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Effects of ultrasonic vibration on polypropylene/graphene nanoplatelet composites

Suihua He and Jingjing Zhang

Ultrasonic vibration can reduce the size and effectively enhance the uniform dispersion of graphene nanoplatelets during extrusion, thus improving the electrical and thermal network in resultant composites.

Ultrasound-assisted extrusion[1–15] is a clean and efficient vibration technology that can be applied to the melt-blending process for nanocomposite (NC) fabrication.[1,2] A number of studies[3,11] have indicated that ultrasonic vibration provides powerful shockwave and shear stresses, and thus promotes better dispersion and exfoliation in polymeric matrices.

In recent years, polymer/carbon-based NCs with fillers of below 100nm have drawn much attention in both academic and industrial research. This is due to their high conductivity, low weight, and ease of processing.[12–15] However, very little work has been devoted to investigating the effect of ultrasound treatment on polymer/graphene nanoplatelet (GNP) NCs. Of particular interest are those with high GNP content, which achieve excellent performance for practical applications (e.g., antistatic and electromagnetic-interference-shielding materials, and conductive plastic[16–18]). Additional information about the effect of ultrasonic treatment on polypropylene (PP)/GNP composites with high GNP content could extend the application areas of these highly scalable, highly available, cost-effective, and high-performance composites.

In our work, we therefore added an ultrasound-assisted extrusion system to the melt-extrusion process for the preparation of PP NCs reinforced with GNPs. A schematic of our experimental setup is shown in Figure 1. We then investigated the relationship between the power of the ultrasonic vibration and the GNP morphology—in terms of exfoliation and dispersion—within the resultant NCs. We also studied the macroscopic properties of the samples.

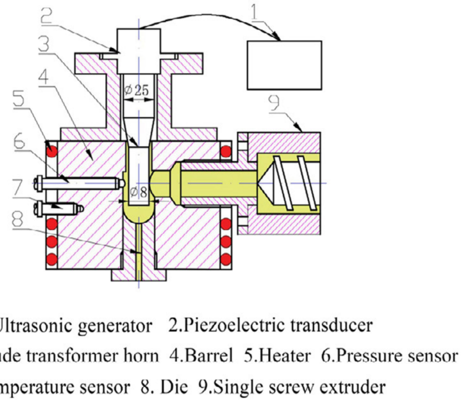

Figure 1. *Schematic showing our experimental setup, which enables ultrasound-assisted extrusion to be carried out. ϕ: Diameter.*

To investigate the morphology of our NCs, we used field-emission scanning electron microscopy (FESEM). Our results showed that the ultrasonic vibration effectively exfoliates and disperses GNPs within the PP matrix: see Figure 2. Moreover, we found that powerful vibration (i.e., 300W ultrasound) reduces the GNP diameter. We also found that more effective GNP exfoliation and dispersion could be achieved in the NCs by lowering the extruder-screw rotation speed and increasing the ultrasonic treatment time. Enhanced dispersion and distribution of GNPs decreases the crystallinity of the resultant NCs. However, decreasing the diameter of the GNPs increases the crystallinity. We were thus able to confirm—by observing the crystallinity within the NCs via x-ray diffraction and differential-scanning-calorimetry pattern analysis—that the NPs were reduced in size, which indicates that they were successfully refined by the ultrasonic vibration.

Our analysis of the rheological properties of the samples revealed that ultrasonic vibration reduces the apparent viscosity of PP/GNP NCs, and that this reduction is more significant at higher GNP content. The decreased viscosity may result in the enhanced GNP distribution that we observed in the finished NCs.

We also studied the thermal and electrical-volume conductivity of the NCs, and found that both are increased with the addition of ultrasonic vibration: see Figure 2. However, as the ultrasonic power

