

# Graphene-Enhanced Polymer Resins for High-Performance Structural Composites

Anh Hoang Dam, Kaja Skålnes Knudsen, and Jon Are Beukes

CealTech AS  
Kanalarmen 22, 4033 Stavanger  
NORWAY

beukes@cealtech.com

## ABSTRACT

*In this work, a low-cost and scalable manufacturing technique was developed to incorporate highly dispersed graphene into epoxy and Polyurethane (PU), which are among the most widely used polymeric materials. The study covered the wide spectrum of graphene materials of different structures, both raw products of synthesis as well as a functionalized one, to be used as reinforced fillers of polymer resins. Additionally, a single-layer or few-layer graphene, as produced by a Plasma Enhanced Chemical Vapor Deposition (PECVD), and Graphene Nanoplatelets (GNPs), which are composed of a dozen or several dozen graphene layers produced from exfoliation of graphite, were also investigated. Furthermore, the properties of epoxy composites reinforced with hybrid graphene fillers and combinations of graphene materials with other fillers is also discussed in this report.*

*The influences of concentration and composition of hybrid graphene mixtures on tensile and flexural behaviour of epoxy resin were studied. Tensile and flexural properties of epoxy resin were improved significantly and reached maximum at low addition of graphene (i.e., below 0.1 wt%).*

*In comparison with pure polyurethane, the graphene-based polyurethane composites exhibited higher tensile strength and modulus improvements, even with a very small amount graphene added. The impact of PECVD graphenes with different flake sizes on tensile properties of PU were investigated. Unlike the graphene-enhanced epoxies, both the tensile strength and Young's modulus of polyurethane improved greater with the addition of large flake-size graphene than with the presence of small flake-size one. Consequently, these graphene-based polymer resins have great potential in the preparation of various high-performance polymer composites for defence and military applications, such as marine, automotive, aerospace, protective equipment, and structures, by improving strength and ballistic performances, and reducing weight.*

**Keywords:** graphene, pristine graphene, PECVD graphene, hybrid graphene, polyurethane, epoxy, graphene polymer nanocomposite

## 1.0 INTRODUCTION

In recent years, polymer composite materials have been widely used in various applications, including automotive, construction, infrastructure, wind turbine blades, sporting goods, and aerospace [1]. The increasing demand of stronger and lighter polymer composites for innovative composite materials has promoted researchers to continuously update existing materials and develop new materials with improved properties and multifunctionalities, so that they can be exploited for improving civilian and military applications [2].

The distinctive one-atom-thick planar structure, along with excellent mechanical strength, electronic transport properties, favourable thermal conductivity, and exceptionally high aspect ratio [3], make graphene an excellent structural and multifunctional nano-reinforcement for developing high-performance and

multifunctional polymer composites. Several promising results regarding improvements in the mechanical performance of graphene-based polymer composites (such as fracture toughness, fatigue, impact strength, tensile strength, stiffness, and surface hardness, etc.) have already been reported by various research groups [4] – [12].

The main goal of this work is to improve mechanical performance of common resins, such as epoxy and polyurethane. The chosen resins are widely used as adhesives, coatings, construction materials and automotive materials for defence applications, industrial tooling and other general consumer products [13] – [15]. This is explored by utilizing different types of graphene materials and by tuning the FORZA technology for graphene production [16]. The reactor system, FORZA, is based on a scalable microwave plasma technology platform. The system can transform carbon containing gases and hydrogen to graphene, which is grown vertically on a variety of substrates, such as stainless steel, inconel, aluminum, quartz, and copper, as well as more complicated structures, including metal meshes, carbon fiber cloths, and particles. The morphology and flake size of the produced graphene can be controlled by changing the growth conditions by varying the growth time, gas compositions, input energy, gas pressures, and temperatures.

The whole family of graphene materials, as well as their graphite or carbon precursors, can be used directly as fillers of polymer resins to provide efficient reinforcement and functional properties of the obtained composites [17] – [21]. Due to the multifunctional behaviour of these fillers, they can improve the chosen mechanical properties of their polymer composites (e.g., tensile strength, flexural strength, elongation, modulus, and/or toughness). This was the reason that research concerning the behaviour of various graphene types on mechanical performance of polymer resins has been conducted. Many critical factors affect the mechanical characteristics of graphene polymer composites, such as the size and aspect ratio of graphene flakes, its concentration within the composites, and the graphene manufacture approach (e.g., liquid-phase exfoliation of graphite, chemical oxidation and reduction, PECVD, etc).

To understand the contribution of the manufacturing techniques on the reinforced behaviour of the graphene used, a plasma enhanced chemical vapor deposition (PECVD) production approach for graphene (bottom-up) and graphene nanoplatelets produced by exfoliating graphite (top-down) were integrated into epoxy resin. The two as-produced graphene materials often have different morphology and number of layers. The former is single- or few-layer graphene, while graphene nanoplatelets is a multi-layer graphene that is available at low cost but often increases the tensile modulus of composite material [22]. The mechanical properties of these two types of graphene were measured and compared.

The weak interfacial adhesion between the graphene layers and polymer matrix, resulting mainly from the atomically smooth surface and chemical inertness of graphene, may make the stress transfer from the matrix to graphene inefficient. Functionalization of graphene surfaces, by introducing suitable functional groups compatible with the polymer not only significantly improves the filler-polymer interfacial interactions but also increases the dispersion of graphene into the polymer [23] – [25], and thus make graphene materials very effective fillers in order to obtain mechanically reinforced composites. Epoxy composites with graphene fillers functionalized with amines were therefore prepared and mechanically tested.

