy adhesives made with M5 or C500 graphene nanoplatelets.

(GNP 0.5 wt%), 125.5 °C for EP-DPCG-0.111 (GNP 1.0 wt%), 126.2 °C for EP-DPCG-0.224 (GNP 2.0 wt%), and 128.1 °C for EP-DPCG-0.340 (GNP 3.0 wt%). The change in curing temperature of the EP-DPCG samples (2.2–5.6 °C) was remarkably lower than those reported in other studies (8–17.1 °C) using polymeric materials as shell materials [11,15,16].

To ensure that the GNPs did not affect the curing behavior of the amine/epoxy adducts, we prepared samples composed of epoxy, curing agent, and GNPs without using the DPC process (EP-G). All samples had similar curing patterns and peak temperatures as the EP-P system, which indicated that the curing mechanism was unaffected by the GNPs.

Fig. 4a shows isothermal heat-flow diagrams of the EP-P and EP-DPCG-0.340 samples at 130 °C, which was close to the curing temperature. Both materials had similar patterns with a peak time of 0.4 min. The curing reaction conversion (α), calculated by dividing the cumulative heat at a specific time by the total exothermic heat of cure, was plotted as a function of time (Fig. 4b). The conversion diagram of EP-DPCG-0.340 was practically the same as that of EP-P, with complete curing conversion seen at 29 min. This confirmed that the curing mechanism at 130 °C was unaffected by the GNP coating layers.

3.3. *Storage stability of the epoxy/core-shell structured curing agent*

Fig. 5a shows the storage stabilities of the prepared epoxy adhesives at 40 °C with different amounts of GNP shell material. In this study, the pot life is defined as the amount of time required for the initial viscosity to double. The pot life of EP-P was 27 days, which was the same as that of EP-DPCG-0.055 (GNP 0.5 wt%) and EP-DPCG-0.111 (GNP 1.0 wt%). SEM images of those samples (Fig. 2) revealed incomplete coating by the GNPs on the curing agent, which did not improve the storage stability. However, increasing the amount of GNPs increased the surface coverage of the curing agent and significantly improved the pot life of the epoxy adhesive. The pot lives of EP-DPCG-0.224 (GNP 2.0 wt%) and EP-DPCG-0.340 (GNP 3.0 wt%) were 39 and 60 days, respectively, which were 40% and 120% higher than that of EP-P. We anticipate the enhanced storage stability after GNP encapsulation is originated from two reasons. First, the GNP shell layers physically protect the reactive functional groups of curing agents and thereby prevent the curing reaction with epoxy prepolymers. Second, GNP encapsulation can alter the surface characteristics of the curing agent toward less compatible with epoxy resin. To confirm the effect of GNPs, we measured the contact angle of epoxy resin on the GNPs and the pristine curing agents. As shown in Fig. S3, the contact angle of epoxy resin on the GNPs (28.5 ± 7.1°) was larger than that on the pristine curing agents (16.7 ± 3.7°), implying the GNP coated curing agents have reduced wetting capability with epoxy resin compared to the pristine curing agent.

Additionally, we confirmed that GNPs did not affect the storage stability of epoxy adhesives that were not prepared with the DPC process. When the GNPs were simply mixed with pristine curing agents and epoxy resin in the EP-G-0.340 composition, the same pot life as for EP-P was observed (Fig. 5b). On the contrary, the pot life of EP-DPCG-0.340 was significantly extended, which indicated that encapsulating the curing agents using the DPC process enhanced the pot life.

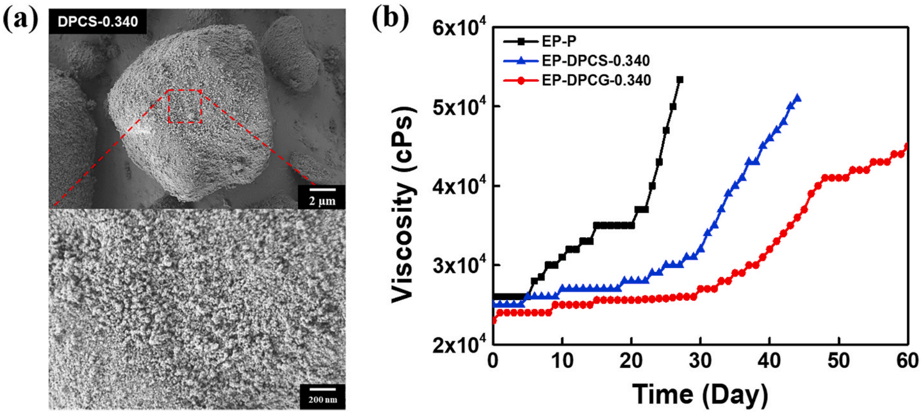

Fig. 7. (a) Surface morphology of core-shell structured curing agents made with fumed silica (DPCS-0.340) and (b) comparative pot lives of one-component epoxy adhesives made with fumed silica or C500 graphene nanoplatelets.

