ON THE MULTI-FUNCTIONAL BEHAVIOR OF GRAPHENE BASED NANO-REINFORCED POLYMERS

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Abstract

The objective of this research is to investigate the influence of few layered Graphene Nano-Platelets (GNPs) on the multi-functionality of nano-reinforced epoxy polymers. Graphene based polymers containing different GNP loading levels [0.5, 1, 5, 10, 15%wt.] were developed by using the three-roll mill technique. Thermal conductivity measurements, thermo-mechanical and mechanical tests were performed in order to explore the effect of GNPs in final properties of nano-reinforced polymers. The results indicate that thermal conductivity of prepared materials increases with the increasing content (>5%wt.) of GNPs into the polymer. Specifically, the thermal conductivity of doped polymers with 15%wt. GNPs showed 130% enhancement over the reference material. Furthermore, the glass transition temperature of nano-reinforced polymers remained almost unaffected from the GNP inclusion. Finally, in the case of mechanical testing, it was found that the modulus (tensile and flexure) of the doped materials increase with the increasing GNP content into the polymers while the corresponding strengths did not follow the same trend. However, the aforementioned strengths were not significantly diminished with the presence of GNPs while the highest increases in tensile and flexural modulus, 48 and 38% respectively, were exhibited by introducing the highest content (15%wt.) into the polymer.

1. Introduction

In recent years the use of nano-materials as fillers in the production of nano-reinforced polymers has attracted increasing interest due to their unique properties and numerous potential applications in the automotive, aeronautic, aerospace and electronic industries. This is due to the fact that the addition of nano-metric additives into polymers may drastically enhance their properties and consequently their multi-functionality. Toward this direction, the majority of research has focused on polymer nano-composites based on carbon nano-species (CNSs). Numerous carbon additives such as carbon black (CB), carbon nanotubes (CNTs), and carbon nanofibers (CNFs) have been utilized to enhance the properties of a pure polymer [1-4]. Since their discovery, graphene nanospecies (GNSs) were considered as potential alternative of the aforementioned carbon nano-species for the development of multi-functional nano-composites due to their superior mechanical, thermal and electrical properties [5-10]. This study focuses on the development of graphene based nano-reinforced polymers with improved multi-functionality. In particular, the effect of GNP loading content in mechanical, thermo-mechanical and thermal properties of final nano-composites is described.

2. Experimental section

2.1 Materials

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The matrix material, used in this study, was an epoxy B-stage system supplied by Huntsman Advanced materials, Switzerland. This system contains the low-viscosity epoxy resin Araldite LY1556, the hardener paste Aradur 1571, the accelerator paste 1573 and the polyamine hardener Aradur XB 3403.
The graphene nanoplatelets (GNPs) were 97% pure and obtained from Cheap Tube Inc., USA. GNPs are consisted of ~4 graphene layers with an average thickness of <4 nm and a typical diameter of 1-2 microns while their surface area is about 750 m^2/g.

2.2 Preparation of samples

Nano-modified suspensions were produced using 3 roll-mill, also known as calender. The distance between the rollers varied from 120 μm down to 5 μm depending on the milling cycle, the sequential gap settings were 120, 40, 13, 5 μm respectively, and five cycles of milling were repeated for each gap setting in order to process the graphene based blends. The speed of the apron roll was maintained at 270 rpm. The other three parts of the B-stage system were added to the prepared mixture and placed in a vacuum chamber to avoid air inclusion. Then, the produced material was poured in silicon rubber moulds and cured, according to manufacturer recommended curing cycle, 2h at 120°C and 6 bars pressure. Following the aforementioned process, graphene based nano-reinforced polymers in different loading levels were developed: 0.5, 1, 5, 10 and 15%wt. GNPs. Neat epoxy samples were also produced for reference.

