

## Rheological Behavior of Graphene/Epoxy Nanodispersions

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### ABSTRACT:

Graphene/polymer nanocomposites are the latest trends in materials science in the recent years, but the technology of their preparation plays a crucial role in obtaining reliable materials with repeatable and enhanced properties. Up to now, there are many unresolved problems in controlling the dispersion of the graphene filler and the corresponding influence on the properties of the final nanocomposite materials. In the present study, we apply rheological methods for controlling the quality of the graphene dispersion. We prepare and characterize epoxy/graphene nanodispersions with graphene contents varying from 0.05 to 1 wt% and explore the effect of different mixing regimes on the dynamic moduli and viscosity, thus assessing the degree of the dispersion. The rheological percolation threshold and relaxation time spectra are determined, in order to evaluate the internal structure of the nanodispersions. The relaxation spectrum is highly efficient to probe the effects of interfaces and interconnections on the relaxation dynamics of molecules in nanodispersions. Rheological results combined with transmission electron microscopy (TEM) observations confirm that the low frequency dynamic viscosity and moduli strongly increase, with increasing the degree of dispersion due to the exfoliation of graphene sheets. The rheological percolation threshold was found at very low concentration depending from the processing conditions. The weight of the relaxation spectra is strongly shifted to higher values, compared to the neat epoxy resin and this effect is much stronger around and above the rheological percolation threshold.

### KEY WORDS:

Epoxy nanodispersions, graphene, rheology, processing, percolation threshold

## 1 INTRODUCTION

Owing to its exceptional physical properties, such as high surface area, excellent thermal conductivity, extremely high mechanical flexibility, and electrical conductivity, graphene has attracted tremendous research interest in the recent years [1-4]. These excellent characteristics have brought great achievements in the design of novel graphene functional materials with tailored properties [5]. In order to improve the properties of polymers, graphene based sheets have been incorporated both into thermosetting [6-11] and thermoplastic polymers [11-15].

Epoxy based materials [16] are used widely because of their superlative mechanical properties, thermal stability, solvent resistance and ease of processing [17]. Epoxies are one of the most adaptable and widely sold high performance material [18]. Some of the applications of epoxy and its nanocomposites include aerospace, automotive, marine, sports materials, construction, structures, electrical and electronic systems, biomedical devices, thermal management systems, adhesives, paints and coatings, industrial tooling and other general consumer products [19].

The superiority of graphene over carbon nanotubes as reinforcements stems from easy access to the graphitic precursor material, the cost, the scalable method, and its orientation flexibility (morphology). In order to achieve optimal enhancement in the properties of graphene/polymer composites, key issues should be resolved, i.e., improved dispersion and alignment of graphene in the polymer matrix for good adhesion/interaction [20-22]. As well known, due to the entanglement of graphene unavoidably occurring during the composite realization, the graphene flakes are usually present in the form of clustered agglomerates, interacting by the intermolecular van der Waals force. Consequently, the dispersion and exfoliation of graphene flakes in a polymer become a challenge [23-28], especially during the phase of preparation, when in mixing them with the polymer, they aggregate in the matrix. Thus, it is safe to argue that the main challenge in designing graphene-based polymer nanocomposites with improved properties is to disperse the individual graphene sheets in the polymer matrix. Among the different graphene precursors used to develop epoxy matrix nanocomposites, expandable graphite (EGS) represents a cheap precursor that can be easily dispersed. Also, known as “intumescent flake graphite”, expandable graphite is a synthesized intercalation compound of graphite that expands and exfoliates when heated. This material is manufactured by treating flake graphite with various intercalation reagents that migrate between the graphene layers in a graphite crystal and remain as stable species.

Indirect methods based on dynamic rheological analyses could efficiently be employed to obtain quantitative measures of the nanofiller dispersion in liquid resins [29-35]. This is mainly based on the fact that the dispersion quality of the nanofillers often affects the viscosity and viscoelastic properties of liquid suspensions in different ways. The development of the rheological parameters of polymer based materials is of major significance for many industrial applications, as far as they determine the technology for production of numerous polymer products that are important for the modern industry. The rheological approach [29] may be used as a highly useful analytical tool in development and optimization of nanocomposites of different matrix polymers and virtually all kinds of nanofillers. It might be used for routine and not expensive control of nanocomposite preparation technology, in order to identify the interesting samples at an early stage of their preparation and to verify the nanocomposite structure. However, rheological characterizations are better to be confirmed by other techniques, such as microscopy.

