Improving nanocomposite performance with graphene oxide and graphene nanosheets

Marya Raji, Hamid Essabir, Denis Rodrigue, Rachid Bouhfid, and Abou el kacem Qaiss

A good dispersion of graphene nanoparticles and nanosheets in polyvinylidene fluoride, achieved by combining solution mixing and melt compounding, improves its mechanical and electrical properties.

Graphene, a 2D material with a honeycomb carbon lattice structure, shows great promise for use as a nanofiller in numerous applications due to its special properties (e.g., high mechanical and electric conductivity, and low manufacturing cost).[1] This is particularly true regarding the addition of graphene to polymeric materials, which show significant improvements at low filler content.

The use of graphene in the production of nanocomposites (NCs) can, however, be limited by the large surface energies that are generated by the strong van der Waals force experienced by the nanoparticles. This force can lead to agglomerations. In the case of graphene nanosheets (GNs), individual GNs tend to stick together in polymer matrices and to rearrange into tactoid (i.e., microcomposite) structures. This behavior reduces the aspect ratios of the filler and thus limits the improvement to the properties of the resultant NC.[2] A suitable processing route is therefore key to preparing graphene NCs with new and improved properties for industrial applications.

We have successfully prepared two types of NCs based on polyvinylidene fluoride (PVDF) with graphene oxide (GO) nanoparticles or GNs as filler. The main objective of our work was to produce highly homogeneous dispersions and distributions of GO and GNs within a polymer matrix.[1] To obtain nanoparticles, we exfoliated natural graphite in solution using potassium permanganate and sulfuric acid to produce GO (as proposed by Hummers and Offeman[3]).[1] We then obtained GNs via the chemical reduction of GO. Our NC fabrication process involves two steps, i.e., a combination of solution mixing and melt-compounding. In the first step, we produced masterbatches of PVDF/GO and PVDF/GN at 10wt.% via solution mixing. In the second step, we diluted the masterbatch to the desired content (1, 2, 3, or 4wt.%) via melt processing (by twin-screw extrusion). We then
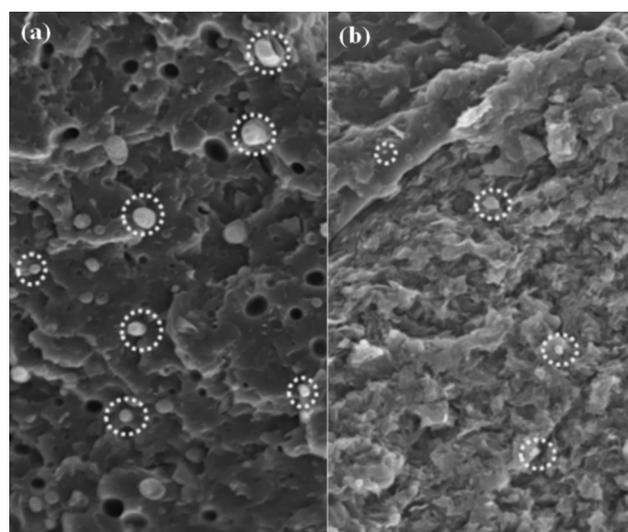

Figure 1. Typical scanning electron microscope images of the polyvinylidene fluoride (PVDF) nanocomposites containing 3wt.% of (a) graphene oxide (GO) nanoparticles and (b) graphene nanosheets (GNs).

pelletized and compression-molded the compounds to produce samples for testing, thus enabling the complete characterization of their morphological, mechanical, and electrical properties. Using our results, we were able to investigate the effect of the processing route on the dispersion and distribution of the nanoparticles inside PVDF.

Figure 1 presents typical scanning electron microscope images of both NCs (PVDF/GO and PVDF/GN) with filler loadings of 3wt.%. These images show that both types of nanoparticles (GO and GNs) are uniformly dispersed and distributed inside the PVDF matrix as a result of the optimized processing conditions that we implemented.[1]

We also studied the effect of GO and GNs on the mechanical properties of the PVDF NCs. The results—see Figure 2(a)—show that the addition of only 3wt.% GO or GNs leads to an improvement in the

tensile properties of the NCs in both cases, with GNs achieving higher values than GO. For example, the Young's modulus increased from 1232MPa for neat PVDF to 1621 and 1321MPa with the addition of 3wt.% GNs and GO, respectively (representing respective increases of 32 and 7%).[1] A higher nanoparticle content (4wt.%) results in lower values, however. This is due to the strong van der Waals force that is experienced between the individual sheets of graphene in the PVDF matrix. The force causes particles to stick together, thus reducing their aspect ratios.[4] We attribute the improvement to the Young's moduli (generally greater for GNs than GO) at low contents to good compatibility between PVDF and the nanoparticles. This compatibility arises due to the high surface area of the components and the fact that the GN

structure has fewer oxygen-containing groups. These features result in better interaction between the filler and the matrix,[5] thus enabling stress to be transferred to the fillers.