2.3 Testing Campaign

Thermal conductivity of the developed materials was measured by using a thermal conductivity analyzer (TCi Mathis). TCi Mathis Analyzer measures directly and rapidly the through thickness thermal conductivity of a sample at room temperature, providing a detailed overview of its thermal characteristics.Four specimens were measured for each tested material type. The dimensions of the measured samples were 25mm x 25mm x 5mm. Moreover, the glass transition temperature of the materials was determined by the use of DMTA 983 of Du Pont (TA Instruments, Inc., USA). The specimens were subjected to Dynamic Mechanical Analysis tests with a testing frequency of 1Hz, a heating rate of 2^0C/min and a temperature range of 25-250°C. Two samples were used for each produced material and the dimensions of the specimen were 50mm x 10mm x 3 mm. Next, tensile and 3-Point Bending tests were performed by the use of an INSTRON 8872. At first, tensile tests of six dog-bone specimens of each prepared material were carried out according to standard: ISO 527-2. The applied rate was 1mm/min. Then, the flexure tests were performed based on standard: ISO 178. At least five rectangular specimens of each material were used and the cross-head rate was 2 mm/min. Finally, Scanning Electron Microscopy (LEO SUPRA 35VP) was used in order to estimate the morphology of used fillers and the statistical dispersion of nano-particles into the matrix.

3. Results and Discussion

3.1 Thermal conductivity measurements

The following bar diagram presents the results of thermal conductivity of the produced reference and nano-reinforced polymers. It is evident, that the reference material appeared insulating behavior while the addition of GNPs into the polymer proved beneficial for the enhancement of thermal conductivity of final products. In particular, it is observed that thermal conductivity of the epoxy system was significantly increased in the case of polymers that are reinforced with higher contents of GNPs (>5%wt.). Furthermore, after the content of 5%wt., it is obvious that thermal conductivity of nano-reinforced polymer increases with the increasing content of GNPs into the polymer. A possible explanation is that with the increasing GNP content, the distance between the adjacent platelets is reduced, as it is evident in SEM images in Figure 7. This fact probably leads to the reduction of the thin, insulated polymer film which exists between the two phases (matrix and filler) resulting in a

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more effective phonon transport between them and as a consequence in better results in the improvement of thermal conductivity. As it can be seen in Figure 1, the highest increase, 130%, was succeeded at the highest GNP content (15%wt.) into the polymer.

