

# ENHANCING MECHANICAL PROPERTIES OF GRAPHENE / EPOXY NANOCOMPOSITES USING FEW-LAYER GRAPHENE PRODUCED BY LIQUID PHASE EXFOLIATION

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## Abstract

In this study, few-layer graphenes (FLGs) were produced by new liquid phase exfoliation (LPE), exfoliation of graphite with weak acid salts. A high concentration dispersion of FLGs in low-boiling point solvents is successfully carried out, achieved by binding molecules with a dispersing function. And then graphene/epoxy nanocomposites were fabricated and tensile properties were evaluated in order to understand the effect of FLGs introduced into the resin. Graphene/epoxy nanocomposite showed improved mechanical properties. Tensile strength and fracture strain were increased by 11.5% and 55.6% compared with as-received one's. Especially, the improvement of fracture strain was outstanding, which indicated that adding FLGs had a positive impact on suppressing effect on crack propagation and improving fracture toughness of matrix resin. These beneficial results were derived from crack trapping by uniformly dispersed FLGs.

## 1. Introduction

These days, Graphene has attracted because of its extraordinary properties. It has demonstrated that monolayer graphene has many attractive properties such as high young's modulus (~1 TPa), strength (130 GPa) and specific surface area (~2,630m<sup>2</sup>g<sup>-1</sup>) [1]. These remarkable properties make graphene suitable for many applications [2] and one of the options is using as the reinforcement of polymers.

Epoxy is the most commonly used thermosetting polymer because it's easy to processing and high strength to weight ratio but its tolerance to damage is not enough. As a solution, enhancing the mechanical properties of epoxy by incorporating few-layer graphenes (FLGs) has been studied intensively in recent years [3]. FLG was considered to be excellent candidate for use as the reinforcement in advanced composite materials to substitute conventional particle reinforcements such as elastomers and carbon nanotubes(CNTs) because of their outstanding properties derived from their 2D honeycomb structures. For example, Rafiee et al. demonstrated that the superiority of graphene nanocomposites to CNTs nanocomposites, as a result of improving strength by 41% and 13% adding 0.1 wt% SWCNT and reduced graphene oxide (RGO) to epoxy [4].

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Graphene oxide (GO) has been widely studied so far because it's easy to produce large-sized flakes. However, GO has some disadvantages derived from oxidation processes used for manufacturing GO. Oxidation processes decrease its mechanical properties and increase its manufacturing cost [5], limiting its versatility as a reinforcing material and possibility for practical applications. Therefore, it is highly desired to produce FLG by other methods than oxidation. As one of the solutions, liquid phase exfoliation (LPE) has received a lot of focus. LPE is exfoliation of graphite in an appropriate liquid, and in most studies, graphene has been produced by LPE of graphite via sonication. However, a weak point of the sonication is its limited scalability [6] and an additional drawback of the sonication is the quality of graphene produced by LPE via sonication is not sufficient, because the sonication damages the crystal purity of the FLGs. At the same time, it's difficult to disperse FLGs in low-boiling point solvents such as acetone and ethanol because of their low surface tension, which makes it challenging to create epoxy based nanocomposites. However, recently, A high concentration dispersion of FLGs in low-boiling point solvents is successfully carried out, that has been considered impossible until now. It was achieved by binding molecules having a dispersing function [7,8]. The proposed solvent mixing method made it easy to make highly dispersed graphene nanocomposites, but the obtainable mechanical properties of nanocomposites produced by the method hasn't been sufficiently studied.

In this study, FLGs was produced using LPE by high power ultra-sonication with functionalization using sodium glutamate. This technique made it possible to produce high-dispersed FLGs into acetone, it made easy to fabricate nanocomposites. FLGs were separated into small-size-FLGs and large-size-FLG under controlled centrifugation conditions. [9] FLGs/epoxy nanocomposites were fabricated to evaluate the influence of size and quality of graphene on strengthening effect and the effectiveness of the FLGs fabricated by the new LPE.

