Effect of the number of layers of graphene on the electrical properties of TPU polymers.

B Galindo1, S Gil Alcolea2, J Gómez2, A Navas3, A Ortega Murguialday1, M Pérez Fernandez2 and R C Puelles2
1 AIMPLAS, Instituto Tecnológico del Plástico, C/Gustave Eiffel 4, 46980, Paterna, Valencia, Spain.
2 Avanzare Innovación Tecnológica S.L. Antonio de Nebrija 8, 26006, Logroño, Spain
3 Instituto de Tecnologías Químicas de La Rioja (Inter-Química), San Francisco 11, 26370, Navarrete, Spain

E-mail: julio@avanzare.es

Abstract. In this paper graphene and few layers graphene were synthesized by a modified Hummers method using flake graphite powders as the starting material. The effect of the incorporation of graphene on the electrical properties of thermoplastic polyurethane (TPU) was investigated via two processing techniques: solution blending and melt compounding. When solution blending is used for the preparation of composites, the obtained electrical conductivity is higher, even at very low loads (0.25% w/w). Moreover, the single layer graphene shows 10,000 times higher electrical conductivity than few layers graphene.

1. Introduction

In the recent years graphene has attracted a great deal of attention due to its potential application in many different areas such as nanoelectronics, ultracapacitors, gas sensors, catalyst supports [1]. Moreover in polymer nanocomposites, graphene is probably the most promising nanofiller due to its high surface area, aspect ratio, tensile strength, thermal and electrical conductivity, EMI shielding ability, flexibility and transparency [2]. In particular, high values of electrical and thermal conductivity have been reported derived from ultra-fast transfer of charge carriers due to its high specific surface area and strong interaction between adjacent carbon atoms and monolayer structure [3].

Currently, a variety of techniques have been developed to prepare good quality graphene nanosheets (GNS), including the mechanical exfoliation, micromechanical cleavage, epitaxial growth (CVD), exfoliation of graphite in the liquid phase through direct sonication, and chemical wetting methods[4,5]. However some disadvantages of these techniques have been reported. Mechanical exfoliation even if high-uniform monolayer graphene flakes are obtained is not scalable and consequently not amenable for mass production of graphene. On the other hand epitaxial growth methods produce pure monolayer graphene sheets however it is a great challenge to transfer sample to insulating substrates for making useful devices.

Among the chemical methods, the Hummers method [6] has been the most popular approach for large scale production of graphene sheets, even though graphene sheets derived by this method contains a significant amount of defects due to the use of strong acids and oxidants (that largely disrupt the sp² bonded carbon network of graphene). The first step of Hummers method provides graphene oxide, which has several in-plane oxygen-containing groups. For reducing GO, two main
approaches have been used in recent years: (1) chemical reduction and (2) thermal annealing. Since Boehm and co-workers [7] early reported a method to prepare graphene by chemical reduction, it has been focused on the synthesis and manipulation of single- and multilayered carbon species [8]. However, reduced graphene produced by the chemical reduction of exfoliated GO has poor electrical properties due to the presence of contaminants and structural defects. Thermal annealing is an alternative route for reduction of GO restoring graphene structure and increasing its conductivity.

Thermoplastic polyurethanes (TPUs) are linear block copolymers characterized by hard and soft segments. Thanks to their particular chemical structure, these materials are very versatile offering a wide range of service temperatures and harness options, excellent tear and abrasion resistance, good resistance to non-polar solvents, high compression and tensile strength [9]. These properties make TPUs suitable for several products such as automotive components, adhesives, medical devices, food processing equipments, and so on. In this regard, it is possible to increase and tailor some specific properties (such as mechanical or dielectric properties) of TPU resins through the inclusion of nanofillers such as graphene.

In this paper we have explored the effects of the number of graphene layers in the electrical properties of the resin through two processing techniques, solution and melt compounding.

2. Experimental

2.1. Materials

Flake Graphite powder Flake Graphite powder with a density of 0.640 g/cm³ particle size of 500 µm obtained from Grafitos BARCO Company SL, Barcelona. For the preparation of graphene samples; KMnO₄ and concentrated H₂SO₄ sodium hydroxide and hydrochloric acid were obtained from COFARCAS (Burgos). Thermoplastic polyurethane (TPU) PEARLTHANE® D15 N70 (TPU; Merquinsa, Barcelona, Spain) with a density of 1,16 g/cm³ (at 20°C) was used as received. N,N-dimethylformamide (DMF; Scharlau, Barcelona S.L., Spain), methanol (MeOH; Scharlau, Barcelona, S.L., Spain), were used as received for the study.