Study of nanocomposite rheology is important for the understanding of processing operations, but it may also be used to examine the nanocomposite microstructure [36-38]. In linear viscoelastic rheology measurements, the low-frequency moduli may provide information on the platelet dispersion; for instance, the presence of a low-frequency storage modulus ( $G'$ ) plateau is indicative of rheological percolation due to formation of a ‘solid-like’ elastic network of filler [39-41].

The properties of graphene/epoxy nanocomposites depend greatly on the degree of graphene dispersion in the pre-polymer at the resin preparation level. Therefore, the evaluation of the dispersion quality following the resin preparation (curing) step is deemed necessary. In the

present work, we take advantage of the accuracy and sensitivity of the rheological analysis to characterize both the dispersion and the interconnection of graphene nanoplates in epoxy based dispersions. The aim novelty of this study is to investigate the effects of different mixing conditions on the dynamic viscosity and moduli at different mixing regimes, as well as to estimate percolation threshold and relaxation time spectra of epoxy/graphene nanodispersions at varying graphene content between 0.05 - 1 wt%. The TEM visualization, combined with rheological characterizations and modeling are applied as an efficient methodology for control of the epoxy/graphene nanodispersions.

## 2 EXPERIMENTAL SECTION

The materials used in this study are epoxy resin D.E.R.<sup>TM</sup> 331 and diluent R-24 purchased from Dow Chemicals Company. Hardener H 10-30 was purchased from Leuna-Harze GmbH (Germany). Graphene was obtained at Frascati National Laboratories - I.N.F.N. (Italy) by microwave (MW) exfoliation method [42-45]. The carbon source was Expandable Graphite (EG) provided by Asbury®. EG was put in a ceramic pot and irradiated in a home microwave oven at the power of 800W. EG was rapidly heated by MW irradiation: the vapor rapidly evolving from intercalated substances produced exfoliation of EG. The comparison between SEM images of EG before and after irradiation clarifies what goes on.

The exfoliation process occurred in tens of seconds: the sample heating was due to a thermal shock given to spark-light events. Spark-lights occurred because of the vaporization of intercalated substances that changed the dielectric permittivity of the atmosphere in the oven, thus spark-lights appeared as an arc discharge phenomenon. Spark-light events quickly increased the sample temperature from 120°C up to 1000°C: the evolution of gases was so vigorous that a fracture in the surface of EG are visible (fig.1b). Graphene was obtained by sonication in ultrasonic bath for 10 min (fig. 1c). Particles were from 4 to 9nm thick (4-11 layers) and from 2 to 10µm large.

Different processing modes were applied for the preparation of nanodispersions, as follows: firstly, we apply 60 min high speed mechanical stirring at 20 000 r/min; then the mechanical mixing phase is followed by the ultrasonic treatment of 30 min at 200 W; lastly, we apply an additional ultrasonic treatment with the high power of 400 W for 15 min or 30 min. The nanodispersions at the different steps of preparation are rheologically characterized for controlling the state of dispersion. The graphene contents in the obtained nanodispersions vary within the range from 0.05 wt% to 1 wt.%.

Then, the appropriate amount of the hardener is added to the epoxy/graphene systems and the curing process is performed under ambient conditions, followed by thermal post curing (2 hours at 100 °C). The mixtures are then poured into molds. The cured samples are prepared for TEM analysis.

The rheological measurements were performed using AR-G2 Rheometer (TA Instruments) with cone-Peltier plate geometry (cone diameter 60 mm). Dynamic viscosity,  $\eta'$ , storage, and loss moduli,  $G'$  and  $G''$ , were measured versus the angular frequency,  $\omega$  of 0.1÷100 rad/s at low strain amplitude of 0.01 (viscoelastic range) and the gap size was of 29 µm between cone and plate. The linear viscoelastic range of the strain amplitude was determined by strain sweep test at the angular frequency of 1 Hz. All rheological measurements were performed at a temperature of 20 °C. The TA Advantage Software was used for data analysis and calculation of relaxation time spectra.

Transmission Electron Microscope (TEM) at 200 kV accelerating voltage was used for the analysis of epoxy/graphene nanocomposites. Thin sheets of < 100 nm thickness were cut from the cured nanocomposite samples using microtome and placed on a standard copper TEM grid, then observed at different magnifications. The phase composition was determined by the selected area electron diffraction (SAED) mode of the microscope.

