

Proceeding Paper

Development and Characterization of Polyaniline/ Hexamethylene Diisocyanate-Modified Graphene Oxide Nanocomposites [†]

Ana María Díez-Pascual ^{*} and José Antonio Luceño-Sánchez

Universidad de Alcalá, Facultad de Ciencias, Departamento de Química Analítica, Química Física e Ingeniería Química, Ctra. Madrid-Barcelona Km. 33.6, 28805 Alcalá de Henares, Madrid, España (Spain); jose.luceno@uah.es

^{*} Correspondence: am.diez@uah.es; Tel.: +34-918-856-430

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Abstract: Polyaniline (PANI) is a cheap and widely used conducting polymer due to its exceptional electrical and optoelectronic properties. However, it is insoluble in conventional organic solvents and degrades at high temperatures. To improve the performance of PANI, carbon-based nanomaterials, such as graphene, graphene oxide (GO), and their derivatives, can be incorporated into a PANI matrix. In this work, hexamethylene diisocyanate-modified GO was used as a reinforcement to prepare PANI/HDI-GO nanocomposites by means of the in situ polymerization of aniline in the presence of HDI-GO followed by ultrasonication and solution casting. The effect of the HDI-GO functionalization degree and concentration on the final properties of the nanocomposites was explored by scanning electron microscopy (SEM), Raman spectroscopy, X-ray diffraction (XRD), thermogravimetric analysis (TGA), tensile tests, and four-point probe measurements. A homogenous dispersion of the HDI-GO nanosheets was found as well as very strong PANI-HDI-GO interactions via pi-pi stacking, H-bonding, and hydrophobic and electrostatic charge-transfer complexes. A continuous improvement in thermal stability and electrical conductivity was found with increasing nanomaterial concentration, the increments being larger with the increasing HDI-GO degree of functionalization. The nanocomposites showed a very good combination of rigidity, strength, ductility, and toughness. The approach developed herein opens up a versatile route to prepare multifunctional graphene-based nanocomposites with conductive polymers for a broad range of applications, including photovoltaic organic solar cells.

Keywords: PANI; graphene oxide; nanocomposites; hexamethylene diisocyanate; characterization

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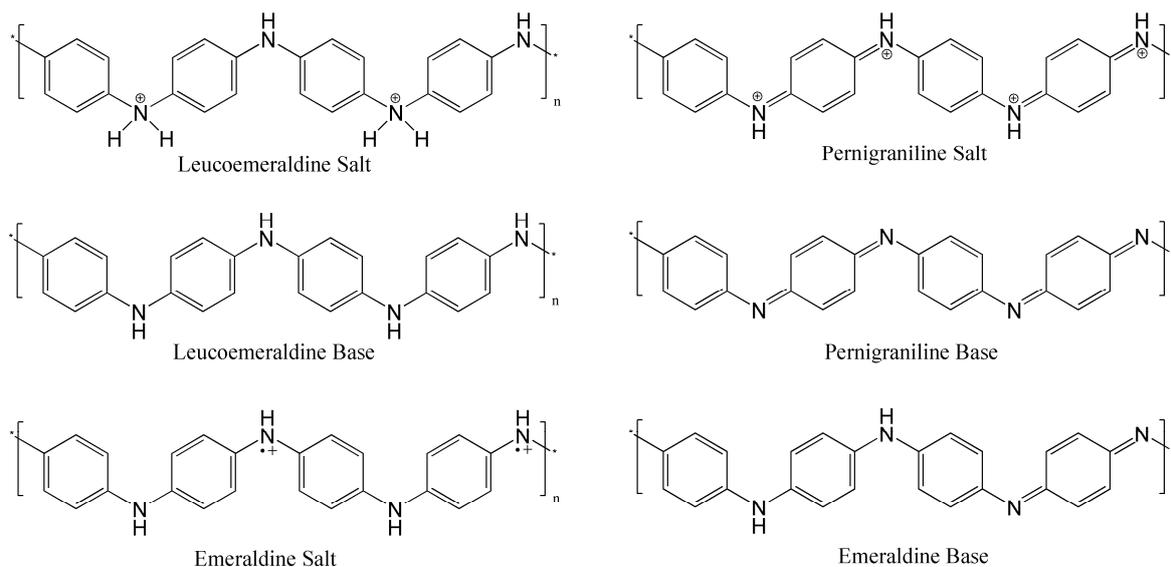
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1. Introduction