## 2. Materials and testing method

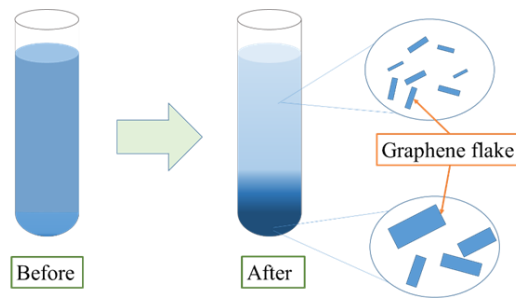
### 2.1 Materials

#### 2.1.1. Fabrication of FLGs

Flaked graphite (Wako Pure Chemical) with an average particle length of 15  $\mu\text{m}$  was used. This graphite was premixed with sodium glutamate, added to 200 ml of acetone, and treated with high power ultra-sonication (UH-600S, SMT) for 30 minutes. And then, the dispersion was centrifuged (Model 2420, Kubota) to control the size of graphene. Those treated at 1500 rpm 45 min were small size FLGs (average particle size 50 nm, thickness about 2 nm) and processed at 500 rpm 30 min were large size (average particle diameter 200 nm, thickness 4 nm) FLGs. In this treatment, a dispersion having a concentration of about 1 to 4 g / L could be prepared. D / G ratio was about 0.2 to 0.3, and high-quality FLGs with high crystallinity could be produced. Table 1 shows the properties of each size of FLGs. Figure 1 shows the schematic of the size-sorting process.

**Table 1.** Centrifugation conditions and properties of graphene.

	Small size graphene	Large size graphene
D / G ratio	0.2~0.3	
Centrifugation condition	1500 rpm/45 min	500 rpm/30 min
Particle size nm	50	200
Thickness nm	2	4
Aspect ratio	25	50



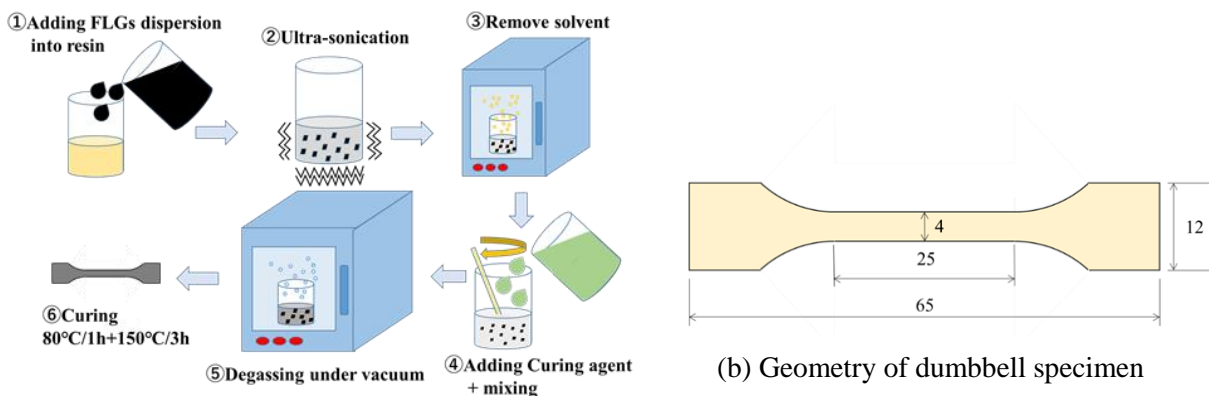
**Figure 1.** Schematic of size-sorting process by centrifugation.

### 2.1.2 Fabrication of graphene/FLGs nanocomposites

The fabrication procedure used to disperse FLGs in a bisphenol A-based thermosetting epoxy is shown schematically in Figure 2[4]. At first, FLGs dispersion was ultra-sonicated for 30 min and then added to epoxy resin (diglycidyl ether of bisphenol A, iER<sup>®</sup> 828, Mitsubishi Chemical) such that the FLG/epoxy mass ratio was 0.1 wt% and 0.2 wt%. The mixture was ultra-sonicated for 1 hour and then heated at 70°C for 12 hours in dynamic vacuum condition to remove acetone. Next, curing agent (jER<sup>®</sup> cure 113, Mitsubishi Chemical) was mixed into the FLGs-resin in a ratio of 100:32 in weight. The mixture was degassed for 2h in dynamic vacuum condition. Then curing was done at 80°C for 1 hour and 150°C for 3 hours. Two kinds of size – sorted specimens were prepared and each sample were labeled as FLG\_S and FLG\_L.

### 2.2. Characterization of FLGs/epoxy nanocomposites

Tensile properties of FLGs/epoxy nanocomposites were measured by using a universal testing machine (AG-I-10kN, SHIMAZU) with crosshead speed of 1.0 mm / min at a room temperature. Figure 2 shows the geometry of dumbbell specimen used in the tensile test. Checking for reproducibility of the results, at least, 3 or 4 samples of each weight fraction of FLGs (AR, 0.1wt%, 0.2 wt%) were fabricated and tested.