### **3 RESULTS AND DISCUSSION**

#### **3.1 Effect of mixing conditions on the dynamic viscosity**

In order to evaluate the effect of different mixing conditions, like the high speed mechanical mixing and the different intensity of ultrasonication treatment (US) on dynamic viscosity, rheological measurements in dynamic mode were carried out. Figure 2 represents dynamic viscosity,  $\eta'$ , vs. angular frequency,  $\omega$ , for epoxy/graphene nanodispersions as varying nanofiller content and the mixing conditions, such as: step (1) - 60 minutes of high speed mechanical mixing (60' Mech), followed by step (2) - 15 min US with the power of 400 W (15' US 400 W), or step (3) - 30 min US with the power of 400 W (30' US 400 W).

According to the obtained results on Figure 2 the viscosity of the dispersions is strongly affected by both the amount of graphene and the mixing regimes. At low filler content of 0.05 wt% graphene, the effect of mixing conditions is very strong. The first step of 60 min mechanical mixing produces dispersions of almost 1 decade higher values of dynamic viscosity at low frequencies compared with the next step of ultrasonication, and a shear thinning behavior is observed. The viscosity increasing after mechanical stirring may be associated with the high-level dispersion/exfoliation to single graphene sheets. However, the next step of sonication after mechanical mixing produces a Newtonian dispersion having viscosity values near that of the neat epoxy pre-polymer. Thus, the ultrasonic field probably facilitates the re-arrangement and assembly of the mechanically well dispersed graphene nanoplatelets in agglomerates.

At higher nanofiller contents, e.g. 0.5 and 1 wt% graphene, the viscosity increases with nanofiller content but the effect of different mixing conditions is less pronounced and 15 min of ultrasonication treatment with the power of 400 W shows slightly higher values compared to mechanical mixing. The probable reason for this is that at higher graphene contents the high-speed mechanical treating at the same conditions is not enough for the good dispersion of the graphene sheets and the effect of dispersing is better at lower filler content. With increasing of the concentration at the same fixed speed and time of mechanical stirring, the filler, is not dispersed in the same manner. This means that at the same speed and time of dispensing, the increase in the concentration does not lead to complete dispersion as at the lower filler content. The small fluctuation of the viscosity curves is probably due to the anisotropic form of the graphene flakes.

#### **3.2 Dynamic characteristics at three mixing regimes, as varying GR content**

In order to compare the rheological behavior of nanodispersions at different mixing regimes as varying nanofiller contents, Figures 3(a-c) represent the storage modulus,  $G'$ , vs. angular frequency,  $\omega$ , for epoxy/graphene nanodispersions, as prepared by mechanical mixing and ultrasonic mixing.

Figure 3(a) represents linear viscoelastic storage modulus,  $G'$ , vs. angular frequency,  $\omega$ , for the mechanically mixed nanodispersions. In the plot of the frequency sweep, the storage modulus ( $G'$ ) of the neat epoxy resin follows a classical linear viscoelastic curve; this is called terminal or liquid-like behavior. For pure epoxy pre-polymer, the typical linear viscoelastic response of a liquid, with scaling laws  $G' \sim \omega^2$  is approached. The storage modulus,  $G'(\omega)$ , of the resin strongly increases by addition of the graphene nanofiller and reaches a low frequencies plateau only at 0.05 wt% graphene, showing non-terminal or solid-like flow behavior. The same situation can be observed in Figure 3(b,c) after 30 min of ultrasonication treatment with the power of 200 W, followed by 15 (b) and 30 min (c) with the power of 400 W, but at the higher concentrations of 0.5 wt% and 0.7 wt%, respectively. These transitions in flow properties of the resin with addition of nanofiller are typical when a percolating network exists [29,46,47]. In other words, such a behavior of the mechanically mixed graphene/epoxy dispersions is an indication for a formation of an intrinsic network of graphene nanoplates in the epoxy matrix at very low concentration of 0.05 wt%.

Figure 3(b) represents storage modulus,  $G'$ , vs. angular frequency,  $\omega$ , for epoxy/graphene nanodispersions as varying nanofiller content from 0.05 wt% to 1 wt% after 30 min of ultrasonication treatment with the power of 200 W, followed by 15 min with the power of 400 W. Storage modulus,  $G'$ , of the resin increases by addition of the graphene nanofiller. At low frequency, storage modulus ( $G'$ ) increases and the dependency on frequency decreases as graphene nanofiller concentration increases and reaches a plateau after 0.5 wt% graphene dispersion, showing solid-like flow behavior. The same situation is on Figure 3(c), which represents the storage modulus,  $G'$ , vs. angular frequency,  $\omega$ , for epoxy/graphene nanodispersions as varying nanofiller content from 0.05 wt% to 1 wt% after 30 min of ultrasonication treatment with the power of 200 W, followed by 30 min with the power of 400 W.