The mechanical performance of polymer composites can be further enhanced by combining graphene fillers that have structural differences. The combination need not necessarily be limited to only graphene fillers, but may be a combination of those from other carbon-based materials (e.g., carbon nanotube [CNT], C60, etc.), inorganic materials, or metallic materials [26]. When the hybrid graphene filler is homogeneously dispersed in the polymer resins at an optimum concentration, their synergetic effect can bring multiple advantages that a single filler may not be capable of offering [27]. In addition to the type of fillers added, the ratio of ingredients in the given hybrid set of fillers needs to be optimized in order to achieve the desired mechanical properties [28] – [30]. In this report, two sets of hybrid combinations, which are (G001 + CNT + G002) and (G001 + CNT + G003), at concentrations that varied from 0.01 wt% to 1 wt%, were investigated. The different

proportions of each component in these hybrid fillers were also studied. Table 1 presents all the types of graphene and combinations used in this study.

**Table 1: Graphene and hybrid graphene used in the study.**

<b>Graphene type</b>	<b>Description</b>
G001	PECVD graphene, small flake size < 0.5 $\mu$ m
G002	PECVD graphene, large flake size < 7 $\mu$ m
G003	Amine-functionalized graphene oxide
GNPs	Graphene nanoplatelets, particle size from 2 $\mu$ m to 5 $\mu$ m
Gmix1	33.3% G001 + 33.3% CNT + 33.3%G002 (by weight)
Gmix2	85% G001 + 10% CNT + 5% G002 (by weight)
Gmix3	85% G001 + 10% CNT + 5% G003 (by weight)
Gmix4	75% G001 + 10% CNT + 15% G003 (by weight)

## 2.0 EXPERIMENTAL

### 2.1 Materials

G001 and G002 are single- or few-layer graphenes produced by a PECVD method and were provided by CealTech AS, Norway. GNPs has particle sizes 2 to 5  $\mu$ m and was purchased from Sigma-Aldrich. Graphene oxide (GO) with an oxygen atomic content of 37.6% was purchased from Abalonyx AS. Carbon Nanotubes (CNTs) used in this study were (-OH) functionalized multiwalled carbon nanotubes purchased from Nanografi. The CNTs had a stated purity of > 96%, a 1 wt% content of (-OH), an inside diameter of 5–15 nm, an outside diameter of 28–48 nm, and a length of 10–25  $\mu$ m. Shin-Etsu Silicones kindly provided (3-aminopropyl) triethoxysilane (APTES).

The epoxy resin used for composite preparation was Epikote 828 and the curing agent used was Lindride 36K; both kindly provided by Comrod AS and used as received. Epikote 828 is a medium viscosity liquid epoxy resin produced from bisphenol A and epichlorohydrin, having a viscosity of 12–14 Pa·s at 25°C and epoxy group content of 5260–5420 mmol/kg. Lindride is a low viscosity and anhydride-based curing agent consisting primarily of methyltetrahydrophthalic anhydride and methylhexahydrophthalic anhydride.

The Polyurethane (PU) used in this study was a High Performance Elastomer (HPE) system, consisting of polyols (HPE 40A Polyol-SL240000 and HPE 85A Polyol-SL285000) and isocyanates (HPE 40-85A ISO-SL000105), and covers a large range of hardnesses, going from a 40 shore A elastomer to a 55 shore D semi-rigid resin. All the polyol and isocyanate components were manufactured by Synthene and distributed by Lindberg & Lund AS. All chemicals were used without any further purification.

### 2.2 Functionalization of Graphene Oxide

A 0.1 g amount of graphene oxide powder was added into 100 mL of anhydrous ethanol. The solution was sonicated for 1 h before 2 g of APTES was added, and the mixture was stirred vigorously at a temperature of 78 °C for 18 hrs. After the reaction, the mixture was filtered and washed several times with deionized water and ethanol. Finally, the amine-functionalized GO was obtained after drying at 50 °C in a vacuum for 12 hrs.

### 2.3 Preparation of Graphene-Based Resin Samples

#### 2.3.1 Graphene-Based Epoxy Composites

First, graphene was dispersed homogeneously into Epikote 828 resin by using a ball-mill Retsch PM100 machine at the speed of 250 rpm. The mixture was then well mixed with the hardener Lindride 36K at the weight ratio of 100:84, and then heated up to 40°C for 30 min under vacuum to get ideal viscosity and to remove bubbles. Finally, the resin was poured into a stainless steel mould. Prior to pouring, the releasing agent was applied gently to the mould surface before the mould was preheated at 60°C for an hour to remove the moisture content. Finally, the samples were poured into the mould and cured at 80°C for 3 hrs, and then 130°C for another 3 hrs.

#### 2.3.2 Graphene-Based Polyurethane (G/PU) Composites

G/PU composites were prepared at three different graphene concentrations: 0.01 wt%, 0.05 wt%, and 0.1 wt%. To prepare the composites, a certain amount of graphene was added into 49g of polyols. The mixture was ball-milled at the speed of 250 rpm using a Retsch PM100 machine. Thereafter, 100g of isocyanates HPE 40-85A ISO-SL000105 were added into the G/polyols. Prior to moulding, the resulting mixture was degassed in vacuum for 15 minutes, and a thin layer of Extra M Release Agent from ChemTrend was applied to the mould, followed by drying at 70°C to remove moisture completely. Finally, the G/PU was casted in the mould. The composites were fully cured after 7 days at room temperature.