(a) Mixing process of FLGs/epoxy nanocomposites [4]

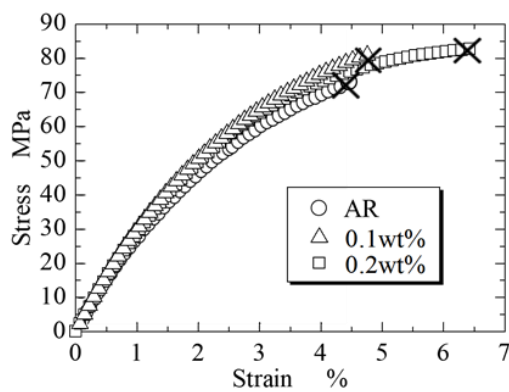
**Figure 2.** Schematics of fabrication of FLGs/epoxy nanocomposites.

### 3. Results and discussions

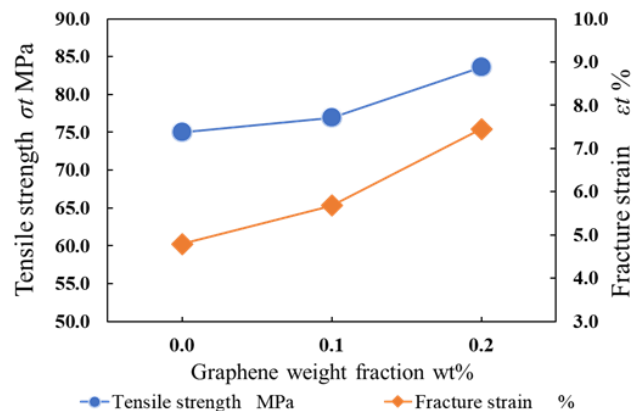
On the purpose of understanding the effect of FLG introduced into the resin depending on the weight fraction of FLG\_L, three kinds of samples, as-received (AR), 0.1 wt%, 0.2 wt%, were fabricated and tested. They were characterized by uniaxial tensile testing to evaluate the mechanical properties. The results of uniaxial tensile testing of AR and FLGs/nanocomposites are shown in Table 2 and Figure 3. Figure 3a shows a stress–strain diagram and Figure 3b shows the mechanical properties of FLG\_L/nanocomposites compared among each weight fraction of FLG\_L. According to Figure 3a and b, the mechanical properties were improved as the weight fraction of graphene increases. The point of these results are improvements of strength and toughness without significant deterioration of stiffness. It means that energy required for destruction was increased. It indicated that fracture toughness of the matrix resin and interactions between FLGs and resin was functioning effectively, which is caused by the sodium glutamate-derived functional group. According to these results, adding FLGs into resin may have a positive impact on suppressing effects on crack propagation.

**Table 2.** Mechanical properties of FLGs/epoxy nanocomposites (FLG\_L)

	AR	0.1 wt%	0.2 wt%
Weight fraction wt%	0.0	0.1	0.2
Tensile strength $\sigma$ MPa	75	77.0	83.6
Fracture Strain $\epsilon t$ %	4.79	5.68	7.46
Young's modulus $E$ GPa	3.1	3.23	3.28