For all mixing regimes as the graphene content increases the storage modulus also increases, becoming more independent of frequency and hence the plateau becomes larger. According to this result and observing the curves, we are able to confirm that the rheological percolation thresholds are close to 0.05 wt% after the first mixing regime of 60 min mechanical stirring. Such a low percolation threshold around 0.05 wt % of graphene is a strong evidence for excellent homogenous dispersion of large graphene nanoplates throughout the matrix. While if ultrasonic filled is applied for dispersing, the percolation threshold appears at higher nanofiller content around 0.5 wt%. We assume that larger graphene nanoplates produced by mechanical mixing are cut by high power of sonication. Recent studies on polymer-graphene nanocomposites have reported percolation thresholds, electrical or rheological, higher than theoretical values [48–52]. The use of melt mixing and even solution mixing of graphene sheets in different polymer matrices has resulted in a percolation threshold within the range 0.5 to 1 vol% of graphene [48–52].

### 3.3 Structure and morphology

The morphologies of epoxy/graphene nanocomposites were characterized using TEM. TEM images of the graphene/epoxy composites can further demonstrate the above conclusions. A representative TEM images of: (a) 0.1 wt%, (b) 0.4 wt%, (c) 0.7 wt% and (d) 1wt% epoxy/graphene nanocomposites at higher magnifications are shown in Figures 4(a-d). As well known, the graphene sheets are highly agglomerated and folded [6,53-56], and, after high speed mechanical stirring at 20 000 rpm and powerful sonicating at 400 W, a well exfoliated graphene sheets and relatively small clusters of the pristine graphene sheets can be observed on Figures 4

(graphene is composed of several such stacked single-layer sheets). For all filler contents, there are well dispersed and even exfoliated graphene layers, which are assembled in micron-sized agglomerated structures (with TEM we can observe only agglomerated structures and single graphene layers are almost transparent).

Figures 5(a-d) show a representative TEM images of: (a) 0.1 wt%, (b) 0.4 wt%, (c) 0.7 wt% and (d) 1wt% epoxy/graphene nanocomposites at lower magnifications. The figure demonstrates a very good distribution of large agglomerates with increasing of the filler content.

Experimental evidence about the debonding of graphene sheets can be observed under TEM [10]. As can be seen in Figures 5(a-d), the gap between the sheet and matrix can be clearly observed. Normally, the diamond knife used in ultramicrotome would induce a relatively high stress during the preparation of TEM specimen. Under such high stress field, the few-layer graphene agglomerates usually delaminate or slips by each other during the fracture process due to the weak adhesion between both the sheet/sheet and sheet/matrix. In addition, a relatively large 2D sheets can bridge micro-crack, which can stabilize and stop developing into large and harmful cracks to the composites. With the micro-crack propagating, however, the poor filler/matrix interface results in the pull-out of graphene sheets when the stress exceeds the filler/matrix interfacial strength [7]. The debonding/delamination or pull-out of graphene was able to trigger and promote the local plastic deformation of matrix such as shear banding to dissipate fracture energy [57]. The above findings suggest that the debonding/delamination and crack bridging of graphene should be the key elements of the toughening effect in the epoxy composites.

### 3.4 Relaxation time spectra

Rheological experiments can be used to more specifically probe the properties of the interfacial region by computation of the linear relaxation spectrum,  $H(\tau)$  [58-60]. Relaxation is due to various processes taking place within the sample, mainly the motion of the whole parts of the polymer molecules. Each relaxation process, or “mode”, contributes a strength and time scale to overall relaxation effect, and  $H(\tau)$  represents the strength of relaxation at each time scale. The linear relaxation model provides the following relation between the relaxation spectrum  $H(\tau)$  and the linear relaxation modulus,  $G(\tau)$  [61,62]:

$$G(T) = \int_{-\infty}^{+\infty} H(T) \exp\left(-\frac{t}{\tau}\right) d \ln \tau$$

where  $\tau$  is the relaxation time and  $t$  is the experimental time.