The interesting properties and applicability of conducting polymers, such as polyaniline (PANI), enable them to be employed as solar cells materials [1–3]. PANI represents one of the most studied polymers in recent decades, mostly due to its exceptional properties and its wide range of uses [1,4]. The synthesis of PANI can be accomplished by electrochemical or conventional approaches, and the oxidation state of PANI can also differ depending on the approach [5]. The possible oxidation states of PANI are depicted in Scheme 1: Leucoemeraldine Salt and Base, Pernigraniline Salt and Base, and Emeraldine Salt and Base.



Scheme 1. Structure of the different forms of PANI: the completely reduced leucoemeraldine, the completely oxidized pernigraniline, and the emeraldine, in the base and salt forms. Taken from [6].

PANI presents good electrical properties, although it has low mechanical performance and undesirable solubility [7]. The addition of nanomaterials to PANI can improve its properties [8]; there are already studies adding graphene-based materials (graphene (G), graphene oxide (GO), and reduced graphene oxide (rGO)) to PANI via in situ polymerization or functionalization procedures [8–12], achieving an improvement in charge carriers transference and strong interfacial adhesion [13]. However, the presence of graphene aggregates can reduce the material properties, so it is critical to enhance the dispersion of the nanomaterial. Previous works have focused on the development of functionalized graphene samples and preparation methods, aiming to optimize the nanomaterial behavior [14–17].

In this work, a procedure to obtain PANI/GO nanocomposites, with a GO homogeneous dispersion, using in situ polymerization techniques is presented. The synthesis involves the use of ammonium peroxydisulfate as an oxidizing agent, GO and hexamethylene diisocyanate-modified graphene oxide (HDI-GO) as the nanomaterials added to PANI, and acid medium. The interaction between PANI and HDI-GO or GO takes place via different options (π - π stacking, hydrogen bonding, and electrostatic and hydrophobic interactions). The nanomaterial synthesized were characterized to study the effect of graphene-based materials on the final properties.

2. Materials and Methods

2.1. Reagents

Aniline monomer ($C_6H_5NH_2$, >99%, $M_w = 93.13$ g/mol, $d_{25^\circ C} = 1.02$ g/cm³), ammonium persulfate ($(NH_4)_2S_2O_8$, 98%, $M_w = 228.20$ g/mol, $d_{25^\circ C} = 1.98$ g/cm³), triethylamine (TEA, >98%, $M_w = 101.193$ g/mol), H_2SO_4 , $KMnO_4$, P_2O_5 , $K_2S_2O_8$, and H_2O_2 were acquired from Sigma-Aldrich. Graphite powder was obtained from Bay Carbon, Inc. Hexamethylene diisocyanate (HDI, >99%, $M_w = 168.196$ g/mol) was purchased from Acros Organics. HPLC grade organic solvents were employed, bought from Scharlau S.L. The deionized water was produced with a Milli-Q Water Purification System. The chemicals were employed as received.

2.2. Synthesis of HDI-GO

The preparation of HDI-GO was carried out following the method showed in previous works [18,19], which is described briefly as follows: (1) synthesis of GO applying

Hummers' method from graphite powder using H_2SO_4 , $\text{K}_2\text{S}_2\text{O}_8$, P_2O_5 , and KMnO_4 ; (2) functionalization of GO with TEA as catalyst and HDI as reagent, added dropwise under $60\text{ }^\circ\text{C}$, inert atmosphere, and stirring for 12 h. Step 2 had two different ratio (GO:TEA:HDI) options, in order to study the functionalization degree (FD) effect on nanocomposite properties: (a) 1:1:1 (FD of 12.3%) and (b) 1:1:1, with a previous ultrasonic tip treatment (FD of 18.1%).

2.3. Synthesis of PANI/HDI-GO Nanocomposites

The synthesis procedure of the PANI/HDI-modified GO nanocomposites was an in situ polymerization of aniline monomers in acid medium in the presence of $(\text{NH}_4)_2\text{S}_2\text{O}_8$.