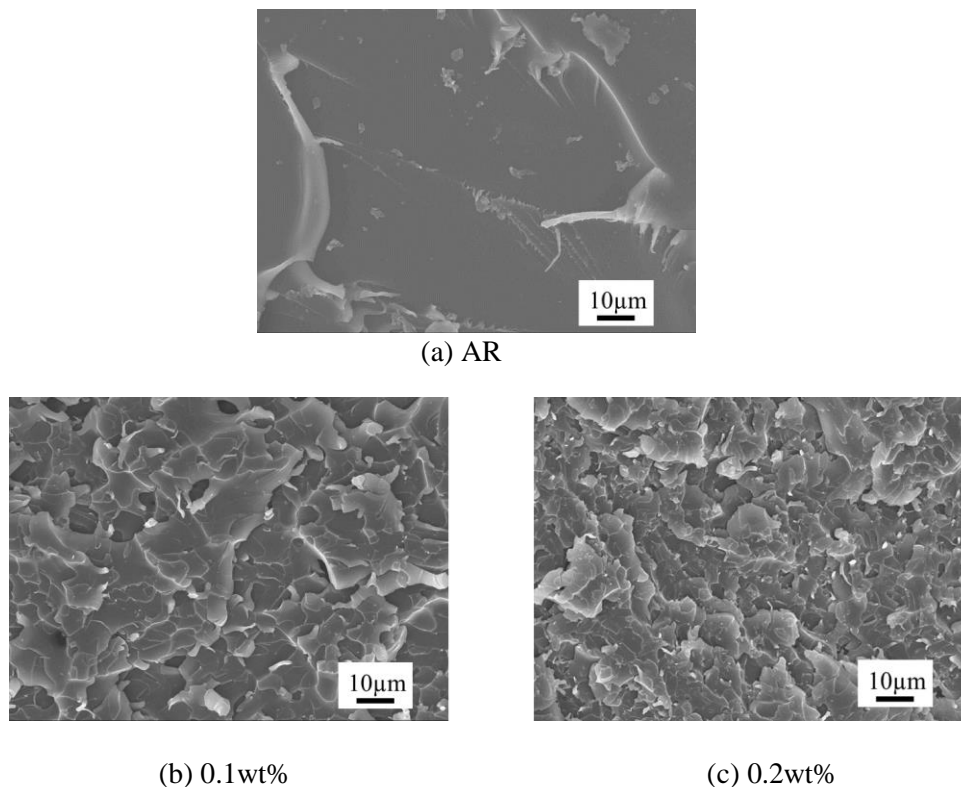
(a) Stress-Strain curve.



(b) Mechanical properties related to weight fraction of FLG\_L

**Figure 3.** Mechanical properties of graphene/epoxy nanocomposites.

Figure 4 shows the result of the observation of fractured surface of specimens after tensile testing. Increasing the weight fraction of FLGs, the fractured surface morphologies of specimens being rougher and uneven shapes being increased. It may be because that the crack propagation could be efficiently barricaded by crack trapping, bridging, bifurcation of cracks and splitting cracks into multiple subcracks, derived from uniformly dispersed FLGs. Since no large aggregations of FLGs were observed, it was indicated that FLGs were highly dispersed even in resins and effectively improved the mechanical properties of nanocomposites.

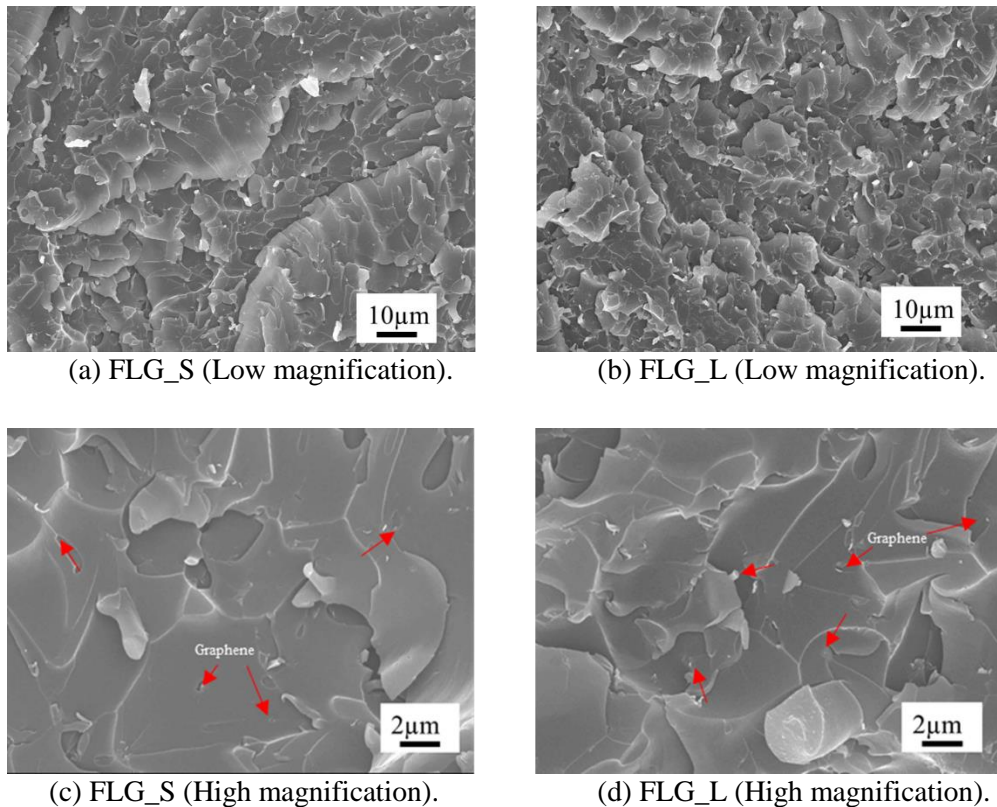


**Figure 4.** FE-SEM images of fractured surface of FLGs/epoxy nanocomposites.

In the following, to investigate the size effect of FLGs on the mechanical properties of nanocomposites, the experimental results of FLG\_S and FLG\_L were compared at weight fraction of 0.2 wt%. Table 3 shows the mechanical properties compared between FLG\_S and FLG\_L and Figure 5 shows the fractured surfaces of each FLGs nanocomposites.