As nanofiller is added, if the mobility of the polymer chains is altered, the relaxation spectra can either shift (if the interface causes global changes in the polymer relaxation times) or broaden (if the interface creates only local changes in polymer relaxation behavior) [29,58]. Figure 6 represents the relaxation time spectra of epoxy/graphene nanodispersions for different graphene contents from 0.05 wt% to 1 wt%. In the relaxation spectra within the range of the high relaxation time region from  $10^{-1}$  to  $10^2$  s, we observed a shifting of relaxation spectra curves to higher relaxation time by increasing of the nanofiller content. By increasing the filler content from 0.05 wt% to 1 wt% the weight of the spectra increased with 3-4 decades. This confirms our

proposal that the mobility of the polymer chains is significantly altered. This effect starts to be significant at very low graphene content of 0.05 wt%.

## 4 CONCLUSIONS

Epoxy nanocomposites containing a small amount of graphene within a range of 0.05 wt% to 1 wt% are investigated using a rheological approach to determine the stage of nanofiller dispersion in the epoxy matrix and the development of rheological properties with filler content, mixing method and mixing time. The influence of mechanical stirring, sonication time and intensity during mixing is examined. The results showed a transition in flow properties of the resin with addition of graphene, typically for the percolating network. Such a behavior was an indication of network formation involving assembly of single nanolayers into 3D network at very low concentration. For the investigated nanodispersions, the very low rheological percolation threshold was estimated at  $\phi_p = 0.05$  wt% graphene filler content after the first stage of 60 min of mechanical stirring. Such a low percolation threshold at 0.05 wt% after mechanical mixing is strong evidence for excellent homogenous dispersion of graphene nanoplates throughout the matrix with used methodology. Although all used methods of dispersion (high speed mechanical stirring and sonication with different power and time), at lower concentrations, the filler is dispersed better, while at a higher concentration, homogenization is not the same at the same types, speeds, and times of stirring. This is a problem that makes very hard to draw up a protocol for the preparation of the nanocomposites. At low concentration at mechanical stirring we assume that graphene is dispersed at large flakes while the ultrasonic field probably cut the graphene sheets. Therefore the percolation threshold at mechanical stirring is 0.05 wt%, but for the composition subjected to ultrasonic mixing the percolation thresholds appear around 0.5 wt%. TEM images of the graphene/epoxy composites have confirmed the above conclusions and showed well exfoliated graphene sheets and relatively small clusters of the pristine graphene sheets.

The relaxation results showed extremely strong effect of interfaces on the changes of the polymer relaxation behavior. The weigh (H) of the spectra was shifted, in composite, to several decades higher values. The effect became much stronger by increasing of the graphene content only above 0.05 wt%. The relaxation spectra calculation was proposed as highly efficient rheological approach to probe the effect of interfaces in graphene/polymer nanocomposites. In the future, we will use these new epoxy resin/graphene nanocomposites as matrices of continuous fiber-reinforced composites to improve their electrical and mechanical properties.

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## Figure Captions

**Figure 1(a,b):** Expandable graphite observed before (a) and after (b) irradiation with microwaves. The exfoliation of EG and holes due to the violent expulsion of gases are clearly visible. Graphene is visible after sonication treatment (c).

**Figure 2:** Dynamic viscosity,  $\eta'$ , vs. angular frequency,  $\omega$ , for epoxy/graphene nanodispersions as varying nanofiller content from 0.05 to 1 wt% at different mixing conditions: 60 minutes of high speed mechanical mixing (60' Mech) at 20 000 rpm, followed by 15 min of ultrasonication treatment with the power of 400 W (15' US 400 W) and by 30 min with the power of 400 W (15' US 400 W).

**Figure 3(a-c):** Dynamic storage modulus ( $G'$ ) vs. angular frequency ( $\omega$ ), for epoxy/graphene nanodispersions, at varying graphene contents in the range 0.05 - 1 wt% and with the following mixing regimes: (a) 60 min mechanical mixing, followed by (b) 30' US at 200W and 15 min US at 400 W; or (c) 30' US at 200W and 30' US at 400 W.

**Figure 4(a-d):** Representative TEM images of: (a) 0.1%, (b) 0.4 wt%, (c) 0.7 wt% and (d) 1wt% epoxy/graphene nanocomposites at higher magnifications.

**Figure 5(a-d):** Representative TEM images of: (a) 0.1%, (b) 0.4 wt%, (c) 0.7 wt% and (d) 1wt% epoxy/graphene nanocomposites at higher magnifications.

**Figure 6:** Relaxation time spectra of epoxy/graphene nanodispersions for different graphene contents from 0.05 wt% to 1 wt% at 15 min of ultrasonication treatment with the power of 400 W.

