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Rheology, electrical conductivity and crystallinity of a polyurethane/graphene composite: Implications for its use as a hot-melt adhesive

Jorge Canales, María Eugenia Muñoz, Mercedes Fernández, Anton Santamaría *

POLYMAT and Polymer Science and Technology Department, Faculty of Chemistry, University of the Basque Country UPV/EHU, P.O. Box 1072, 20080 San Sebastián, Spain

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ABSTRACT

Homemade graphene based polyurethane composites elaborated using a facile melt mixing method were studied. The polyurethane (PUR) was a hot-melt adhesive and the research was carried out considering the perspective of electrically conductive adhesive composites. The crystallization of PUR was significantly modified by graphene; for instance the crystallization temperature was shifted to higher temperatures. Avrami equation results indicated that the composites constituted nucleated axialites, instead of espherulites. These results were used to explain the initial decrease of conductivity, followed by a recovery, observed during the crystallization process.

The observed huge conductivity enhancement, together with the increase of the crystallization temperature, opens interesting perspectives in the development of electrically conductivity adhesives which offer a rapid welding.

1. Introduction

The amount of papers on polymer composites that contain graphene oxide and graphene nanoparticles is increasing in recent years, approaching to the number reached by carbon nanotubes (CNT) based polymer composites. Both types of composites can actually compete in the development of new materials with improved mechanical properties, as well as electrical and thermal conductivity.

Most of the outcomes of graphene or graphene oxide based polymer composites are summarized in several reviews and feature articles [1–6] published in the last lustrum. Besides of an analysis of the advantages of these composites, such as, high tensile strength, thermal and electrical conductivity, EMI shielding ability, flexibility, and low thermal expansion characteristics with low loading, the literature reflects some basic aspects that are at stake: (a) Functionalization or not of graphene sheets (b) Dispersion of graphene or graphene oxide in the polymer matrix avoiding stacking (c) Monitoring shape changes and orientation of the sheets (d) Alteration of rheological properties linked to processing (e) Understanding the physical changes of the polymer matrix, like polymer-filler bridging and crystallization.

Several methods to obtain graphene, including chemical vapor deposition (CVD) on metal surfaces and thermal reduction of exfoliated sheets of graphene oxide, have been reported in the literature [2]. The last method in particular involves a disruption in the conjugated electrical structure of graphene reducing its electrical conductivity. But, the hydrogen interactions between the remaining oxygen-containing groups and some polymers (like urethane based polymers) lead to improve the interfacial interactions between the graphene and the polymer. This favors the way to obtain well dispersed graphene based polymer composites, notwithstanding issues similar to those of CNT based polymer composites are still present, such as rheological and thermal alterations. The latter are very relevant in the case of semi-crystalline polymer matrices, because the most affected physico-chemical aspect is the crystallization process.

Graphene/polymer composites based on semi-crystalline polyurethanes have deserved the attention of a number of papers [7–20], but the case of polyurethane matrices used as hot-melt adhesives has been scarcely treated [21]. In the present work we study the rheological properties, the electrical conductivity and the crystallinity of a polyurethane composite that includes graphene sheets obtained through thermal reduction of exfoliated sheets of graphene oxide, from the perspective of its potential use as an electrical conductive hot-melt adhesive.

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* Corresponding author. Tel.: +34 943 018184; fax: +34 943 015270.
E-mail address: antxon.santamaria@ehu.es (A. Santamaría).

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2. Experimental part

2.1. Materials

The polymer matrix used to elaborate the nanocomposites was a semicrystalline thermoplastic polyurethane (PUR) produced by Merquinsa (Spain). This polyurethane is currently commercially available to be used as a Holt Melt adhesive. The hard segment is formed by a diisocianate and chain extending short chain diol, and the soft segment is formed by the long chain diol. The aromatic diisocyanate is Diphenylmethane diisocyanate (MDI), the chain extender is a short-chain diol, 1, 4-butanediol, and the long chain diol is ε-polycaprolactone. The composition deduced from NMR is 10% hard segment and 90% soft segment.

Homemade graphene (HG) was obtained from graphite oxidation and subsequent thermal exfoliation and reduction of graphite oxide. A modification of the procedure described by Hummers [22] was employed. Graphite flakes of 45 μm and grade 230, supplied by Asbury Carbons, were mixed with adequate proportions of $NaNO_3$ and H_2SO_4 in a flask refrigerated with a vessel which contained ice. After stirring for an hour, $KMnO_4$ was added, carefully, to avoid an increase of the temperature above 20 °C. Once this process was finished, the vessel with the ice was removed and the mixture was stirred for two hours; an increase of temperature up to 35 °C was observed. Adding water the temperature suddenly increased to 98 °C. To eliminate the excess of $KMnO_4$, water and H_2O_2 were added.