**Table 3.** Mechanical properties of FLG\_S and FLG\_L

		FLG_S	FLG_L
Graphene content	wt%	0.2	
Tensile strength $\sigma_t$	MPa	80.6	83.6
Fracture strain	$\epsilon_t$ %	6.69	7.46
Young's modulus E	GPa	3.50	3.28
Aspect ratio		25	50



**Figure 5.** FE-SEM images of fractured surface of FLGs/epoxy nanocomposites.

According to Table 3, the mechanical properties of FLG\_L were superior to those of FLG\_S. Using large size FLGs, Young's modulus, tensile strength and fracture strain were improved by 5.77%, 11.5% and 11.6%. These results indicated that as the size of graphene increases, reinforcement ability of graphene becomes more impressive.

Figure 5 shows that there were no aggregations of FLGs, even in the case using large size of FLGs. And FLGs making fractured surfaces rougher were observed.

#### 4. Conclusion

In this study, by applying the premixed process with sodium glutamate, highly dispersed FLGs in acetone were prepared. FLGs were added into epoxy resin as a reinforcement, and their tensile properties were evaluated in order to discuss the effect of FLG as a reinforcement of epoxy resin. The sample of 0.2 wt% of FLG\_L showed improved mechanical properties. Young's modulus, tensile strength and fracture strain were improved by 6.2%, 3.7% and 55.6%. Interestingly, fracture strain was significantly improved, derived from suppressing effect on crack propagation by uniformly dispersed FLGs. FLG\_L was also improved with increasing the size of FLGs. It might be because inhibition of crack propagation was more efficient with the increasing size of FLGs. As the size of graphene increases, precipitation tends to occur more easily and it's difficult to maintain the dispersed state for long time. As one of the solutions, the new method including premixing process makes it possible to fabricate and maintain large size of graphene.

## References

- [1] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos and I. V. Grigorieva, A. A. Firsov, Electric Field Effect in Atomically Thin Carbon Films. *Science*, 306:172–182, 2014.
- [2] K. S. Novoselov, V. I. Fal'ko, L. Colombo, P. R. Gellert, M. G. Schwab and K. Kim, A roadmap for graphene. *Nature*, 490:192–200, 2012.
- [3] Rasheed Atif, Islam Shyha and Fawad Inam, Mechanical, Thermal, and Electrical Properties of Graphene-Epoxy Nanocomposites—A Review, *Polimers*, 48, 281, 2016.
- [4] Mohammad A. Rafiee, Javad Rafiee et al., Enhanced Mechanical Properties of Nanocomposites at Low Graphene Content, *ACS Nano*, 3, 12: 3884-3890
- [5] Ji Won Suk, Richard D. Piner, Jinho An and Rodney S. Ruoff, Mechanical Properties of Monolayer Graphene Oxide. *Nanoscale*, 5:38–51, 2013.
- [6] Keith R. Paton, Eswaraiah Varrla et al., Scalable production of large quantities of defect-free few-layer graphene by shear exfoliation in liquids, *nature materials*, 13: 624–630, 2014.
- [7] Yoshihiko Arao, Yoshinori Mizuno, Kunihiro Araki, Masatoshi Kubouchi, Mass production of high-aspect-ratio few-layer-graphene by high-speed laminar flow, *Carbon*, 102: 330–338, 2016.
- [8] Yoshihiko Arao, Fumiya Mori, Masatoshi Kubouchi, Efficient solvent systems for improving production of few-layer graphene in liquid phase exfoliation, *Carbon*, 118: 18–24, 2017.
- [9] Yanbang Zhang, Guozhi Jia et al., Size effect on near infrared photothermal conversion properties of liquid-exfoliated MoS<sub>2</sub> and MoSe<sub>2</sub>, *Superlattices and Microstructures*, 105: 22–27, 2017.