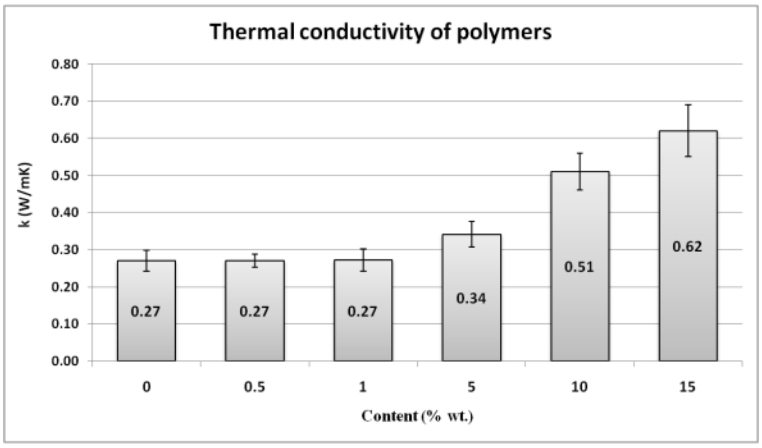

Figure 1: Thermal Conductivity of produced polymers

3.2 Thermo-mechanical tests

Thermo-mechanical tests were performed in order to define the glass transition temperature of developed nano-reinforced polymers. The glass transition temperature (Tg) of developed materials that resulted from DMA tests are presented in Figure 2. It is observed that Tg values of nano-reinforced polymers are lower in comparison with that of the reference material. Even though it was not observed any enhancement of Tg with the addition of GNPs into the polymer, it is evident that their presence in the reference material did not lead to a significant degradation of Tg. This fact is in contrast to what was expected based on literature. Generally, it is believed that the macromolecular movement in the nano-reinforced polymer is restricted by the presence of the nano-filler, affecting positively the Tg of the polymer. Nanometer size particles limit the segmental motion of polymer chains and as a result the need for higher temperatures in order to transit the material from glassy state to rubbery state [11]. As it is obvious, the results in this study were not in agreement with the aforementioned theory. According to the literature [12], the good adhesion between matrix and filler, the geometry and volume fraction of nanofillers and finally the curing conditions are the basic factors that can significantly affect Tg. Taking into consideration that the curing conditions were the same for all the tested materials it is concluded that the quality of the adhesion and the geometry of the fillers maybe were not the appropriate for the improvement of glass transition temperature.

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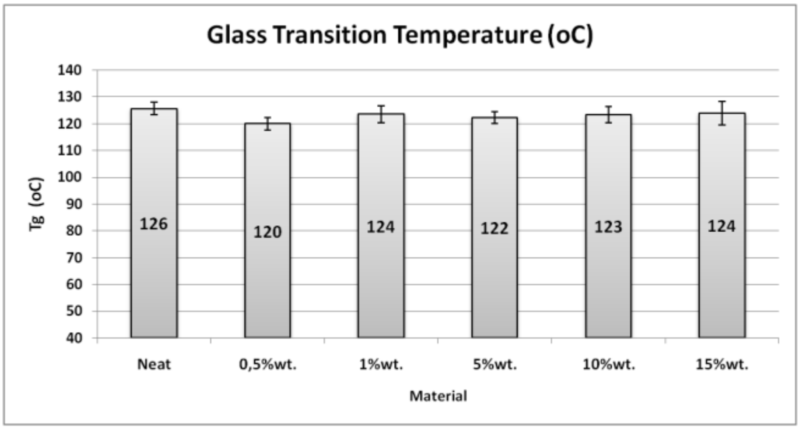

Figure 2: Thermo-mechanical properties of produced polymers

3.3 Mechanical Tests

The following figures present the results obtained from the performance of tensile and flexure tests.
It is worth mentioning that tensile and flexure properties showed similar trends. Specifically, the modulus increases with the increasing content of GNPs into the polymer while the strength of the final products is not improved with the addition of GNPs. This fact is in accordance with literature. It is well known that the modulus of particulate reinforced composites is mainly depending on the moduli, rigidity, volume fraction and dimensions of the composite constituents, rather than the interfacial connection between filler and matrix. On the other hand, their strength is mostly depending on the interfacial adhesion among the filler and matrix [13]. The degradation of strength can be attributed to the inevitable aggregation between GNPs as shown in SEM micrograph (Figure 8a). Additionally, GNPs tend to bend/buckle and roll up as shown in SEM micrograph (Figure 8b). The above observations probably contributed to the deterioration of the effective aspect ratio and specific surface area of GNPs resulting in a weak interfacial adhesion between matrix and filler which prevented the improvement of mechanical properties. However, it should be mentioned that the GNP presence in the polymer did not lead to a significant degradation of tensile and flexure strength while the nano-reinforced polymers with 15%wt. GNPs exhibited the highest increase in tensile and flexural modulus, 48 and 38% respectively.