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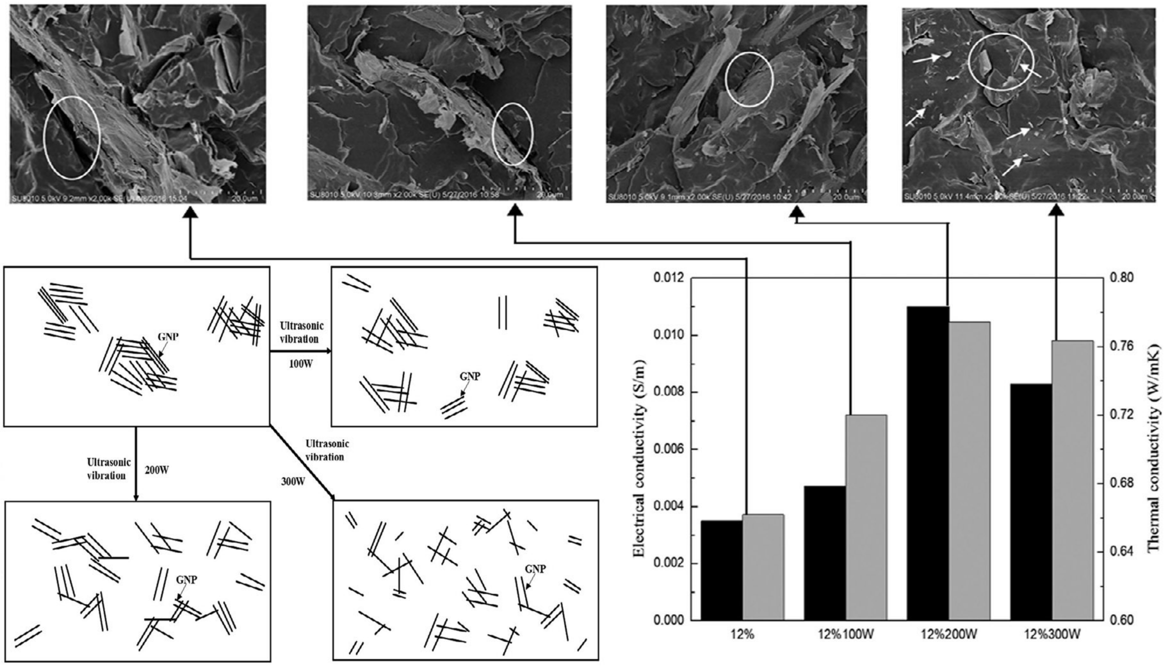

Figure 2. Schematic illustrations (bottom left) show the dispersion mechanisms of graphene nanoplatelets (GNPs) in polypropylene (PP) during extrusion under different ultrasonic powers. The graph (bottom right) shows the electrical (black) and thermal (gray) properties of PP/GNP composites (with 20%wt GNP) treated with ultrasound at a range of powers (i.e., 100, 200, and 300W). A PP/GNP composite prepared without ultrasound is also shown for comparison. Scanning-electron-microscope images (top) show the composite morphologies, with certain areas circled to highlight the evolution of GNP morphologies for different treatments. The arrows point out the reduced size of the GNPs at the highest power (300W).

increases further, the conductivity begins to decrease. It is likely that this effect arises due to the higher shear stresses, which enable high-level exfoliation of GNP agglomerations and thus lead to better GNP dispersion. Initially, improved GNP exfoliation and dispersion increases the likelihood of GNPs coming into contact with each other within the composite, leading to the formation of a conductivity pathway. However, the reduced conductivity in composites subject to ultrasound powers of 300W indicates that high shear stresses do not enhance the conductivity of the NCs. We attribute this to the GNP agglomerates being broken down into GNPs with smaller diameters, thus reducing the chance of contact between them (and, in turn, the formation of a conductive network) within the NC, thereby decreasing its conductivity.

To investigate the thermal behavior of the NCs, we used thermogravimetric analysis. We found that, due to the different mechanisms of electrical and thermal conductivity, the increased amplitude of the thermal conductivity within the NCs is much lower than that of the electrical-volume conductivity. Our TGA analysis confirms that only slight degradation occurred during the processing of PP/GNP nanocomposites in the presence of ultrasonic vibration. Furthermore, the thermal performance of the samples suggests that they remain suitable for high-temperature processing and applications.

In summary, we have developed an ultrasound-assisted extrusion system, and have used our system to fabricate PP NCs reinforced with GNPs. Our results show that this method is feasible for use in the industrialized production of such NCs. In addition, because the treatment is mechanical, our method enables the preparation of high-performance composites without the need for any chemical pretreatment. The ultrasound process also results in reduction of the viscosity of the NCs. As such, it will benefit the productivity of the extrusion process, and the distribution of GNPs in the PP matrix. Moreover, our TGA results proved that the treatment leads to only a slight degradation of the PP, and is therefore suitable for high-temperature processing and applications. In the next stage of our work, we will further study the effects of ultrasonic vibration on the conductive network formation of GNPs of different sizes. We also plan to further analyze our experimental

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results by using computer simulation, and aim to propose an applicable mathematical model to describe the effects of ultrasonic vibration on GNP-network formation within NCs.

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Author Information

Suihua He and Jingjing Zhang
Guangdong University of Technology
Guangzhou, China

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