### 2.4 Characterization and Mechanical Testing

The graphene types used in this study were characterized by means of Raman spectroscopy, Scanning Electron Microscopy (SEM), and transmission electron microscopy (TEM). Raman spectra were collected on a Renishaw inVia micro-Raman spectrometer with a 532 nm Ar laser excitation; the graphene powders were placed on microscope slides and a small glass cover placed on top, and secured by adhesive tapes. TEM was conducted on a JEOL JEM-2100 microscope with 200 kV accelerating voltage; graphene was dispersed in Isopropyl Alcohol (IPA) and the dispersed flakes were deposited on a TEM support grid. SEM was performed on a JEOL JSM-7500F microscope with 5 kV accelerating voltage in which graphene powders were placed on carbon tapes.

Mechanical properties of nanocomposite materials were measured by an Instron Applications Laboratory Model 5985. Tensile strength tests were performed according to the standard DIN EN ISO 527-2. Dog-bone shape samples were used for the testing. Samples have a gauge length of 50 mm, 10 mm width, and thickness of 4 mm. Tensile tests were performed with a constant cross head speed of 1 mm/min for epoxy and 100 mm/min for PU material. Flexural strength (3-points flexural) tests were performed according to standard ASTM D790-03; specimen sizes for this study were: 80 x 10 x 4 mm. A minimum of seven specimens were tested for each formulation as required to reduce the uncertainty of the measurement.

## 3.0 RESULTS AND DISCUSSION

### 3.1 Graphene Characteristics

The characteristic quality of graphene was investigated by using Raman spectroscopy. The typical Raman spectra of graphene has D, G, and 2D peaks (Figure 1). The D peak appears at 1320 – 1350  $\text{cm}^{-1}$  and is the defect band that represents a ring breathing mode from the  $\text{sp}^2$  hybridized carbon rings. The G band appears around 1570 – 1585  $\text{cm}^{-1}$  and represents an in-plane vibrational mode involving the  $\text{sp}^2$  hybridized carbon atoms. The 2D band peak appears around 2650-2700  $\text{cm}^{-1}$  and can be used to investigate whether the layers of graphene are single, double, or multi-layers. In some cases, D' band also arises from a defect-induced double-resonance process [31].

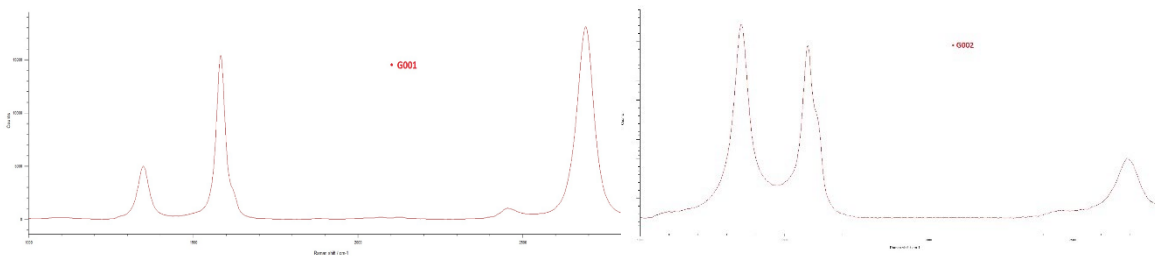


Figure 1: Raman spectra of G001 (left) and G002 (right).

Table 2: Raman characteristics of graphene G001 and G002.

Graphene type	D	G	2D	I <sub>D</sub> /I <sub>G</sub>	I <sub>2D</sub> /I <sub>G</sub>
G001	1345.0	1580.0	2690.3	0.38	1.16
G002	1348.6	1579.6	2691.2	1.71	0.59

The 2D band of the G001 peak has a high intensity, a symmetric shape, and a symmetric D peak, which indicates a single-layer graphene. This is further confirmed with the I<sub>D</sub>/I<sub>G</sub> ratio of 0.38 and the ratio I<sub>2D</sub>/I<sub>G</sub> of 1.16, as shown in Table 2. The higher ratio of I<sub>D</sub>/I<sub>G</sub> in G002 compared to that in G001 probably arises from the fact that G002 is more hydrogenated and has more interaction between the individual flakes, due to the production parameters in the PECVD process. This may partly result in a change in hybridization (e.g., from sp<sup>2</sup> to sp<sup>3</sup>) or a change in the sp<sup>2</sup> configuration. The strong D band peak and D' band peak also may suggest a more nanocrystalline structure and the presence of graphene edges and defects, such as distortion, vacancies, and straining to graphitic lattices, which are prevalent features of PECVD graphene; the high defect density in PECVD graphene is referred to energetic particles from the plasma interacting with the growing surface [32] – [35]. This is further seen by a lower I<sub>2D</sub>/I<sub>G</sub> in these samples. However, the electron diffraction pattern of G002 (see Figure 5) shows characteristics of a highly crystalline material, which suggests it is indeed single layered graphene.

Figure 2 and Figure 3 represents a typical surface morphology of the large vertical graphene sheets as grown by PECVD [16] from a mixture of CH<sub>4</sub> and H<sub>2</sub>. These SEM images show obvious differences in size and morphology between G001 and G002. These graphenes were produced using different process parameters (e.g., gas ratios, plasma densities, temperatures, pressures, etc.). G001 exhibits a small flake size and densely packed structure. While G002 has a maze structure with a larger flake size and relatively wide spacings. The cross section view in Figure 3 (right) represents the grown height of approx. 7 μm for G002.

TEM images of G001 graphene at low magnification showed wrinkled graphene sheet structures with flake sizes around 500 nm (Figure 4). The electron diffraction (not shown) pattern indicates single or few-layer graphene. The electron diffraction pattern of G002 in Figure 4 confirms the hexagonal-packed lattice structure of single-layer graphene. The TEM images of GNPs on the contrary suggest a presence of multiple graphene layers with relatively smooth surfaces (Figure 5).