The first step involves the solution of 0.1 mL of aniline monomer with 25 mL of 1M HCl, and later the desired mass of HDI-GO (0.25, 0.50, 1.00, 2.50, or 5.00 mg). This mixture was ultrasonicated with a top for 5 min and later an ultrasonic bath for 30 min. Parallely, 0.60 g of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ was dispersed in 25 mL of 1M HCl, and later mixed dropwise into PANI-HDI-GO solution. The polymerization reaction, which starts when the solution becomes a green color, was carried out under stirring and in an ice bath for 12 h. In order to remove the residual polymers and oligomers, the reaction's products were filtrated and washed with deionized H_2O , ethanol, and hexane until colorless, and later, an oven was used to dry the products at $80\text{ }^\circ\text{C}$ for 48 h.

In order to study the effect of HDI, and its FD, on the addition of GO, a sample of 5.00 mg pristine GO (10 wt%) and PANI single samples were prepared, and also two different HDI-GO sets (HDI-GO1 and HDI-GO6). Films based on the nanocomposite mixtures were obtained by dropping 5 mL of the sample in a glass and drying in the oven under the same conditions as the composites.

2.4. Instrumentation

The ultrasonication treatments were applied using a Selecta 3,001,208 ultrasonic bath and a 24 kHz Hielscher UP400S ultrasonic tip. A SU8000 Hitachi microscope was used for scanning electron microscopy (SEM) analysis. Raman spectra were obtained using a Renishaw Raman microscope. The thermal stability was studied using a TA Instruments Q50s thermobalance.

3. Results

3.1. Morphology of Nanocomposites

The structures and morphology of the different samples (PANI, GO, HDI-GO, and the nanocomposites obtained) were analyzed by SEM. The SEM micrographs are presented in Figure 1.

The images of HDI-GO 6 reveal a stacked structure of graphene flakes, attributed to the linking between HDI chains and the GO surface due to the functional groups. The samples appear heterogeneous, since they comprise a mixture of raw GO sheets and HDI-modified sheets; a similar morphology was found for the HDI-GO 1 samples.

However, when the GO-based materials were mixed with PANI particles, surfaces fully covered by PANI were observed. This result is consistent with previous works [20, 21], since the use of HCl produces the adsorption of PANI in the graphene surface by electrostatic attraction. Furthermore, given that the HDI-GO has negative charge, it was expected that the PANI would stick to the surface more strongly due to the positive charge of PANI emeraldine salt form. Additionally, other kinds of interactions between PANI and HDI-GO structures can take place, such as pi-pi stacking, hydrophobic interactions, and hydrogen bonding.

The polymerization method showed that the polymeric matrix covered the HDI-GO surface homogenously. This allows us to yield composites in which the intercalation of HDI-GO in PANI is effective and no-agglomeration or phase separation takes place, in contrast with previous works [22,23]. The spaced layers of HDI-GO enable the diffusion on PANI particles between them, and later its deposition onto the surface as a thin coating.