Figure 1(a,b):

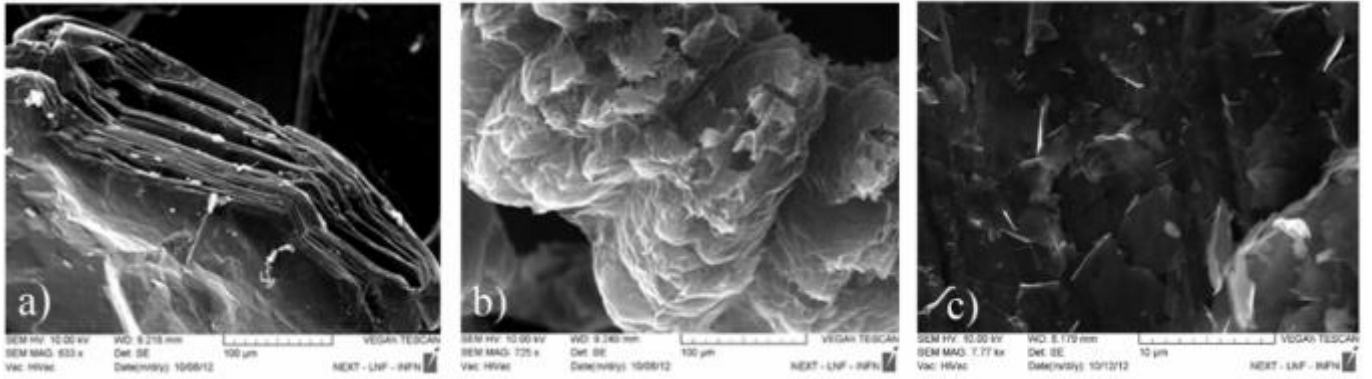


Figure 2:

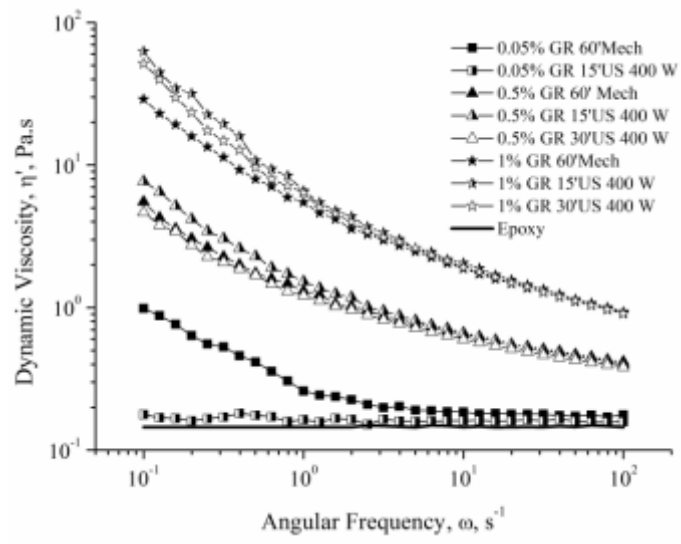
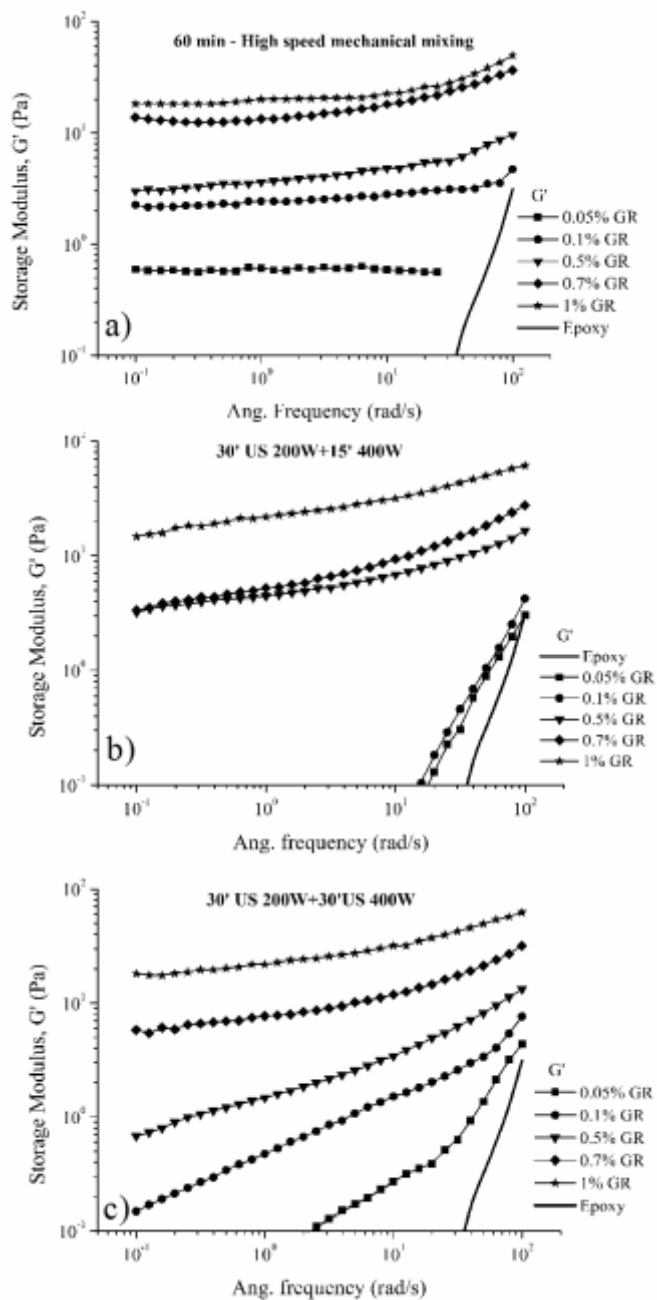