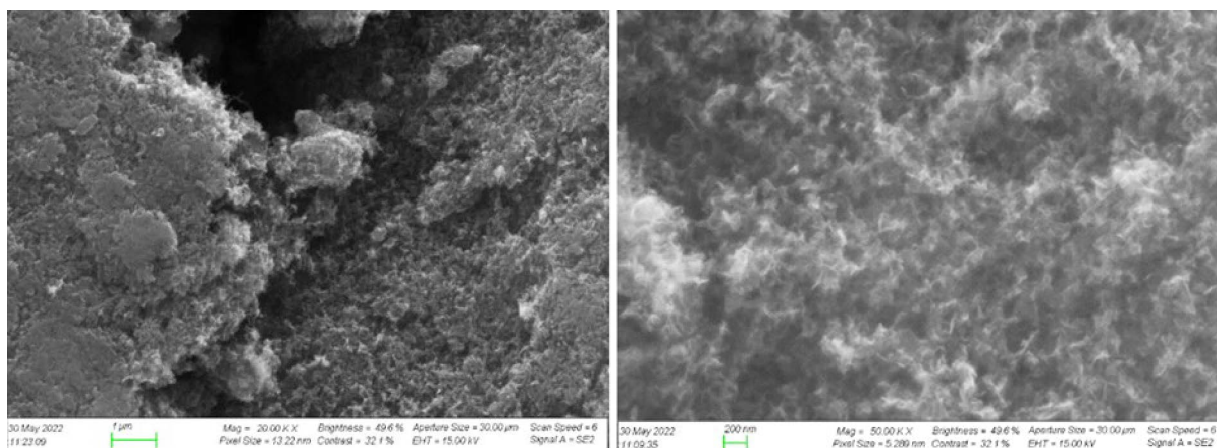


Figure 2: The SEM images of graphene G001.

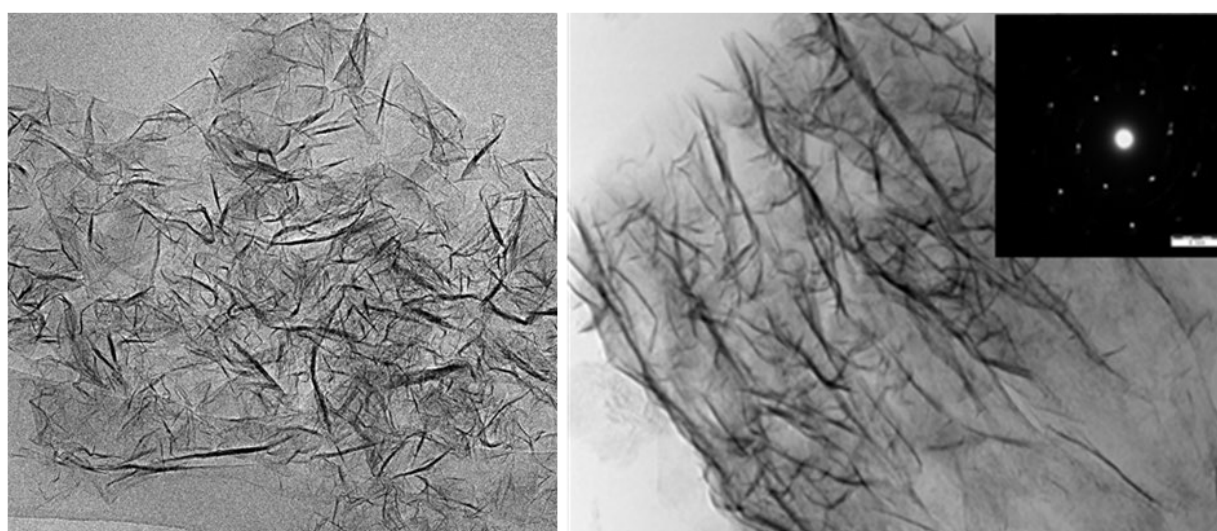


Figure 3: The SEM images of graphene G002: top-view of the grown vertical graphene sheet (left) and cross section view of graphene sheets (right).

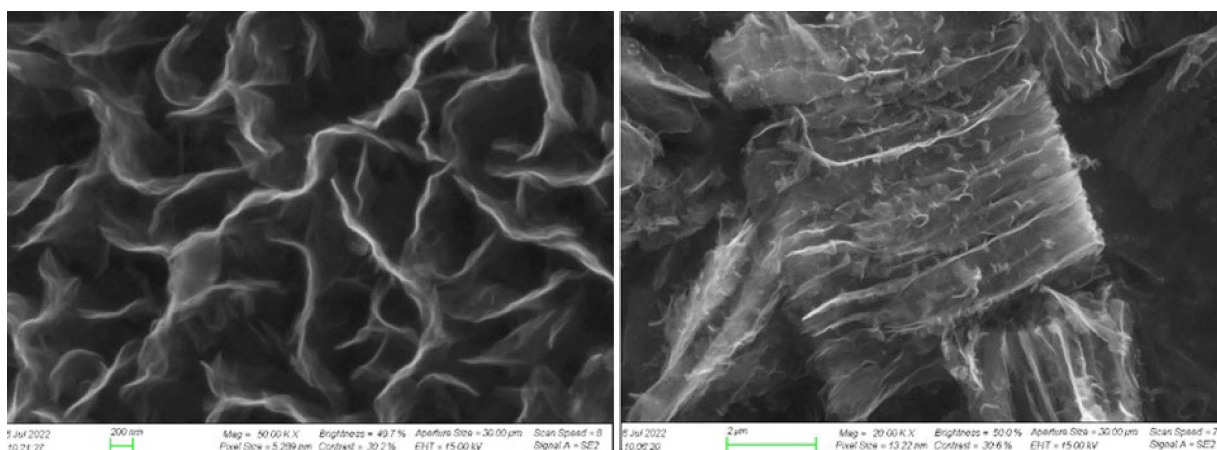


Figure 4: TEM images of G001 graphene (left) and G002 graphene (right). Inserted Selected Area (Electron) Diffraction (SAED) pattern showing high crystallinity from single-layer graphene.