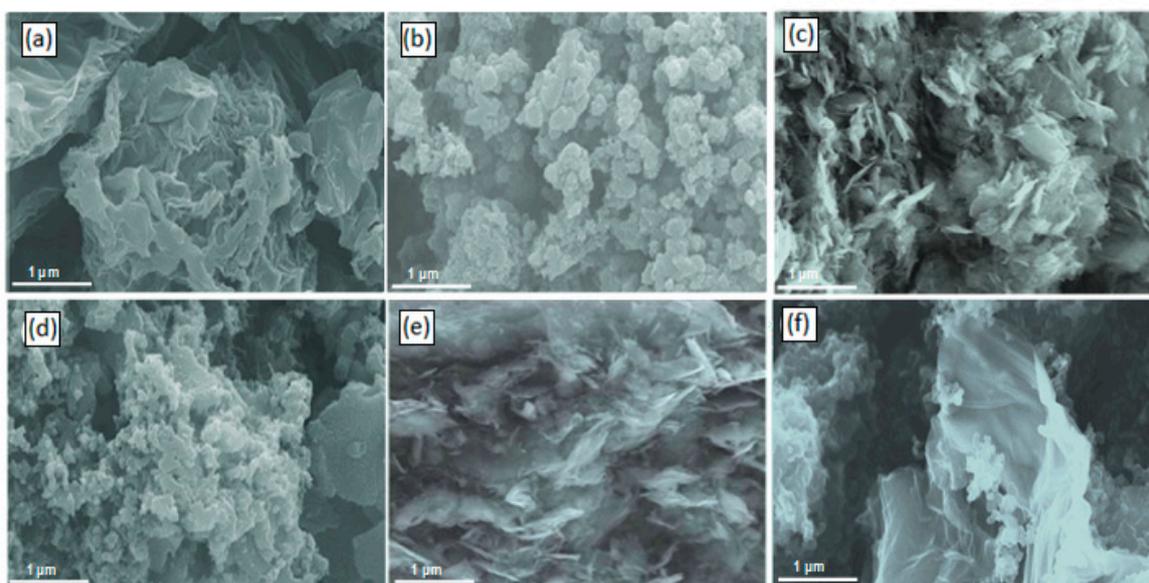


Figure 1. SEM micrographs of samples: raw GO (a), neat PANI (b), HDI-GO 6 (c), PANI/HDI-GO 6 (10 wt%) (d), HDI-GO 1 (e), and PANI/HDI-GO 1 (10 wt%) (f). Taken from [6].

A similar morphology was observed for all the nanocomposites with HDI-GO. The samples with HDI-GO 6 presented a smooth surface, and a direct relation between the nanomaterial amount and degree of interpenetration. The arbitrarily distribution of graphene flakes onto the PANI matrix can be a potential aid to create conductive paths though the material. However, the sample with 10 wt% HDI-GO 1 presented a lower interpenetration structure. The GO sheets were more separated due to the addition of PANI particles, which implies a larger level of exfoliation.

3.2. XRD Patterns

The XRD patterns prove the viability of the in situ polymerization method presented. The sample of pure PANI showed a peak at $2\theta = 25.3^\circ$, which was also presented in the diffractograms of every nanocomposite, but at lower 2θ and with a lower intensity. This fact is explained by considering the loading of nanomaterials [24]: the higher the amount of GO, the lower the intensity and the lower the 2θ .

Furthermore, the downshift was more noticeable for the samples with HDI-GO compared with those with GO, and also more marked with higher FD. As this shift is related to the interlayer distance, it is reasonable to think that the sample with a higher amount of HDI will have more separated flakes and can hold more PANI particles on their surface and between layers.

In the case of GO, the interlayer was smaller than in the HDI-GO samples (for 10 wt%: 0.8 nm vs. 1.18 (HDI-GO1) or 1.33 nm (HDI-GO6). This is another fact that supports the idea of higher interlayer spacing implying the higher intercalation of polymeric chains.

3.3. Raman Spectroscopy Results

The characteristic peaks of PANI ($400\text{--}1800\text{ cm}^{-1}$) and GO (disorder D band at 1345 cm^{-1} , and tangential G band at 1595 cm^{-1}) can be observed in the nanocomposite spectra. Additionally, the HDI-GO spectrum showed similar peaks to GO, but more intense due to the increased number of defects related to HDI and upshifted, attributed to a change in the electronic structure of GO in the presence of electron-acceptor groups [25]. Furthermore, the ratio between the intensity of the D and G band is indicative of the disorder [26]: the higher the ratio, the higher the number of defects; this ratio was about one for GO; meanwhile, for the HDI-GO1, it was 1.55 and for the HDI-GO6, it was 1.73.

The spectra of the nanocomposites were similar to that of PANI, but the peaks were slightly shifted to higher wavelengths, and their intensity was reduced. There were differences when comparing PANI/GO and PANI/HDI-GO samples: those with GO presented a small upshift of the bands, while PANI/HDI-GO1 and PANI/HDI-GO6 samples exhibited a strong upshift. These results are yet another confirmation of the presence of PANI chains on the GO or HDI-GO surface. Furthermore, the FD has an effect on the peaks: the higher the FD, the larger the modification of the peaks.

3.4. Thermal Stability

The thermal decomposition of the samples was investigated by TGA experiments under nitrogen atmosphere, and the thermographs are presented in Figure 2.

Some similarity can be observed by comparing PANI, GO, and HDI-GO samples with the PANI/GO and PANI/HDI-GO composites.

PANI presented a first decomposition step related to a deprotonation, probably caused by the HCl molecules of the dopant [13], and a second step due to the elimination of the groups attached to the PANI backbone. The GO sample only showed one step around 250 °C, which is attributed to the removal of functional groups [18]. HDI-GO also presented two steps: the first is related to the decomposition of the remaining functional groups, and the second correlates with the decomposition of HDI chains.

The thermographs of nanocomposites presented two steps of degradation, like PANI, but with a higher thermal stability. These significant changes, larger in HDI-GO samples, imply that the addition of GO and HDI-GO nanomaterials to a PANI matrix improves the stability of the samples, increasing the degradation temperatures at every step. This improvement can be related to the PANI/HDI-GO interaction. The HDI-GO flakes protect PANI from the heat. This kind of stability enhancement was previously reported for PANI/graphene nanoplatelets [27]. Furthermore, it can be observed that the higher the loading of HDI-GO, the higher the thermal stability, and also, the higher FD, the higher stability. This fact can be explained considering that the strong interactions between PANI and HDI-GO restrain the polymeric rotational movement, so the stability is improved.

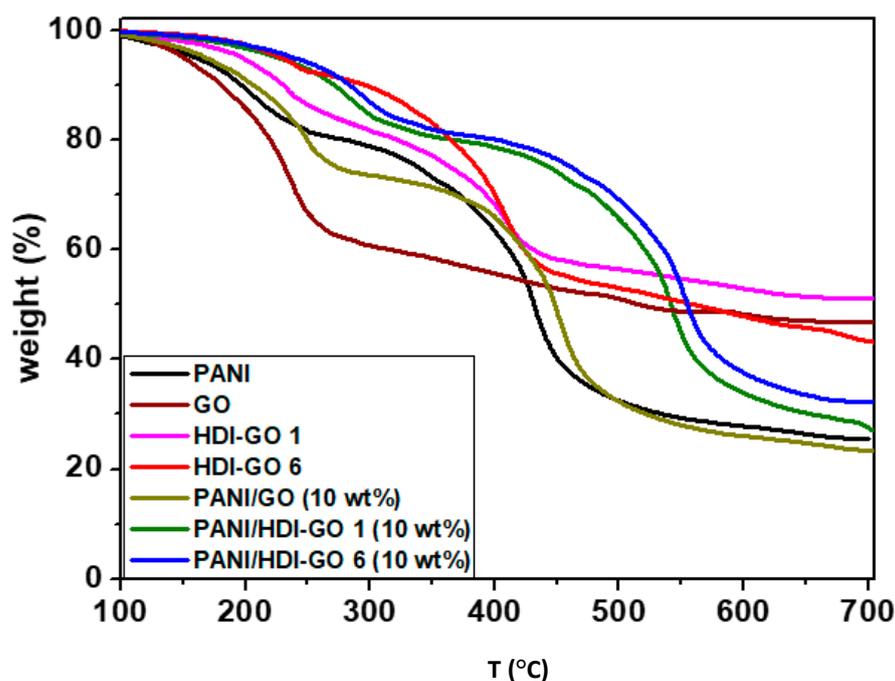


Figure 2. TGA curves under inert atmosphere of neat PANI, GO, HDI-GO 1, HDI-GO 6, and the nanocomposites with 10 wt% nanofiller loading. Taken from [6].

4. Conclusions

In this work, nanocomposites based on PANI/HDI-GO mixtures were prepared; the synthesis involved an in situ polymerization of aniline monomers with HDI-GO nanofillers in acid medium with $(\text{NH}_4)_2\text{S}_2\text{O}_8$ as an oxidizing agent. In order to study the effect of HDI-GO on the properties of the nanocomposites, the samples were characterized by different techniques. Experimental results show that the sample morphology consists of a dense network of PANI matrix particles deposited onto the GO-based material surface. The interactions between PANI and HDI-GO are mainly hydrogen bonding, pi-pi stacking, electrostatic, and hydrophobic interactions. It was noticed that the higher the concentration of HDI-GO, the higher the thermal stability and the electrical conductivity of PANI composites; further, the conductivity also increased with increasing HDI-GO functionalization degree. This new procedure for synthesizing PANI/HDI-GO nanocomposites offers the opportunity to develop new multifunctional graphene/polymer-based materials for a broad range of applications.

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