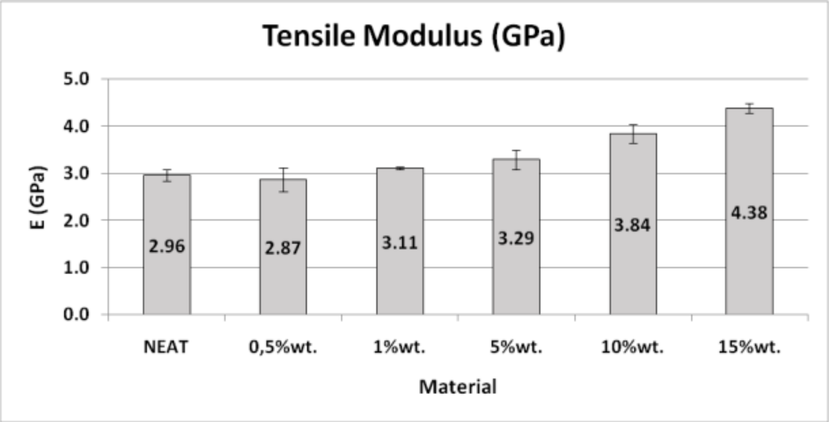

Figure 3: Tensile modulus of produced samples

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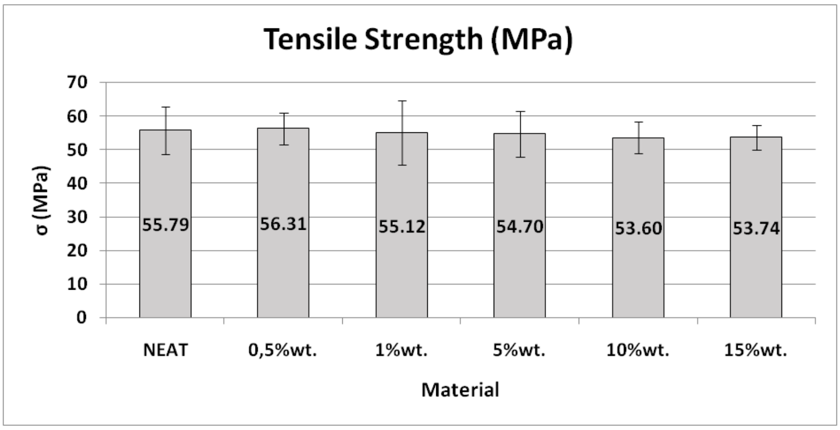