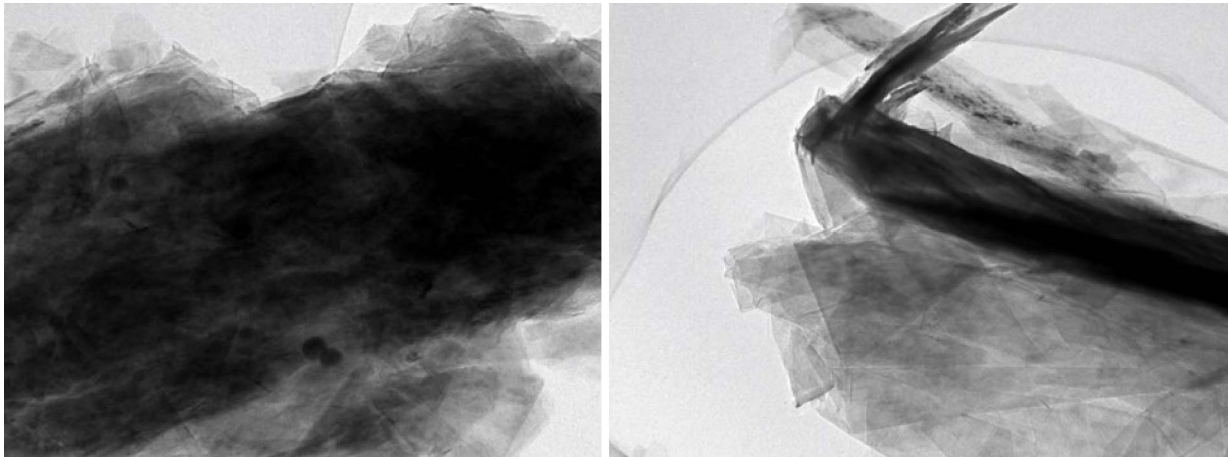


Figure 5: TEM images of GNPs.

### 3.2 Mechanical Properties of Graphene Epoxy Nanocomposites

#### 3.2.1 Impact of Graphene Type on Mechanical Properties of Epoxy

##### 3.2.1.1 Tensile Properties

Five graphene and hybrid graphene types were selected and incorporated into epoxy Epikote 828 at a concentration of 0.3 wt%. For each sample, tensile strain was tested in seven specimens until rupture of the specimen. Average standard tensile properties at break for all samples is illustrated in Figure 7.

All the graphene-containing epoxy resin samples developed in the project showed significant increases of both tensile strength and elongation at graphene concentrations of 0.3 wt%. The small-size PECVD graphene G001 showed the highest improvement, with an increase of up to 88% in tensile strength and 182% in elongation compared to the pure epoxy resin sample, followed in performance by the larger-sized PECVD graphene G002. The enhancement is explainable with the large aspect ratio and high interfacial contact area of the graphene. Moreover, an increase in tensile strength and elongation of epoxy resins containing graphene resulted due to the surface roughness of graphene (wrinkled surface), which caused an enhanced mechanical interlocking with the epoxy chains and, consequently, better adhesion [36].

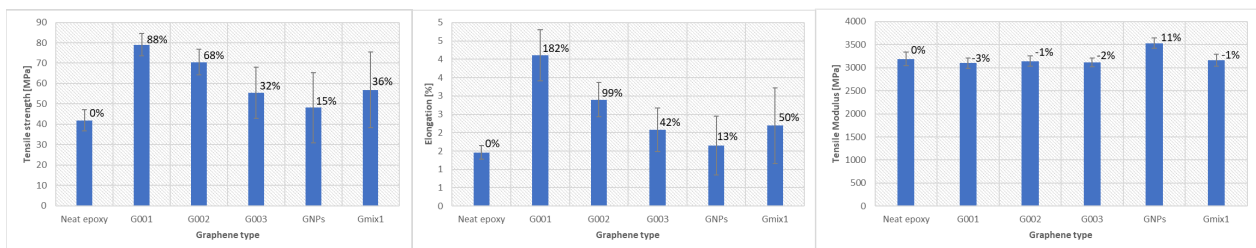


Figure 6: Tensile properties of neat epoxy and graphene-based epoxy resin at graphene concentration of 0.3 wt%.

Among the graphene samples, multi-layer GNPs showed the lowest improvement in tensile strength (15%) and elongation (13%). However, as expected, GNPs has the highest tensile modulus with an increasing of 11% compared to neat epoxy (not shown). Other graphene composites showed insignificant or negative improvement in modulus. It is interesting that adding a nanofiller results in improved strength and elongation,

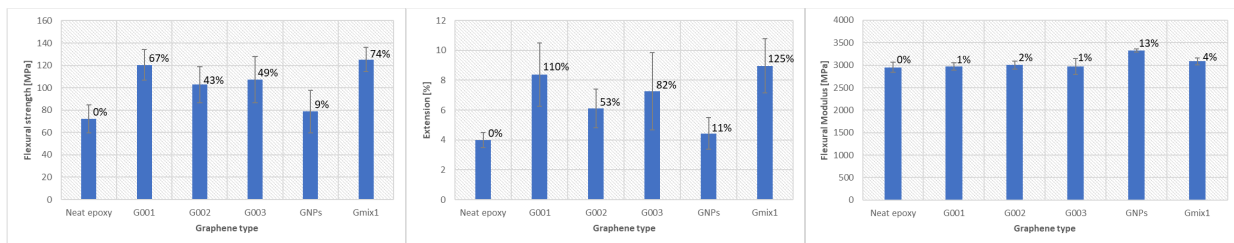
but has a minor impact on the modulus. This probably refers to the improved toughness of resins by these graphene fillers. The epoxy resin material fails due to the creation of cracks in the matrix and further crack length increases, followed by failure of samples. It is well known that the tougher materials have an efficient mechanism of internal energy absorption, which restricts the crack propagation, thus allowing it to maintain the desired level of durability in the real field of application under massive variations in operating conditions.