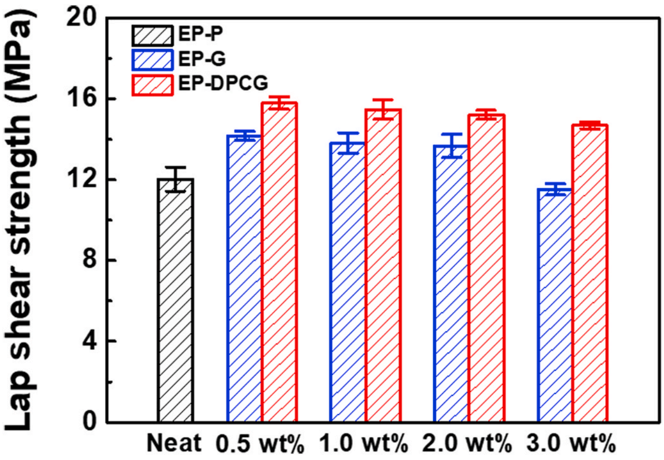

Fig. 8. Lap shear strengths of one-component epoxy adhesive joints prepared by simple mixing (EP-G) and using the DPC process (EP-DPCG) as a function of GNP content.

3.4. *Effect of the size and shape of shell materials on storage stability*

To investigate the size and shape effect of shell material on the storage stability of the epoxy adhesive, we prepared the core-shell curing agent with different shell materials at a fixed weight ratio (1:0.340). First, the encapsulation was carried out using GNPs having four-times larger lateral size (M5; 2 μm) than the other GNPs used in this study (C500; 500 nm). Fig. 6a shows the surface morphology of the core-shell structured curing agent made with M5. Unlike DPCG-0.340, dense coating layers of GNPs were not formed and GNP aggregates were observed for DPCM5-0.340. This is because the size difference between the core and shell material was insufficient to realize an efficient dry coating process. Although the pot life of EP-DPCM5-0.340 was doubled to 50 days compared with EP-P, it was not longer than that of EP-DPCG-0.340, since the coating layer was not dense and incompletely formed.

We also prepared the core-shell structured curing agent with fumed silica nanoparticles having an average diameter of 7 nm. Fig. 7a shows a SEM image of DPCS-0.340. Although the fumed silica nanoparticles densely encapsulated the outer surface of the curing agent, the storage stability of EP-DPCS-0.340 was 44 days, which was less than that of EP-DPCG-0.340 (Fig. 7b). Unlike GNPs, fumed silica nanoparticles could not adhere strongly to the surface of the curing agent during the DPC process due to their shape and small contact areas. During the paste-mixing process of particularly high viscosity compositions, some of the fumed silica separated from the curing agent, which reduced the pot life. These data indicate that identifying the optimal shape and size of the shell materials is important to ensure good encapsulation of the core materials and thereby improve storage stability.

3.5. *Effect of GNPs on the lap shear strength of one-component epoxy adhesive-bonded joints*

Previous studies reported that lap shear strength improved when nanofillers were added to epoxy resins [9,31–44]. To identify the effect of GNPs as nanofillers and their dependence on the processing method, we investigated the lap shear strength of EP-G and EP-DPCG as a function of GNP content (0.5, 1.0, 2.0, and 3.0 wt%) (Fig. 8). Both samples had improved lap shear strength compared with EP-P. At 0.5 wt%, the lap shear strength increased by 17% for EP-G and 31% for EP-DPCG. With higher GNP content, the lap shear strength of both EP-G and EP-DPCG gradually decreased. Interestingly, the EP-DPCG samples exhibited higher lap shear strengths than the EP-G samples regardless of the GNP content: 15.8 vs. 12.0 MPa for 0.5 wt%, 15.5 vs. 14.2 MPa for 1.0 wt%, 15.2 vs. 13.8 MPa for 2.0 wt%, and 14.7 vs. 11.5 MPa for 3.0 wt %. We assume that the DPC process promoted dispersion of the GNPs in the epoxy adhesives, thereby improving the lap shear strength [21,45].

The dispersion state of the GNPs in the epoxy adhesives was examined by transmission optical microscopy. First, we analyzed the morphology of the curing agent in the epoxy adhesives before and after curing. The curing agents initially appeared as solid transparent particles in the EP (Fig. S4a), but they completely dissolved once the temperature exceeded the melting point of the curing agents (Fig. S4b). After the GNPs had been incorporated by the DPC process (EP-DPCG) or