Figure 4: Tensile strength of produced samples

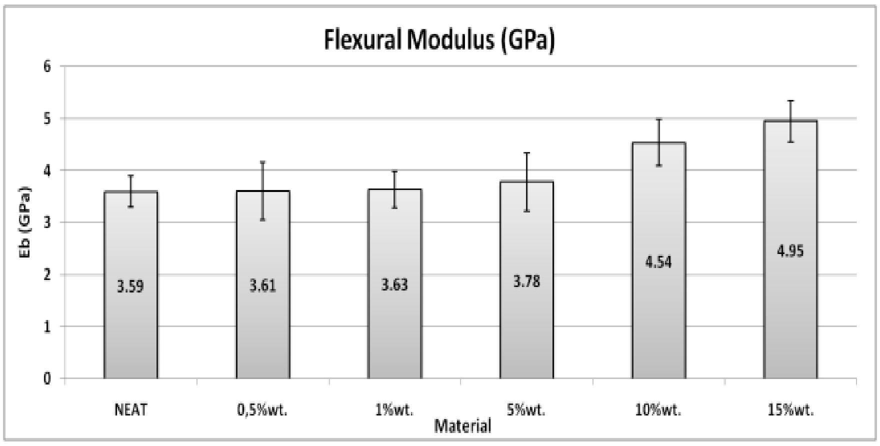

Figure 5: Flexural modulus of produced polymer

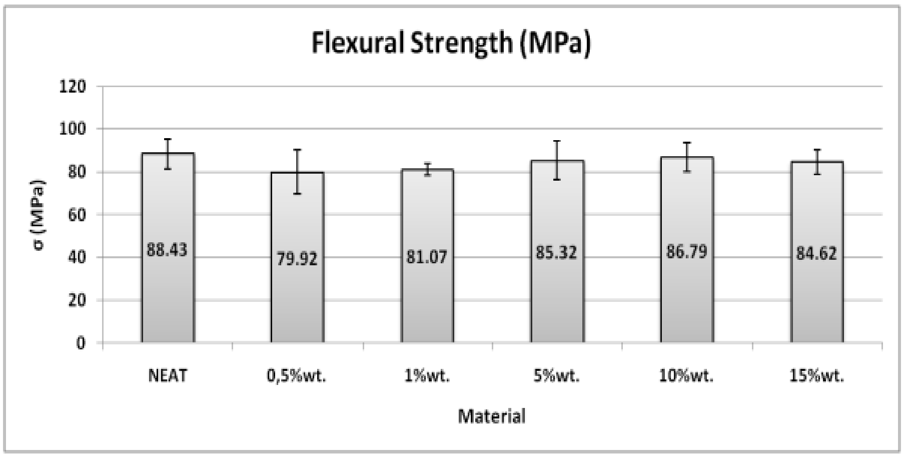

Figure 6: Flexural strength of produced polymer

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3.3 SEM

The representative SEM micrographs of the nano-reinforced polymers filled with different weight contents of GNPs are shown in Figure 7. It can be shown from the figures that the GNPs are fairly good dispersed in the nano-reinforced polymers. However, it is observed that the increasing filler content in the epoxy leads to the creation of more intense aggregation between the particles.