The tensile test results showed that the efficiency of filler-induced increases in epoxy strength and elongation follows the trend: G001 > G002 > Gmix1 > G003 > GNPs.

**3.2.1.2 Flexural Properties**

Flexural properties of the six samples, including a pure epoxy resin and five graphene-containing epoxy resin samples at concentration of 0.3 wt%, were measured by using the 3-points flexural test. For each sample, seven specimens were tested until rupture.

All five graphene-enhanced epoxy samples showed an increase in the average flexural strength and extension, as compared to the pure reference sample. A maximum increase of 74% in strength and 125% in extension was obtained by the addition of hybrid graphene Gmix1 while multi-layer GNPs showed the smallest increase in flexural strength (9%) and extension (11%). However, GNPs exhibited the highest improvement in flexural modulus with an increase of 13% (not shown).



**Figure 7: Flexural properties of neat epoxy and graphene-based epoxy resin at graphene concentration of 0.3 wt%.**

In regard to the flexural strength and flexural extension of the samples, the following trend was seen: Gmix1 > G001 > G003 > G002 > GNPs.

**3.2.2 Impact of Graphene Concentration on Mechanical Properties of Epoxy**

Gmix2/epoxy and Gmix3/epoxy samples at various concentrations of 0.01 wt%, 0.1 wt%, 0.3 wt%, and 1 wt% were made. To understand the impact of ingredient proportion, Gmix1/epoxy and Gmix4/epoxy were prepared at a graphene concentration of 0.3 wt%. The mechanical properties of these samples were then measured and compared.

**3.2.2.1 Tensile Properties**

The measurements for tensile properties of Gmix2- and Gmix3-based epoxy resins versus graphene concentration are shown in Figure 8. In general, elongation properties exhibited a similar trend to that shown by tensile strength and both improved significantly with addition of graphene, even with a very small amount (0.01 wt%). The optimal concentration of graphene falls into a low value range (0.01 – 0.1 wt%).

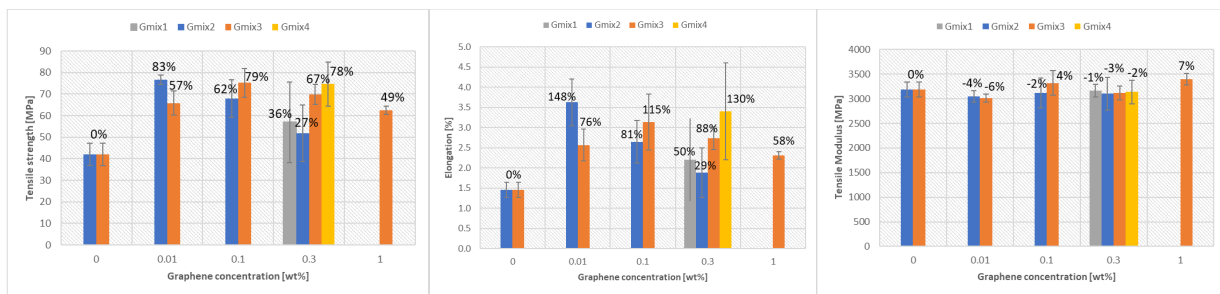
Neat epoxy resin demonstrated a tensile strength value of 42±5 MPa and an elongation value of 1.46±0.17%, which increased to 66±5 MPa and 2.57±0.32%, respectively, with the addition of 0.01 wt% Gmix3. It further reached a maximum of 75±5 MPa and 3.14±0.57%, respectively, at a Gmix3 concentration of 0.1 wt%.



A further increase in the Gmix3 concentration to 0.3 wt% and 1 wt% decreased the tensile strength to  $70\pm 4$  MPa and  $62\pm 2$  MPa, and the value of elongation to  $2.74\pm 0.25\%$  and  $2.31\pm 0.08\%$ , respectively. Apparently, at above a 0.1% weight fraction, the effectiveness of graphene diminishes, possibly due to the degradation in dispersion quality of graphene in the epoxy matrix. This highlights one of the disadvantages of graphene in that it is challenging to disperse graphene properly at higher weight fractions.

Both the tensile strength and the elongation of resin containing 0.01 wt% Gmix2 exhibited the highest improvement, with values of  $77\pm 2$  MPa and  $3.62\pm 0.47\%$ , respectively. Increasing the concentration of Gmix2 from 0.01 to 0.3% was accompanied by significantly decrease of both the tensile strength and elongation.

In comparison, at low concentration (i.e., 0.01 wt%), the Gmix2-based resin showed higher tensile strength than Gmix3-based resin; when increasing concentration to 0.1 wt% and higher, the Gmix3 is superior to Gmix2. The difference between the two hybrid graphenes is that the pristine graphene G002 was used in Gmix2 and the functionalized graphene oxide G003 was included in Gmix3. This indicates that functionalized graphene oxide G003 plays an important role in dispersing and stabilizing graphene in epoxy, especially at high graphene concentrations. In conclusion, it is recommended to use pristine graphene G002 in a hybrid graphene set, if a small quantity of graphene is used; however, when graphene concentration increases to a critical point, where highly dispersed graphene becomes challenging, the presence of functionalized graphene oxide G003 will be favourable.