2.2. Synthesis of graphene sheets

The graphene and few layers of graphene particles were synthesized by a modified Hummers method using flake graphite powders as the starting material. In this methodology, graphite flakes are suspended in a water solution of different strong oxidants (during 36 h to obtain few layers graphene and 48 h to prepare graphene monolayer); the resulting cake is washed and filtered to provide the graphite oxides. A subsequent step of controlled reduction by means of chemical reductants and thermal treatment provides the different qualities of graphene.

2.3. TPU/graphene nanocomposites preparation

Graphene and graphite TPU Nanocomposites (0.25% w/w) were prepared via 2 methodologies: Melt compounding and solution blending. Solution blending nanocomposites were prepared as follows: TPU was dissolved in DMF, on the other hand, the required quantity of graphene and graphite was dispersed in DMF and sonicated in an ultrasound bath. The TPU dissolution was added and the mixture was stirred in order to get a homogeneous solution. After that, it was poured slowly into methanol to precipitate the polymer-graphene nanocomposite. The material obtained was dried overnight at 70°C in a vacuum oven.

Melt compounding nanocomposites were prepared as follows: a Masterbatch (concentrated) compound was prepared through the solution methodology described before. The masterbatch obtained was diluted using an internal mixer (BRABENDER PL 2000, Germany) for 6 minutes at
190ºC. The obtained nanocomposites via solution blending and melt compounding were compression moulded at 180ºC to obtain a 500 micron film for electrical conductivity measurement.

2.4. Characterization techniques

The morphology of graphene sample was obtained by scanning electron microscopy (SEM) images using a Hitachi S-2400. The morphology and thickness were characterized by atomic force microscopy (AFM) NT-MDT model NTEGRA PRIMA. The dimension and the number of layers were also evaluated using a transmission electron microscopy (TEM) experiments were performed on a JEOL model JEM-2010 electron microscope. For microscopy characterization, the samples were dispersed in isopropyl alcohol and sonicated with a Hielscher UP200S sonicator.

Raman spectra were recorded with a Raman Horiba Xplora using an excitation wavelength of 532 nm. Scans were recorded in the range from 400 to 3200 cm⁻¹. For lineal measurements the electrodes were at 1 cm of distance and 250 V polarization technique was used. TPU/nanocomposites were analysed with a scanning electron microscopy PHENOM World desktop SEM PRO-X.

3. Results and discussion

3.1. Graphene characterization

High-yielding and good-quality of few layers of graphene and single/bilayer of graphene are obtained by exfoliation of sheets of graphite using the modified Hummers method as shown by electron and atomic force microscopy (Figures 1, 2, 3 and 4). The coarse graphite powder is in fact composed of multiple layers of graphene; the exposure to strong oxidizing agents cause layers to spread obtaining graphitic oxides (GO). GO reduction via thermo-chemical treatment leads to a total exfoliation of graphite and in consequence graphene structures made of one or more layers are obtained maintaining XY plane while reducing the apparent density of the materials (Table 1).

| Table 1. Properties of synthesized graphene products |
|-----------------------------------------------|
| Product               | Reaction time. | Apparent density. | XY plane measured by SEM |
|-----------------------|----------------|------------------|--------------------------|
| Graphite              | ---            | 0.640            | 0-500                    |
| Few layer graphene    | 36             | 0.020            | 20x20                    |
| Mono/bilayer graphene | 48             | 0.006            | 20x20                    |

High resolution TEM is used to characterized the degree of exfoliation of graphite. Figure 1 shows TEM images of few layers graphene. The distinguishable red-white lines running almost parallel in some parts and in zigzag in other zones may be a reflection of the wrinkled nature of graphene. This wrinkle and folding nature is also seen in Figure 2 for the mono/bilayer graphene. SEM (Figures 3 and 4) images demonstrated the effectiveness of the modified Hummers method for the exfoliation of graphite flakes obtaining few and monolayer graphene products. The XY plane size has been reduced from 500 microns of the graphitic crystal to 20 x 20 µm size to graphene.
The AFM is a powerful non-destructive technique for precisely identifying the number of graphene layers by measuring the step height profile. Figure 5 and 6 show a representative tapping mode AFM image of graphene and few layers of graphene sheets and the height profile in selected locations. The sizes and thicknesses vary, but as a whole, all the thicknesses of few layers graphene are roughly around 1 to 2 nm, and less than 1 nm for single layers graphene.