Figure 3(a-c):



**Figure 4(a-d):**

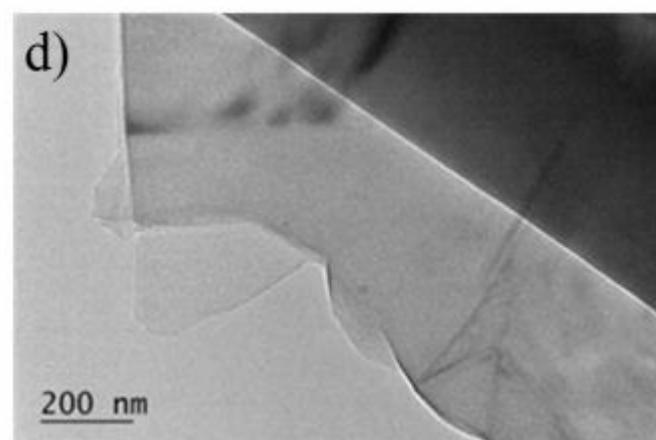
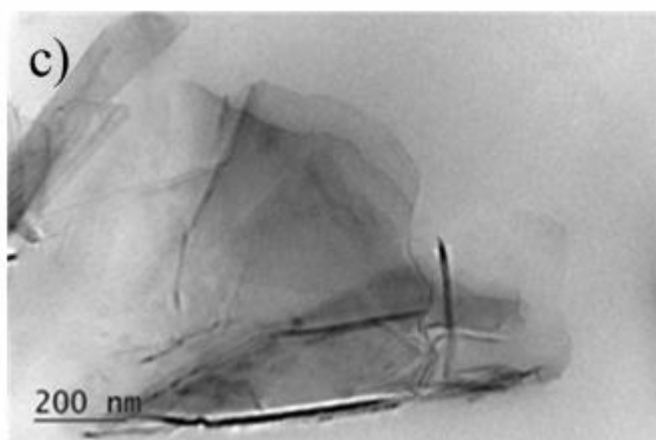
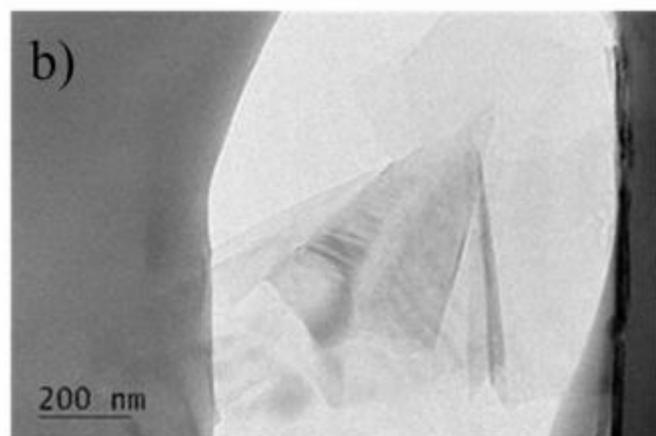
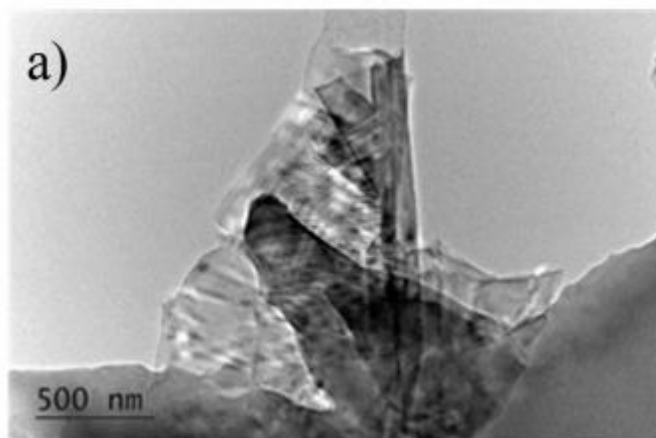