**Figure 8: Tensile properties of hybrid graphene-based epoxy resin as function of graphene concentration.**

At a concentration of 0.3 wt%, the improvement of tensile strength and elongation follows the order: Gmix4 > Gmix3 > Gmix1 > Gmix2, or, in other words:  $(75\%G001 + 10\%CNT + 15\% G003) > (85\%G001 + 10\%CNT + 5\% G003) > (33.33\%G001 + 33.33\%CNT + 33.33\% G003) > (85\%G001 + 10\%CNT + 5\% G002)$ . As mentioned above, the hybrid Gmix3/epoxy exhibits greater tensile properties than the hybrid Gmix2/epoxy at a relatively high concentration of 0.3 wt%. Moreover, when the content of the functionalized graphene oxide G003 in the hybrid set increases from 5% (i.e., in Gmix3) to 15% (i.e., in Gmix4), the tensile properties of graphene-based epoxy increases. This once again confirms the role of G003 for dispersing and stabilizing graphene in epoxy.

### 3.2.2.2 Flexural Properties

Typical average flexural properties of Gmix2- and Gmix3-based epoxy resins are shown in Figure 9. The flexural properties of resin increased by the presence of both graphene Gmix2 and Gmix3 and exhibited a similar trend as that shown for tensile properties. A significant improvement in flexural strength was found for a very small loading of 0.01% by weight of Gmix2 and a decrease was observed with further loading. The flexural strength and extension were maximized at loadings of 0.1% by weight of Gmix3.

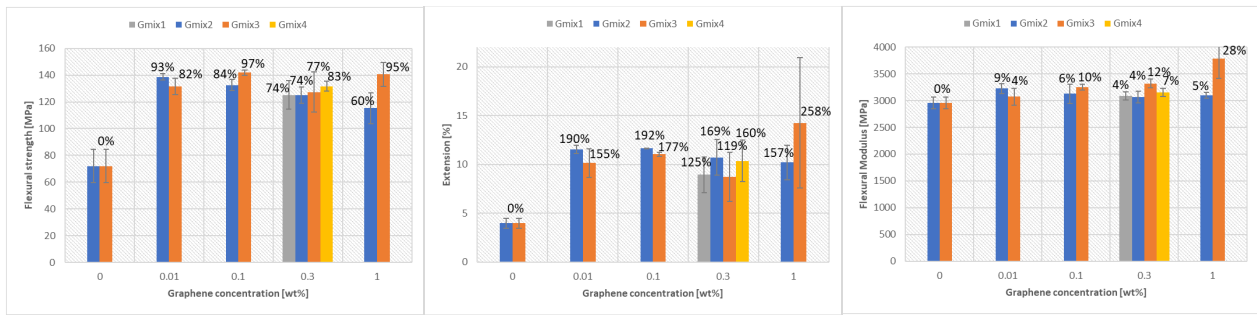


Figure 9: Flexural properties of Gmix2- and Gmix3-based epoxy resin.

The flexural strength and the flexural extension of the neat epoxy were found to be 72 MPa and 4 mm, respectively. With the addition of 0.01, 0.1, 0.3, and 1 wt% Gmix3, the flexural strength of resin increased by 82%, 97%, 77%, and 95% and the extension increased by 155%, 177%, 119%, and 258%, respectively.

Unlike tensile modulus, the flexural modulus of the resin improved with addition of graphene at any concentration. Compared with the neat epoxy, the flexural modulus of Gmix3/epoxy resin improved by 4%, 10%, 12% and 28%. The flexural modulus of Gmix2 epoxy resin increased by 9%, 6%; 4%, and 5% with the presence of 0.01%, 0.1%, 0.3%, and 1 wt%.

The behaviours of Gmix2 and Gmix3 on flexural strength at a given loading were similar to those on tensile strength. Gmix2 is favourable at low loading while Gmix3 performs better at higher loading. At concentration of 0.3 wt%, the improvement of tensile strength follows the order: Gmix4 > Gmix3 > Gmix1 = Gmix2. This suggests that at high graphene concentration, the functionalized graphene oxide G003 should be added more in the hybrid graphene set.

### 3.3 Mechanical Properties of Graphene/PU Nanocomposite

Figure 10 presents the tensile properties of the G001/PU and the G002/PU nanocomposites as a function of graphene concentration. The figure indicates that the incorporation of both G001 and G002 led to an increase in tensile strength and Young's modulus of the composites, as compared to the neat PU.