Raman spectroscopy is a powerful tool for examining the quality of the graphene materials. The main features in the Raman spectra of carbonaceous materials are the so-called G and D peaks, which lie at
around 1560 and 1360 cm\(^{-1}\) respectively. The Raman spectra of few layers and single layers graphene are displayed in Figure 7. There are three peaks at 1350 cm\(^{-1}\) (D peak), 1580 cm\(^{-1}\) (G peak) and 2714 cm\(^{-1}\) (2D peak). The D peak, is derived from the edge effects, disorder and lost of graphitic structure. In addition, the intensity ratio (ID/IG) is about 0.6 for the few layers and 0.4 for single layer one, which is much less than most chemical reduction reports [10].

![Raman spectra of Few layers and single layer graphene](image)

**Figure 7.** Raman spectra of Few layers and single layer graphene

3.2. TPU nanocomposites

The influence of two processing methodologies melt compounding and solution blending on the electrical performance has been studied on TPU graphene nanocomposites. Table 2 show the electrical properties of 0.25% w/w graphene TPU nanocomposites prepared by both methodologies. The electrical conductivity is found to increase when the exfoliation of the graphitic structure is completed. Thus mono/bilayer TPU nanocomposites show 10,000 times higher conductivity than few layer graphene where bulk graphite composites were out of the measurement limit of the equipment. In addition solution blending methodology showed for the mono/bilayer nanocomposite 10 times higher electrical conductivity.

| Methodology          | Product        | % filler | linear conductivity (Sxcm\(^{-1}\)) |
|----------------------|----------------|----------|-----------------------------------|
| Solution blending    | Mono/bilayer graphene | 0.25    | 2,33.10\(^{-08}\)                |
| Melt compounding     | Mono/bilayer graphene | 0.25    | 2,16.10\(^{-09}\)                |
| Solution blending    | Few layer graphene | 0.25     | 1,25.10\(^{-12}\)               |
| Melt compounding     | Few layer graphene  | 0.25     | 1,26.10\(^{-12}\)               |
| Solution blending    | Graphite        | 0.25     | out-range                         |
| Melt compounding     | Graphite        | 0.25     | out-range                         |

Figure 8 and 9 show the SEM microphotographs of cryofractured surface morphology of the TPU/mono-bilayer graphene nanocomposites in order to observe the dispersion and distribution of the nanofiller and the physical interaction with the TPU matrix. It can be observed that graphene has homogenously been dispersed among the TPU matrix.
Figure 8. SEM image of mono/bilayer TPU produced by melt compounding

Figure 9. SEM image of mono/bilayer TPU produced by solution blending

4. Conclusions

We have prepared graphene and few layers graphene using a modified Hummers method with highly restoration of the graphitic structure, as it can be seen by SEM, AFM and RAMAN measurements. Using solution blending and melt compounding, we have obtained TPU composites of graphene and few layers graphene. When solution blending is used for the preparation of composites, we observe higher electrical conductivity, even at very low concentration of graphene 0.25% w/w. We also observe that single layer graphene shows 10.000 higher electrical conductivity than few layers graphene.

Acknowledgments

This work was has been performed within the framework of the project NANOMASTER (from the European Community's Seventh Framework Programme FP7/2007-2013 under grant agreement n° 285718).

5. References

[1] Wang G X, Shen X P, Yao J and Park J, 2009 Carbon 47 2049
[2] Potts J R, Dreyer D R, Bielawski C W and Ruoff R S 2011 Polymer 5
[3] Geim A K, Novoselov K S 2007 Nat. Mater 6 183
[4] Stankovich S, Dikin D A, Piner R D, Kohlhaas KA, Kleinhammes A, and Jia Y, et al. 2007, Carbon 45:1558
[5] Dreyer R D, Murali S, Zhu Y, Ruoff RS and Bielawski C W. Journal of Materials Chemistry 2010
[6] Hummers WS and Offeman RE 1958 J Am Chem Soc. 80 1339.
[7] Boehm H. P, Claus A.; Fische G, Hofmann U Proceedings of the Fifth Conference on Carbon, 1962, 73.
[8] Park S and Ruoff R. S 2009 Nat. Nanotechnol 4,217
[9] Fernandez M, Landa M, Muñoz M E, Santamaria A 2010 International Journal of Adhesion and Adhesives 30 609
[10] Fan Z J, Kai W, Yan J, Wei T, Zhi L, Feng J, Ren Y, Song L, and Wei F 2011 ACS nano 5 191