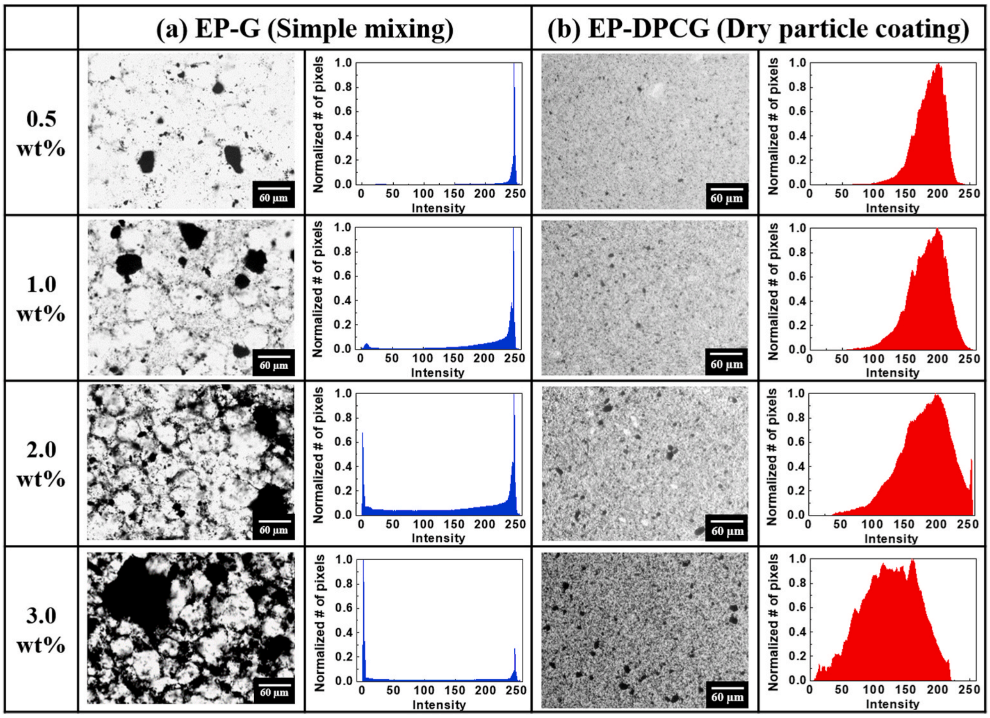

Fig. 9. Optical microscopy images and gray-scale intensity histograms after curing of (a) EP-G and (b) EP-DPCG adhesives as a function of GNP contents.

the simple mixing process (EP-G), both samples showed dispersed GNPs (Fig. S5). For the EP-DPCG samples, most GNPs were located on the surface of the curing agents, while they were poorly dispersed in the EP-G samples.

Fig. 9 shows the micron-scale dispersion of the EP-G and EP-DPCG samples, for different GNP contents, after the curing agents had completely melted. Based on the optical images, the GNPs were more uniformly dispersed in the EP-DPCG samples but large agglomerates (diameter: > 20 μm) were observed in the EP-G samples. This is because the GNPs spread across the outer surface of the curing agents as they dissolved in the EP. The numerical dispersion of the GNPs was obtained from the OM images by calculating the distribution of the gray-scale intensity at each pixel. Gray-scale values range from 0 (black) to 255 (white). In transmitted light, the gray color appeared when the GNPs were well-dispersed, whereas a strong dark color with intensity ranging from 0 to 50 was observed when they were poorly dispersed and stacked. For the EP-G samples containing more than 1.0 wt% GNPs, distinct peaks were observed for the very dark-colored regions, indicating GNP agglomeration. Notably, in the OM image of EP-G-0.340 (GNP 3.0 wt%), which had the lowest lap shear strength, most pixels had intensities ranging from 0 to 50, which implied severe aggregation of the GNPs. In contrast, for all of the EP-DPCG samples, there was no distinct peak in intensity in the range of 0–50, since most of the GNPs were uniformly dispersed. The distribution curve moved toward lower intensity values with increasing GNP content. Thus, the DPC process improved the dispersion quality of GNPs in epoxy resins, thereby improving the lap shear strength of epoxy adhesives.

4. Conclusions

We developed a simple dry coating process to provide core-shell structured curing agents that enhanced the storage stability of one-component epoxy adhesives. Encapsulation of the core materials was much better with smaller GNPs than with larger GNPs or silica nanoparticles. With the GNP-coated curing agents, the pot life of our epoxy adhesives increased by up to 120%, while the curing temperature slightly increased by up to 5.6 °C compared with the pristine epoxy adhesive. Additionally, the lap shear strength of our adhesives increased by up to 20% because the GNPs provided reinforcement and the DPC process assisted the dispersion of the GNPs in the cured EP. We expect this simple and solvent-free coating approach to provide a route to a variety of core-shell structured materials for industrial applications.

Notes

The authors declare no competing financial interest.

Author statement

Sung Min Jee: Conceptualization, Investigation, Validation, Writing – Original Draft; **Cheol-Hee Ahn**: Supervision, Project Administration; **Jong Hyuk Park**: Conceptualization, Supervision, Project administration, Funding acquisition; **Tae Ann Kim**: Writing – Review & Editing, Supervision, Project administration; **Min Park**: Conceptualization, Supervision, Project administration, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.compositesb.2020.108438.

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