The most significant effect that arises in our NCs is an improvement in their electrical conductivity compared with that of PVDF. We attribute this behavior (which conforms to our expectations) to the intrinsic properties of these graphene nanofillers (i.e., they provide percolated pathways for electron transfer, thus introducing electrical conductivity into NCs even at low contents).[6] The electrical conductivity of PVDF/GO, PVDF/GN, and neat PVDF is compared in Figure 2(b), where a substantial improvement is exhibited as a function of filler content. For example, the results show that electrical conductivity increased from 5.9×10^{-14} S/cm for neat PVDF to 6.8×10^{-9} and 1.2×10^{-11} S/cm for NCs containing 3wt.% GNs and GO nanoparticles, respectively.[1] Our results also confirm the successful reduction of GO to form GNs. The higher electrical conductivity values (by about two orders of magnitude) that we observed for PVDF/GN compared with PVDF/GO arise due to the substantially larger aspect ratio of GNs compared to GO.[7] The remarkable increase in the electrical conductivity (by five orders of magnitude compared with neat PVDF) achieved with GNs at a low filler loading (3wt.%) also suggests restoration of the graphitic network of sp^2 bonds.[8]

In summary, we have developed a two-step methodology (combining solution mixing and melt-blending) that can successfully produce PVDF nanocomposites with well-dispersed GN and GO nanoparticles. Our results show that a low content (3wt.%) of GNs is able to substantially improve the tensile modulus (by 32%) and electrical conductivity (by five orders of magnitude) compared with neat PVDF. We are now investigating the potential of these materials for use in several applications, such as solar/fuel cells, electronics, and piezoelectric sensors.

Figure 2. *(a) Young's modulus and (b) electrical conductivity of PVDF/GO and PVDF/GN nanocomposites as a function of nanoparticle content.*

Author Information

Marya Raji, Hamid Essabir, Rachid Bouhfid, and Abou el kacem Qaiss
Laboratory of Polymer Processing
Moroccan Foundation for Advanced Science, Innovation and Research (MAScIR)
Rabat, Morocco

Marya Raji is a PhD student at Mohammed V-Rabat University in collaboration with MAScIR. His research focuses on the synthesis, preparation, and functionalization of nanocharges.
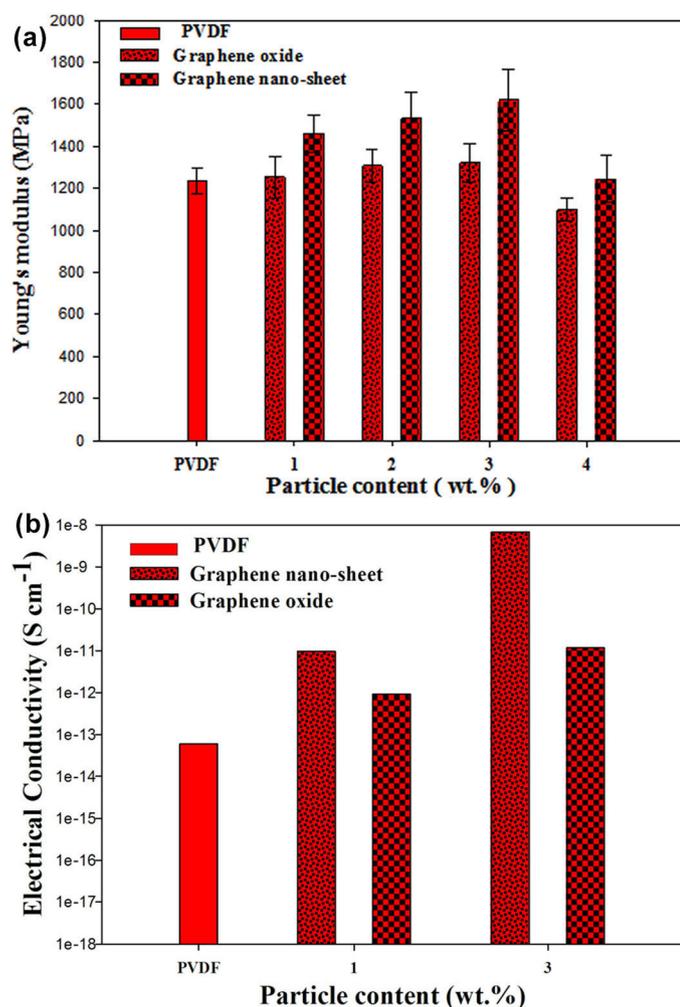
Hamid Essabir is a researcher in the composite and nanocomposite center at MAScIR, where he leads the polymer processing laboratory. He obtained his PhD from ENSA Agadir. His research interests include polymer processing, rheology, and composite and nanocomposite materials.

Rachid Bouhfid is a researcher in the composite and nanocomposite center at MAScIR. His research interests include organic synthesis, preparation, and functionalization of nanocharges based on clay, nanocellulose, and graphene.

Abou el kacem Qaiss is a researcher in the composite and nanocomposite center at MAScIR, where he leads the polymer processing laboratory. He obtained his PhD from Université Laval, Quebec (Canada). His research focuses on polymer processing, rheology, the physical chemistry of polymeric systems, and composite and nanocomposite materials.

Denis Rodrigue
Chemical Engineering
Université Laval
Quebec, Canada

Denis Rodrigue is a professor of chemical engineering. His work focuses on polymer processing and characterization, the rheology of complex systems, and recycling.

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