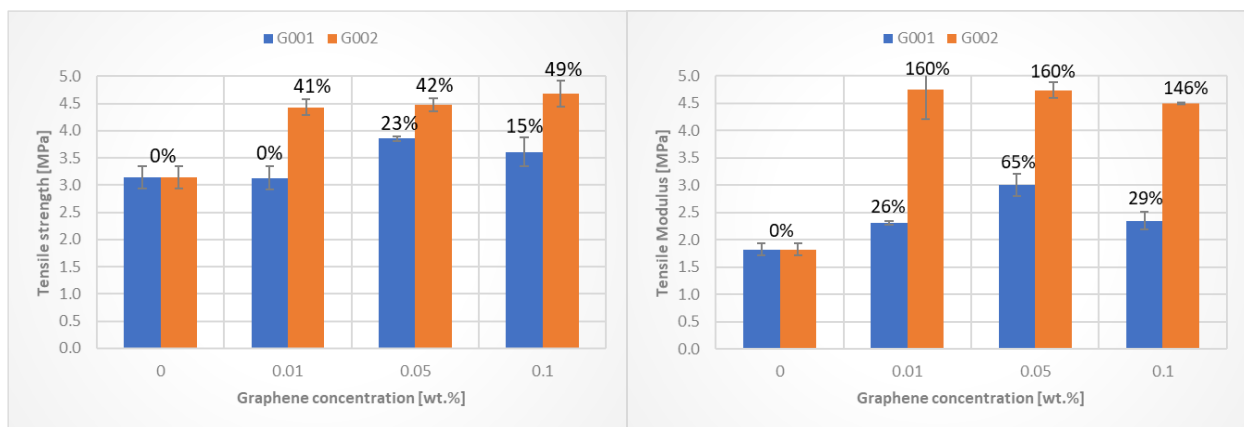


Figure 10: Tensile strengths and Young's modulus of graphene-based PU nanocomposites.

The G002-based PU nanocomposites showed significant enhanced tensile strength at a very low graphene loading level of 0.01 wt%, and further increase in loading resulted in negligible further increase in the tensile strength. It was found that the elongation at break decreases with the addition of G001 and G002, while the tensile strength and Young's modulus were significantly improved and achieved a maximum at loadings of around 0.01 – 0.1% by weight of G001. The data indicates that for the G002/PU composite, the Young's modulus maximum could possibly be even below 0.01 wt%. This behaviour is typical of many graphene/polymer systems, of which there are a number of reports in the literature [36]. Both the Young's modulus and the tensile strength of the polymer are typically found to increase with the loading of graphene, while the elongation at break is decreased.

It is clearly seen that PU nanocomposites prepared with the large flake size graphene G002 present higher tensile strengths and Young's modulus (Figure 10) for all the nanofiller contents than the nanocomposites prepared with the small flake-size graphene G001. These findings are consistent with those of Coleman, et al. [37] and Gong, et al. [38]. They also found that for a given loading of graphene, the level of reinforcement effect decreased as the graphene flake size was reduced.

#### 4.0 CONCLUSION

This study shows that the magnitude of improvement in the properties of composites with graphene depend on the structure of the graphene fillers (i.e., dimensions and number of graphene layers). The impacts of graphene flake size on the mechanical properties of epoxy resin and PU resin were different. In contrast with graphene-based epoxy nanocomposites, which showed the smaller flake-size graphene having greater improvements for mechanical properties, the large flake-size graphene-based PU nanocomposite exhibited much higher tensile properties. Introduction of hybrids and various combinations of graphene materials with other fillers of different structures and properties into the epoxy matrix can provide the composites with untypical properties and may also result in new functions based on synergistic effects. The properties of the hybrid graphene / epoxy composites were strongly associated with the functionalized surface of graphene toward improved dispersibility, compatibility and adhesion between epoxy phase and nanofillers, especially at high graphene loading.

The graphene content required to significantly improve mechanical properties of polymer resins has been as small as <0.01 wt%, which is orders of magnitude lower than other nanofillers such as nano-clays, CNT, nano-TiO<sub>2</sub>, metal / metal oxide nanoparticles, and silica nanoparticles. This such low weight fraction requirement of graphene suggests that graphene shows great promise as nanofiller for the next generations of advanced composite materials for both civilian and military applications. Because of these excellent enhancements in properties, graphene reinforced polymer nanocomposites possess great potential to be used in construction, automotive, electronics, aerospace and for other sectors. However, there are a number of fundamental scientific issues that need to be addressed in order to realize the full impact of this enabling enhanced materials technology. For example, more characterization efforts on graphene/polymer nanocomposites are still necessary to understand the issues related to the correlation between the structure of polymer and graphene fillers, and their dispersion and interaction. Other relevant mechanical properties, such as fracture and fatigue properties, impact strength, damage tolerance, damping response, high strain rate response, torsional / flexural response, and so on, are needed to complete the picture. It is also important to determine the impact of graphene on thermal and electrical properties of polymer composites. Finally, it could be most valuable to study the apparent enhanced fire resistance property of graphene / polymer composites, since this property is one of the main obstacles for polymeric materials to replace metal or inorganic components.

### 5.0 ACKNOWLEDGEMENTS

Amalie Grønvold, Tale Frafjord Tungesvik, and the Norwegian Defence Research Establishment are thanked for valuable discussions and preliminary measurements of strength of different graphene-enhanced resin systems. Jenny Niphawan Opsanger, Joachim Hope Kyllingstad, and Mats Aspeseter Rødne are acknowledged for their technical assistance.

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## 7.0 AUTHOR BIOGRAPHIES

**Anh Hoang Dam** is the Senior Material Chemist at CealTech AS. He has a PhD. in Chemical Engineering at the Norwegian University of Science and Technology (NTNU). He has more than 11 years of hands-on experience in polymer material science and technology and over 7 years of professional experience working with graphene and nanomaterials.

**Kaja Skålnes Knudsen** has a Master's degree in nanoscience from the University of Bergen, where she worked on developing multidrug delivery by nanocarriers in cancer treatment. Since 2018, she has worked as a scientist at CealTech AS, developing and analysing graphene-enhanced materials for different applications.

**Jon Are Beukes** is the CEO of CealTech AS. He is a Dr.Scient. in Physical Chemistry from the University of Copenhagen and the University of Oslo. He has 5 years of experience as a Beamline Scientist at the European Synchrotron Radiation Facility (ESRF) and worked for 2 years with complex materials at NTNU. Recently, he has spent 15 years leading research groups and commercializing plasma technologies for multi-purpose applications.