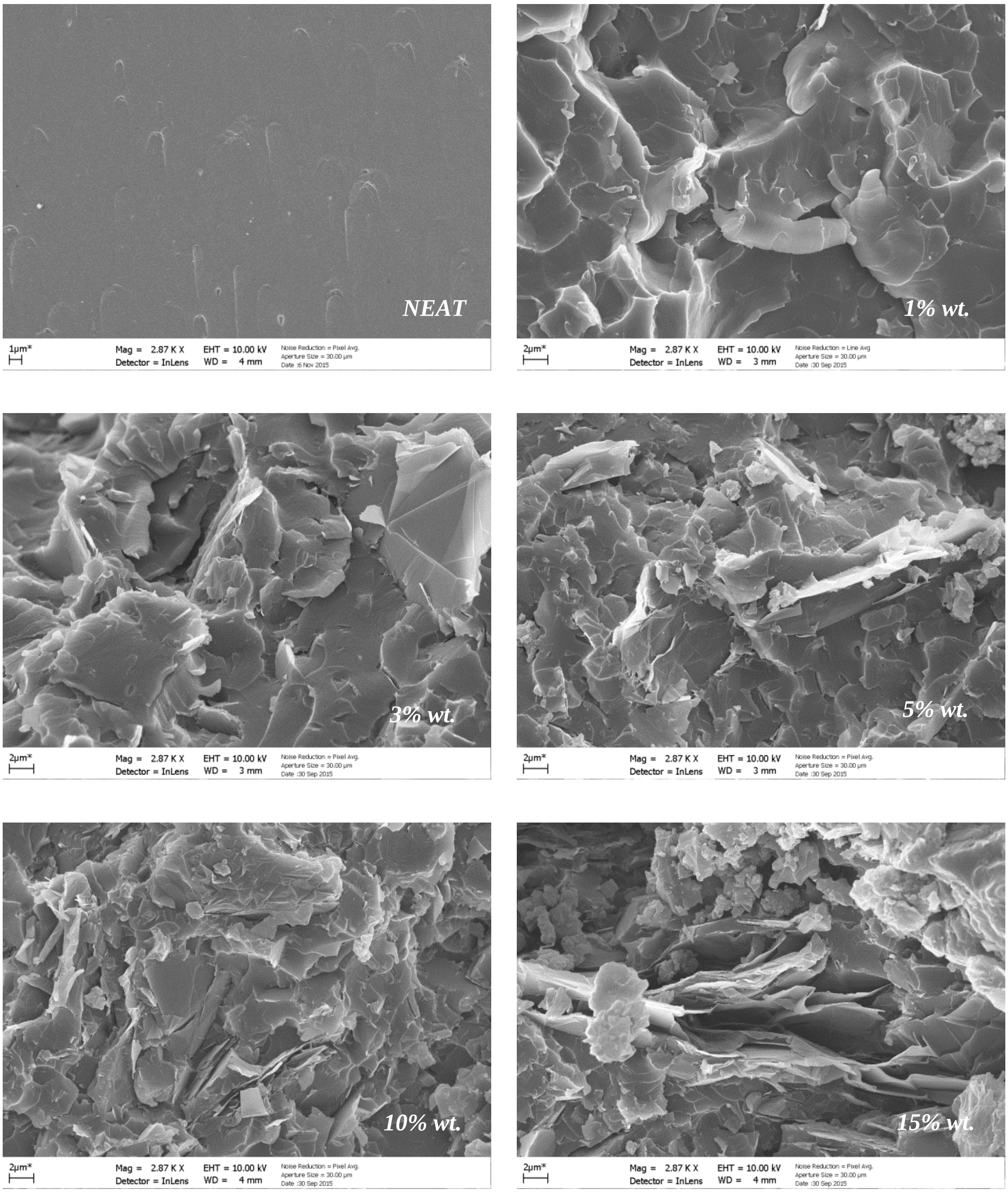

Figure 7: SEM-images of the reference and nano-reinforced polymers filled with different contents of GNPs

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Figure 8 presents the agglomeration between the particles, the buckling and the rolling up of GNPs that were observed in the case of 0.5%wt. GNP nano-reinforced polymer.

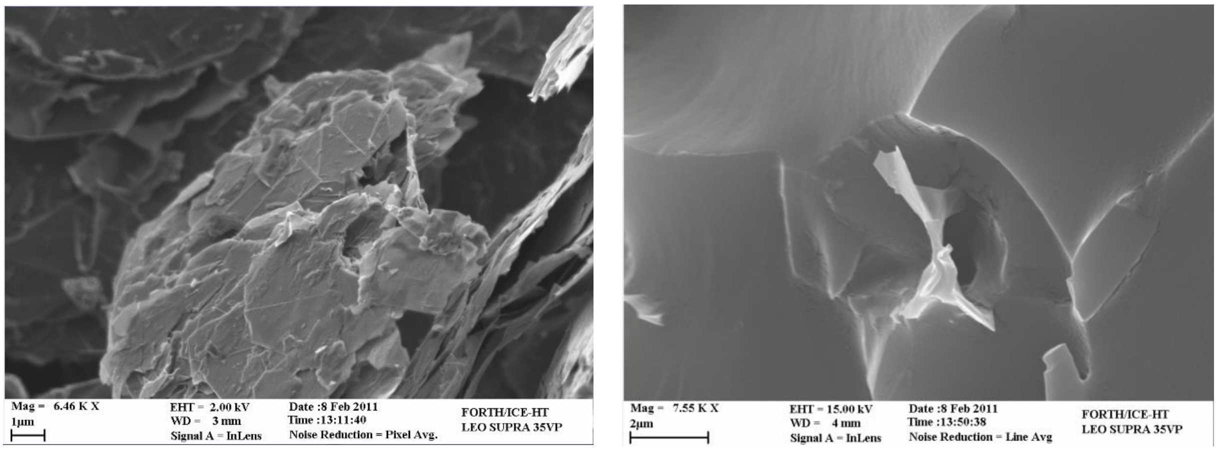

Figure 8: SEM micrographs of (a) GNP agglomeration, (b) buckled and rolled up GNP (0.5%wt. GNP nano-reinforced polymer)

4. Conclusions

Thermal conductivity of nano-reinforced epoxy polymers increased with the inclusion of high GNP contents (>5%wt.) into the polymer. It was found that the addition of 15%wt. GNPs into the epoxy matrix caused an increase of 130% in thermal conductivity of developed materials. In addition, the glass transition temperature of nano-reinforced polymers was not influenced by the GNP introduction. Finally, it was observed that tensile and flexure properties of graphene based polymers have similar trends. Specifically, the modulus increases with the increasing content of GNPs into the polymer while the strength of the final products is not enhanced with the addition of GNPs.

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