In-situ preparation of epoxy-based hybrid materials with graphene oxide and partially exfoliated graphite filler

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Carbon–based composites have become the interesting materials due to their low cost and wide field of applications including aircraft components, solar cells, sensors, transistors, supercapacitors, electronic and automobile devices, etc. [1-4] The combination of excellent mechanical and physical properties of carbon fillers with poor properties of some polymeric matrices often causes a significant improvement in material strength, conductivity, hardness, etc. [5-9]. Nevertheless, the main problem is always to receive a good dispersion and hinder the agglomeration process of high surface additives. For instance, the preparation method of stable single layer graphene solutions from natural graphite is still performed mainly through a chemical way. However, it is difficult to obtain the same single-layer effect in polymer matrices [10-12]. Therefore, the development of less drastic innovative technique could help in production of a new class of nanocomposites. Accordingly, our goal was to obtain stable graphene and graphene oxide dispersions in epoxy matrix using different sonication methods. Such homogenous materials could be further used in synthesis of organic-inorganic nanohybrids.

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In this study, we reported the preparation of graphene and graphene oxide solutions in a solvent as well as in an epoxy resin. In the first synthesis step, natural graphite was exfoliated using high intensity cavitation field in a pressure batch-ultrasonic reactor (UIP 2000hd, 20 kHz, 2000 W, Hielscher Ultrasonics GmbH) [13]. As a result, high quantity of graphene was produced and further oxidized to graphene oxide in water solution [14]. In order to improve the adhesion between the inorganic filler and epoxy matrix, the received GO was functionalized with a tetrafunctional amine (MDEA, Lonzacure™ M-DEA, Lonza) using water-bath ultrasounds at 60˚C. The obtained dark violet precipitation was easily homogenized with diglycidyl ether of bisphenol A (DGEBA) in ultrasounds. The rheology of such mixtures, differing in GO : DGEBA ratio, was studied. In the case of samples containing 1.3 wt. % of GO shear thinning behavior was observed. This solid-like flow behavior indicated formation of epoxy-amine network. In contrast, the samples with lower amount of functionalized GO showed a Newtonian behavior. Such homogenous epoxy precursors were cured to obtain bulk hybrid materials possess increased rubber and Young's modulus, hardness and thermal stability.

We also investigated the exfoliation process of natural graphite with addition of various ionic liquids (IL) as lubricating and stabilizing agents [15]. To receive well dispersed and stable solutions we used an optimum ratio of IL : graphite = 10 : 1. Surprisingly, the obtained degree of exfoliation was relatively high after 3h of sonication connected with cooling of the sample in water bath and conditioning under vacuum. This technique worked well in a solvent solution (dichloromethane) as well as in an epoxy resin (DGEBA). Thus prepared stable suspensions were further used in the synthesis of hybrid epoxy nanomaterials. Only the amount of 0.07 wt. % of graphite and 0.7 wt. % of IL was sufficient to significantly improve the thermomechanical properties of final materials. In such filler loading the glass transition temperature remained comparable with the neat matrix, what implied lack of re-agglomeration process. The obtained composites were fully translucent and homogenous, showing increase in rubber and Young's modulus, toughness and thermal stability.

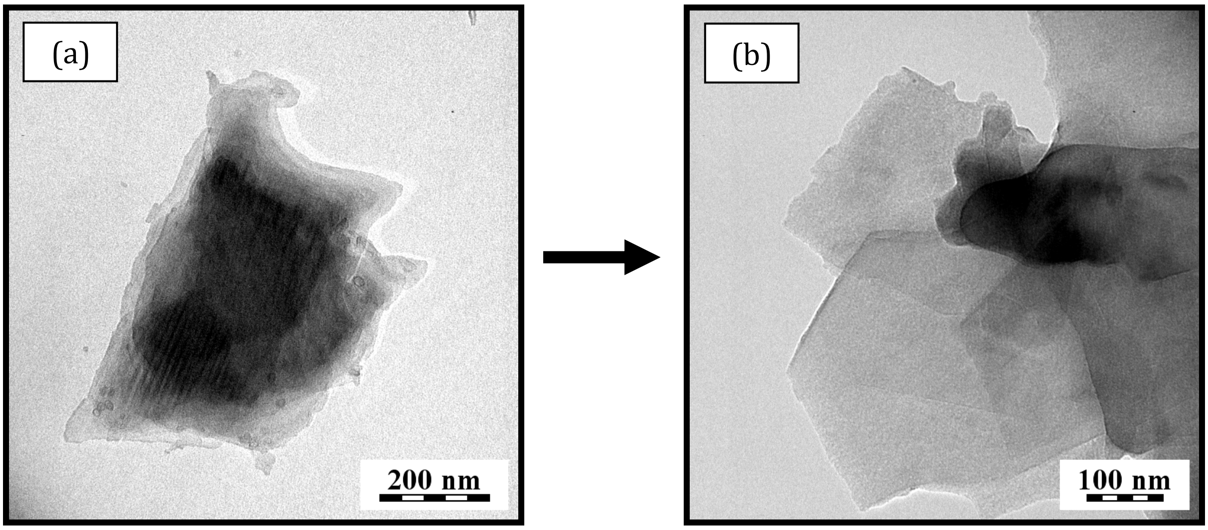

Figure 1: TEM images of graphite-epoxy solutions after treatment in ultrasounds with no (a) and 0.7 wt. % IL (b) addition.

To conclude, we developed a new and simple method of graphite exfoliation and stabilization of the product by suitable IL. The addition of ILs helped to improve the adhesion between inorganic filler and organic matrix, what resulted in increased mechanical properties of the final hybrid materials. The functionalization of graphene oxide by amine hardener led to improved filler-epoxy matrix interphase [16].