The resulting graphite oxide was dashed and filtered with a HCl solution several times (until the tests with $AgNO_3$ revealed absence of chloride) and was dried by lyophilization. Posterior reduction and exfoliation of the graphite oxide was reached with a rapid thermal expansion, following the procedure described by Aksay et al. [23] which consists in placing the graphite oxide in a tube furnace preheated to 1000 °C and argon atmosphere for 30 s. Rapid heating (>2000 °C/min) splits the graphite oxide into graphene sheets through the evolution of CO_2 gas.

2.2. Characterization of graphene

X-ray diffraction spectra of graphite, graphite oxide and graphene (Supplemental information) were obtained. A strong and sharp diffraction peak of pristine graphite at 26.6° completely disappeared after oxidization and instead a new peak around 11° appeared. This indicates that graphite oxidation and expansion of interlaminar spacing, due to the insertion of functional groups [24–26], was taking place. After thermal exfoliation, there was no apparent diffraction peak detected, which signifies that the periodic structure of graphene oxide was eliminated and graphene nanosheets were formed.

AFM results obtained in a Nanoscope IV multimode AFM controller (Bruker/Veeco/Digital Instruments), using tapping mode with etched silicon TESP probes (spring constant 42 N/m), are displayed in Fig. 1. In this figure agglomerated graphene sheets, with a typical wrinkled shape, are observed. Expanding the image allows analyzing the height which is only 2 nm, indicating that the agglomerates are constituted by 2–3 graphene sheets.

2.3. Composites preparation and rheological and thermal measurements

The composites were prepared dispersing the home made graphene in the polyurethane matrix by melt mixing method in a Haake Mini-Lab twin screw extruder (Thermo Electron Corp).

The dynamic viscoelastic behavior in the molten state was investigated using a TA-Instruments ARG2 viscoelastometer with parallel-plate shear geometry. Frequency sweep tests were carried out to study the effect of frequency on the shear elastic modulus, G', in the terminal viscoelastic zone. The experiments were accomplished in the linear regime at the temperatures indicated in the text.

Analysis of the isothermal crystallization of pure polyurethane and polyurethane/graphene composites at the indicated temperature were carried out by Differential Scanning Calorimetry measurements in a DSC Q2000 equipment (TA Instruments).

2.4. Electrical conductivity measurements

The ARES Rheometer Dielectric Analysis option (DETA) with an Agilent E4980A Bridge was used to determine the electrical conductivity. Electrodes were 25 mm diameter stainless steel plates which allowed making tests in the liquid and in the solid state, typically with samples of 0.5 mm thickness. The measurements were carried out using a voltage of 1 V. Dielectric data, permittivity and dielectric loss were recorded for each sample as a function of temperature and frequency during isothermal and temperature sweep test. The real part of the conductivity as a function of the angular frequency ν, is calculated from the imaginary part of the dielectric constant $\varepsilon''(\nu)$ through the relation:

$$\sigma'(\nu) = \varepsilon_0 2\pi\nu\varepsilon''(\nu) \tag{1}$$

where $\varepsilon_0 = 8.85 \times 10^{-12}\ \mathrm{F\,m^{-1}}$ is the vacuum permittivity. The real part of the conductivity, σ', is referred as the electrical conductivity.

Electrical conductivity isothermal results were obtained in a frequency range of 20 Hz to 1 MHz, under the following conditions: (a) In the molten state at $T = 120$ °C, after an annealing time of $t = 120$ min and (b) In the solid state, after cooling the annealed samples to $T = 20$ °C.

It is known that annealing in the molten state brings about an electrical conductivity enhancement in polymer/graphene composites [27–32], as well as in other polymer composites which contain electrically conductive fillers. In view of these results, our choice was to take the maximum possible annealing time without degradation ($t = 120$ min at $T = 120$ °C).

An example of the variation of the conductivity with frequency observed for the nanocomposites is shown in Fig. 2. DC value was calculated from the frequency independent conductivity data associated to the low frequency regime. The results shown in Fig. 2 are similar to the behavior reported for many polymer/MWCNT composites [33–42]. However, such response has been scarcely reported for polymer/graphene composites; in particular only in the case of an isotactic polypropylene/graphene composite [12,30,43,44].

The continuous variation of the DC conductivity with temperature was studied at 20 Hz (within the frequency independent conductivity zone), in the range from 120 to 0 °C at a cooling rate of 1 °C/min., with samples submitted to an annealing time of $t = 120$ min at $T = 120$ °C.

3. Results and discussion

3.1. Rheology and electrical conductivity in the molten state

The study of the rheological properties of polymer composites is relevant regarding two fundamental aspects: (a) Analysis of the processing performance of the system (b) Evaluation of the interactions between nanoparticles and polymer chains. In this section we focus on the latter issue, analyzing the dynamic viscoelastic response of our polyurethane/graphene composites in the terminal zone, i.e. when the oscillation frequency tends to zero. In particular, the variation of the elastic modulus (G') with frequency for