Figure 5(a-d):

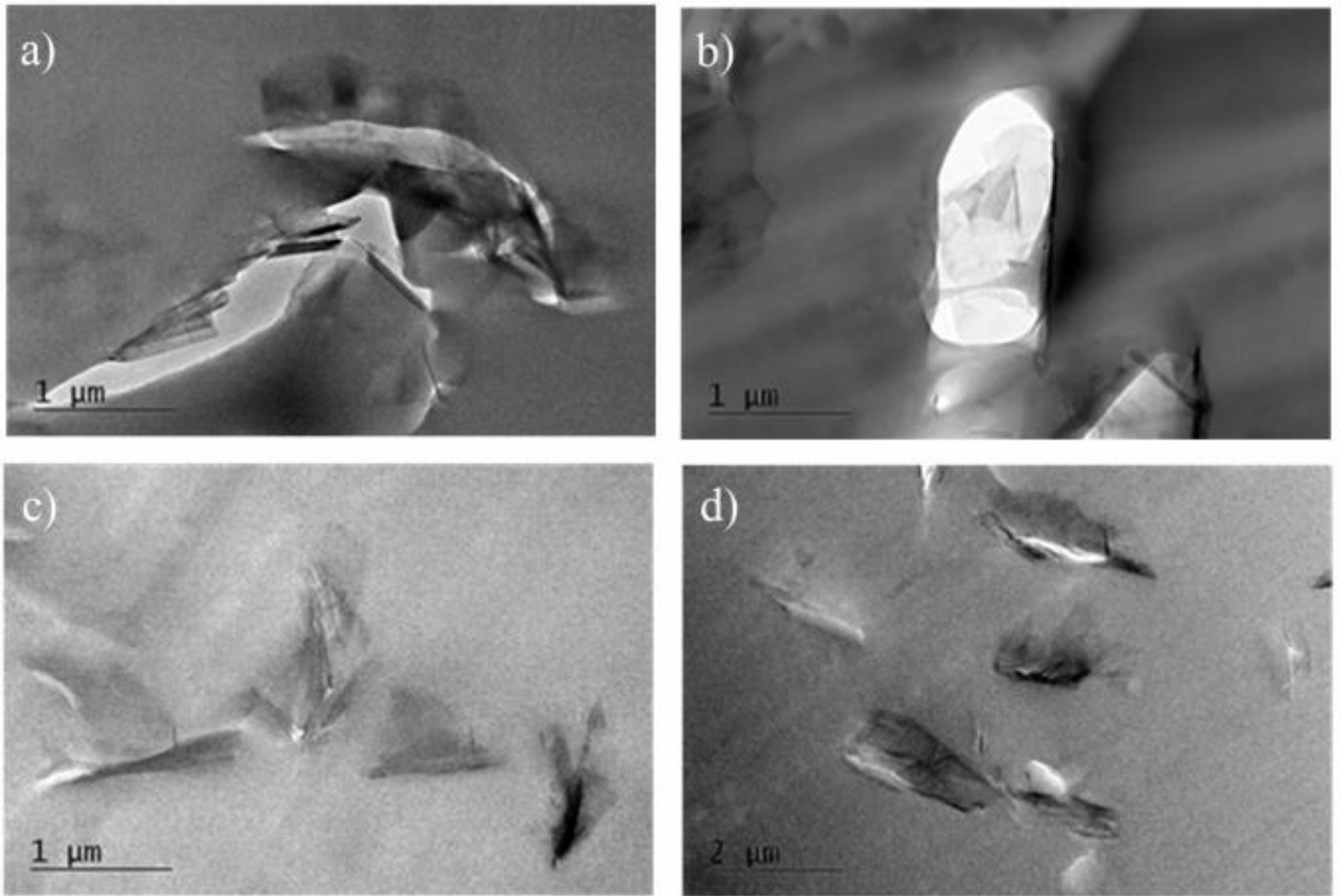


Figure 6:

