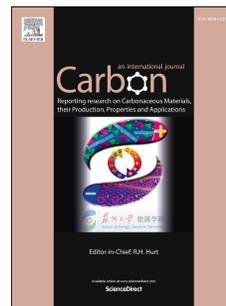


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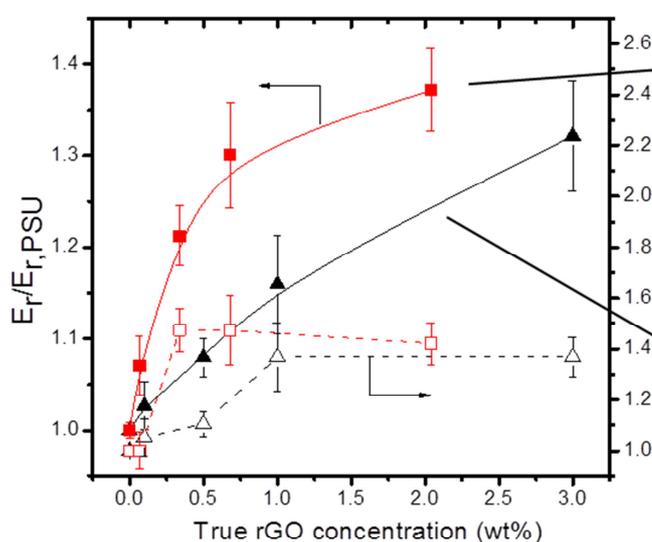
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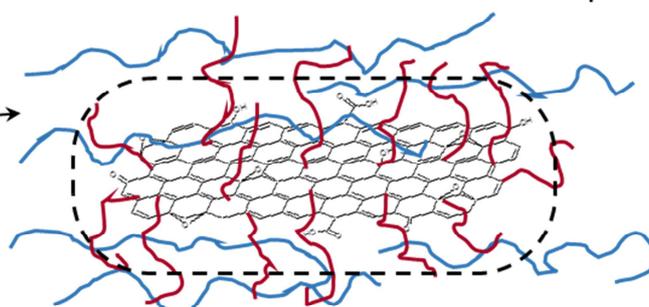
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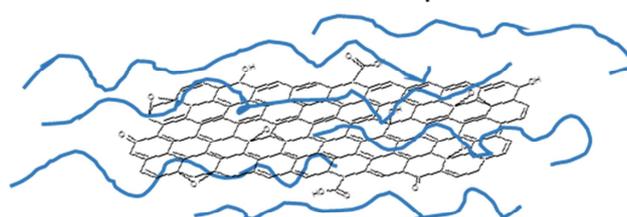
Graphical abstract



PSU functionalized rGO/PSU nanocomposite



rGO/PSU nanocomposite



Effect of polysulfone brush functionalization on thermo-mechanical properties of melt extruded graphene/polysulfone nanocomposites

Janire Peña-Bahamonde¹, Verónica San-Miguel¹, Juan Baselga¹, Juan P. Fernández-Blázquez², Gabriel Gedler³, Rahmi Ozisik³, Juan C. Cabanelas^{1*}

¹*Carlos III University of Madrid, Department of Materials Science and Engineering and Chemical Engineering (IAAB), Av. Universidad 30, 28911 Leganés, Madrid, Spain*

²*IMDEA Materials Institute, C/ Eric Kandel 2, 28906 Getafe, Madrid, Spain*

³*Rensselaer Polytechnic Institute, Department of Material Science and Engineering, Troy, NY 12180, U.S.A.*

Abstract

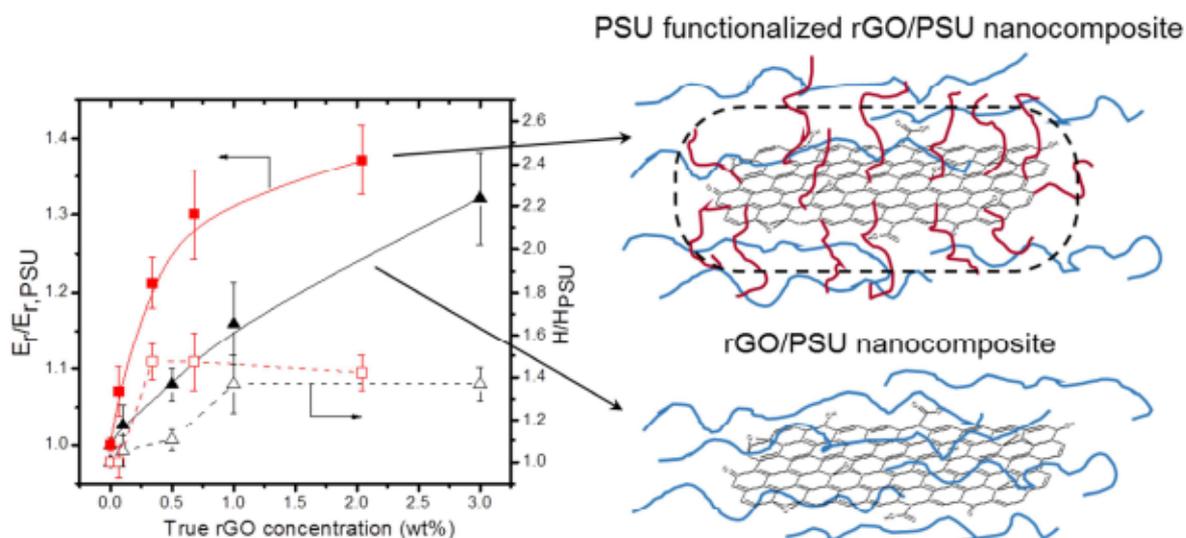
The current work reports the preparation of nanocomposites of polysulfone (PSU) reinforced with reduced graphene oxide (rGO) by a solvent-free extrusion-injection method. In order to improve nanofiller dispersion, rGO was covalently grafted with PSU brushes via click chemistry. Several rGO/PSU nanocomposites with concentrations up to 3% (by weight) were prepared with both unmodified and PSU-grafted rGO. Morphology of the rGO/PSU nanocomposites were characterized via FE-SEM and TEM, which revealed a better dispersion state when rGO was grafted with PSU. Thermo-mechanical characterization of the rGO/PSU which improved the overall mechanical properties compared to unmodified rGO/PSU composites. An increase in the glass transition temperature (T_g) of the PSU matrix was also observed. Nanocomposites did not reach complete rheological percolation, therefore, the results have been explained in terms of the entanglement of grafted and matrix PSU chains leading to improved interphase effects. The presence of

*Corresponding author: Juan C. Cabanelas, Phone: +34-916248386, Fax: +34- 91-6249430, E-mail: caba@ing.uc3m.es

grafted polymer chains also increased the sliding capacity favoring the sample deformation with subsequent toughness improvement. The proposed solvent-free extrusion-injection method is easily scalable and enables the potential uses of rGO/PSU nanocomposites.

Keywords: Nanocomposites, homopolymer brushes, graphene oxide, polysulfone, melt extrusion.

Graphical abstract



Highlights:

- Nanocomposites of polysulfone with functionalized rGO with PSU brushes have been prepared.
- Nanoreinforced composites were prepared by a solvent-free extrusion-injection method.
- Grafting of PSU brushes to rGO favors dispersion in PSU matrix improving the interfacial interaction.
- An improved thermal and mechanical behavior compared to unmodified rGO/PSU nanocomposites was achieved.

1 Introduction

Polymer matrix nanocomposites have attracted noteworthy attention due to the improved properties that can be achieved at low filler concentrations compared with conventional composites. In recent years, a huge scientific production has been performed on graphene-based polymer nanocomposites because of the excellent properties of graphene [1],[2]. Graphene improves mechanical, thermal, electrical, and gas barrier properties of polymers, showing a great potential for use in a vast array of diverse applications in energy, electronics, aerospace and automotive industry [2],[3],[4],[5],[6],[7],[8],[9],[10],[11]. Most research in graphene nanocomposites has involved testing of their mechanical and electrical properties [12],[13],[14],[15].

Among potential polymeric matrices, high-performance thermoplastic polysulfones (PSUs) are of great interest because they exhibit great chemical inertness, enhanced oxidative resistance, thermal and hydrolytic stability, as well as high mechanical strength [16],[17]. Additionally, PSUs might be easily processed as a film, and therefore, they are good candidates for use in various applications such as gas separation, hemodialysis, nano/ultra-filtration, metal to metal adhesives, fuel cells, drug delivery, or fiber reinforced composites.[18] The laminar structure and high specific surface of graphene nanosheets may improve thermal and mechanical properties of polysulfone as well as its biocompatibility and biofouling through graphene's antibacterial properties.[19] Graphene oxide (GO) was first incorporated into PSU matrices by Ionita et al. using a phase inversion method [20],[21], and the nanocomposite showed an enhancement in both mechanical and thermal properties. Most recent studies in GO/PSU systems start from solution fabrication methods [22],[23],[24]. In the current study, we present an original approach based on the preparation of homopolymer nanocomposites by covalent functionalization of rGO surface with PSU chains prior to blending with the polymer matrix. To the best of our

knowledge, the study of graphene/PSU nanocomposites functionalized with PSU brushes has not been reported so far [25].

A key challenge for the preparation of graphene nanocomposites is to obtain the appropriate dispersion of graphene within the polymer matrix. Graphene is usually difficult to disperse in polymers due to its high specific surface area, and van der Waals and π - π interactions [26],[27]. Solution processing methods have a limited use because of the poor solubility of PSU in most common solvents due to its highly aromatic and polar character. The few good PSU solvents (N-methylpyrrolidone, N,N-dimethylacetamide, trichloro-, and tetrachloroethane) are difficult to remove and they present harmful health effects. Melt mixing is a more simple method, however, it usually leads to poor graphene dispersion. An important issue is the particular method employed in the obtention of the graphene sheets, as it affects graphene surface chemistry, and therefore, the compatibility of graphene with the polymer matrix. The procedure to obtain GO usually involves thermal or mechanical exfoliation of graphite accompanied by chemical oxidation. Oxidation disrupts the carbon sp^2 network and decreases the conductivity and mechanical performance. In terms of electrical conductivity, GO is often considered an electrical insulator, and its mechanical performance, although still outstanding, is inferior to that of graphene. In this way, GO sheets are thermally and/or chemically reduced to partially recover the original graphene structure. Reduced graphene oxide (rGO) is more difficult to disperse than GO and tends to form aggregates. However, reduction is rarely complete, and therefore, the presence of residual oxygen functional groups (epoxy, ether, carbonyl) may improve dispersability in organic solvents and polymer matrices, and they can also be used to facilitate further surface modification [28]. Significant efforts have been made to modify rGO surfaces to make them more compatible with the polymer matrices [29],[30],[31]. Modification of rGO with polymeric brushes may improve the solution processability [32] and the dispersability of GO in the polymer matrix by forming strong interfacial interactions.

In a previous paper [33], we reported a successful method to obtain chemically functionalized rGO with PSU brushes. The surface modification improved the antibacterial properties through bacterial trapping in the grafted polymer. In the current work, we present, for the first time, preparation and mechanical testing of novel graphene/PSU nanocomposites based on the use of rGO that are functionalized with PSU brushes.

An important factor to be considered is the particular method used in the preparation of the nanocomposite. Many authors reported the production of graphene nanocomposites by solution mixing [25]. It is well-known that solution mixing may result in composites with inferior mechanical properties, and therefore, in the current work, melt blending was used. Moreover, lack of hazardous chemicals makes melt blending an environmentally friendly processing method. In fact, melt extrusion, followed by injection molding, is a widely used procedure in the industry for the fabrication of thermoplastic nanocomposites. It is also noteworthy that this process is easier to scale up for large-scale production for commercial applications. Nanocomposites containing up to 3% (by weight) surface modified rGO have been prepared via melt mixing using a twin-screw extruder. Their morphology, and mechanical and dielectric behavior was characterized and compared against composites containing non-modified rGO and neat PSU. Results showed a significant improvement in the mechanical properties of the surface modified rGO nanocomposites, which is attributed to better charge transfer in an extended interphase, even though a percolated network of rGO nanofillers was not observed

2 Experimental

2.1 Materials

Graphene oxide (GO) was synthesized from natural graphite powder (Alfa Aesar, universal grade, ~200 mesh, 99.9995% purity) using a modified Brodie's method [34]. Then, GO was reduced in hydrogen atmosphere at 500 °C to obtain reduced

graphene oxide (rGO). Direct observation by TEM revealed few layer graphene stacking, from 6 to 9 graphene layers by aggregate.

A commercially available polysulfone polymer purchased from BASF (Ultrason S2010, $M_n \sim 14,000$ g/mol, high polydispersity) was used as polymer matrix. PSU from Sigma Aldrich ($M_w \sim 35,000$ g/mol, $M_n \sim 16,000$ g/mol) was used for graphene modification. Synthesis and characterization of rGO modified with polysulfone brushes were performed as previously reported [33]. Briefly, the synthesis followed the well-known nitrene chemistry. Previous to grafting, an azide group was introduced to the polysulfone chain and subsequently a covalent linkage was established via 1,2-cycloaddition to the sp^2 carbon network of the rGO by forming a stable aziridine linkage. Two different modified graphenes were prepared depending on the position of the azide functionalization on the PSU backbone: at the chain end (rGO-PSU end) or randomly along the polymer chain (rGO-PSU mid).

The grafted PSU chains represented 29 and 32% of the rGO-PSU mid and rGO-PSU end by weight, respectively, as determined by TGA (see authors' previous work in reference [33]). The rGO-PSU end composite had the longer polymer brushes ($\sim 16,000$ g/mol) with a grafting density of 3.53 chains per 10,000 carbons. For rGO-PSU mid, the mean molecular weight of the anchored polymer chain may be estimated as $\sim 8,000$ g/mol, because each grafted polymer chain generated two branches, and therefore, the grafting density was calculated to be 6.16 chains per 10,000 carbon atoms.

2.2 Nanocomposite preparation

Incorporation of reduced graphene oxide and polymer-modified rGO nanosheets in the polysulfone matrix was performed by melt mixing using a HAAKE Minilab micro-compounder, equipped with a conical counter-rotating silicon carbide hardened twin-screw extruder. Nanocomposites containing 0.1-3.0 wt% nanoreinforcement were fabricated by mixing with PSU pellets in the twin screw. The mixture was cycled for 10 min at 340 °C at a screw rotating speed of 150 rpm in order to obtain a good

dispersion of the nanosheets in the polymer matrix. The molten polymer strand was quenched at room temperature and pelletized. The extruded pellets of neat PSU and nanocomposites were injection molded using a Battenfeld Microsystem 50 micro-molding machine at a mold temperature of 135 °C, barrel temperature of 350 °C, die temperature of 345 °C, injection speed 500 mm/s, injection pressure of 989 bar, and cycle time of 20 s to obtain bone shaped specimens measuring 16x3x1 mm and disks of 0.45 mm thickness and 7 mm radius. After the injection, samples were subjected to heat treatment at 170 °C for 1 hour to remove any residual internal stresses. Figure S1 shows representative injected specimens of various nanocomposite samples. Only at the lower graphene content (0.1 wt%), the composite is light grey, and above 0.5 wt%, the material becomes completely black. In all cases, the specimens presented a homogeneous macroscopic appearance.

Table 1 presents all materials studied in the current work. The naming conventions used is PrG(*x*) for unmodified graphene nanocomposites, and PrGend(*x*) and PrGmid(*x*) for nanocomposites with rGO-PSU end and rGO-PSU mid nanoreinforcements, respectively. The number (*x*) inside the parentheses indicates the apparent percent concentration of rGO (including the brush if present) by weight. Obviously, in the case of modified rGO, the contribution of the grafted PSU chains leads to a lower weight percentage of the rGO sheets in the nanocomposite. The true rGO concentrations are also indicated in Table 1.

Table 1. List of all samples studied, and the apparent and true rGO concentrations of nanocomposites.

Sample	Apparent rGO Concentration (wt%)	True rGO Concentration (wt%)
PSU	–	–
PrG(0.1)	0.10	0.10
PrG(0.5)	0.50	0.50
PrG(1.0)	1.00	1.00
PrG(3.0)	3.00	3.00
PrGmid(0.1)	0.10	0.07
PrGmid(0.5)	0.50	0.35
PrGmid(1.0)	1.00	0.71
PrGmid(3.0)	3.00	2.13
PrGend(0.1)	0.10	0.07
PrGend(0.5)	0.50	0.34
PrGend(1.0)	1.00	0.68
PrGend(3.0)	3.00	2.04

2.3 Characterization techniques

Thermogravimetric analysis (TGA, Perkin Elmer STA 6000) was carried out to study the thermal stability of the nanocomposites under N₂ atmosphere in a temperature range of 50-900 °C at 10 °C/min. Rheometry (AR2000EX, TA Instruments) was employed to study the viscoelastic behavior of the nanocomposites. Frequency sweeps from 0.1 to 100 rad/s were performed at 290 °C. For all measurements, modified and unmodified graphene nanocomposites were tested within the linear viscoelastic strain range.

The morphology of the samples and the dispersion state were investigated by transmission electron microscopy (TEM, JEOL-JEM-2010) and scanning electron microscopy (SEM, Nova NanoSEM 230). For SEM measurements the surface of the samples was analyzed after cryogenic fracturing and coating with gold. TEM samples were cut to a thickness of 60 nm with an ultramicrotome at 0.7 mm/s.

Dynamic mechanical thermal characterization (DMTA, TA instrument Q800) of all compounded materials was performed with injection molded specimens in tension mode in a temperature range of 50-220 °C. A heating rate of 2 °C/min and a frequency of 1 Hz were employed during DMTA experiments.

The electrical conductivity was determined using a digital multimeter (Agilent HP34401). Dielectric spectroscopy (Novocontrol Alpha Analyzer, type K) was performed over laminar samples of around 1 mm thick with a circular area of 2.5 cm in diameter.

Tensile tests were performed with a Shimadzu Autograph-1KN at a crosshead speed of 1 mm/min and at room temperature according to UNE-EN ISO 527-2 standard with bone-shaped injection molded samples. Each mechanical test was carried out at least five times. Nanoindentation tests were performed with Hysitron TI 900 Tribodenter. For each sample, 21 measurements were done in 3x7 pattern over a cross-section of the specimen with a Berkovich tip applying a load of 8000 μ N.

3 Results and Discussion

3.1 Nanocomposite morphology

It is essential to determine if the graphene nanoplatelets are well dispersed within the PSU matrix since an inadequate dispersion may result in less than expected change in the material behavior and it could even negatively affect the polymer matrix properties. The morphology of the composites was evaluated by microscopy. SEM micrographs of nanocomposites prepared with the highest loading (3 wt%) are presented in Figure 1. The effect of rGO on the composite microstructure is clearly observed. The smooth and uniform cryo-fractured surface of pristine PSU (Figure 1a) is representative of a brittle fracture with little plastic deformation. The fracture surfaces became rough after rGO addition (Figure 1b-d). The SEM images of the fracture surfaces also provide evidence of a relatively good dispersion of graphene embedded in the PSU matrix, although some small aggregates can be detected on the nanocomposites. The boundaries between the rGO sheets and the PSU matrix

are not defined, which suggests a strong interfacial adhesion. PrGmid and PrGend nanocomposites (Figure 1c and 1d, respectively) showed a higher plastic deformation compared to PrG, owing to a better dispersion. The improved dispersion in PrGmid and PrGend could be attributed to the entanglements formed between the PSU brushes on rGO and the matrix PSU chains. The cohesive fracture produced cavities at the fracture surface, due to the dragging of the matrix material by the graphene, suggesting an interfacial adhesion within the grafted chains and the polymer matrix.

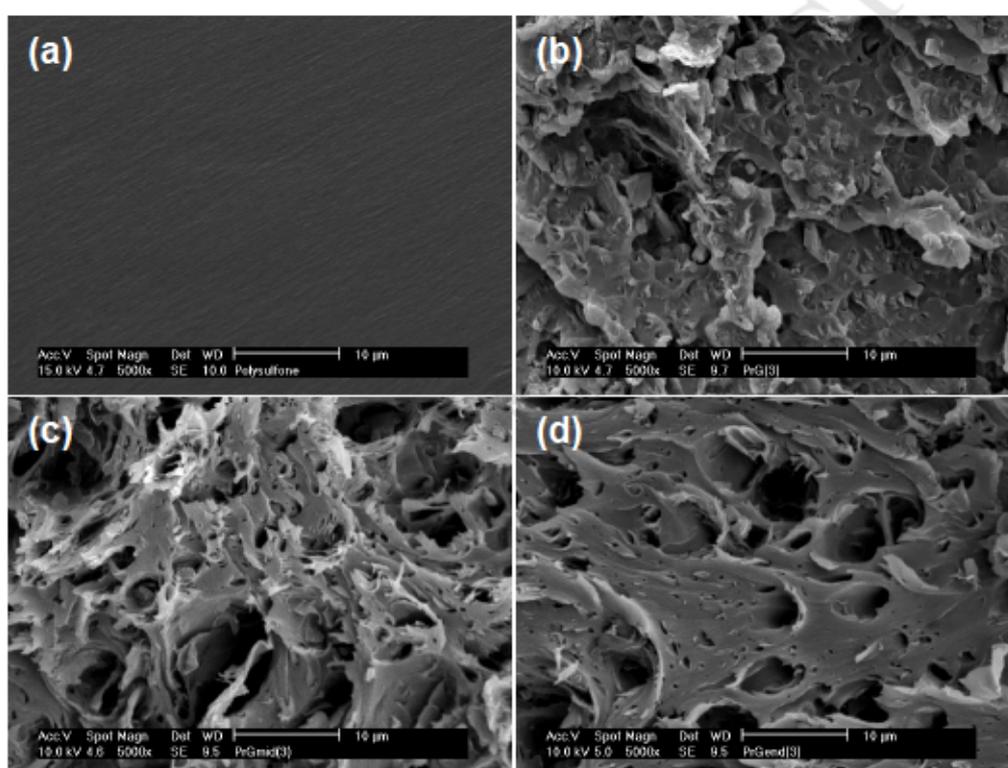


Figure 1. SEM images of (a) neat PSU, (b) PrG(3.0), (c) PrGmid(3.0), and (d) PrGend(3.0). The scale bar is 10 μm .

Examination of PrG, PrGend, and PrGmid nanocomposites by TEM revealed a distribution of delaminated graphene nanosheets (Figure 2). The graphene stack thickness for PrG nanocomposites was estimated to be around 50 nm (Figure 2a), reflecting a certain amount of aggregation as suggested by SEM. Nanocomposites prepared with polymer-modified rGO showed a drastic decrease in the aggregates

thickness, with values between 5 and 15 nm (Figures 2b and 2c). This could be attributed to the presence of polysulfone brushes, which might have improved the compatibilization between the rGO nanosheets and the polymer matrix, and therefore, preventing aggregation. It is also possible that rGO sheets slide with respect to each other and form smaller stacks during extrusion and injection molding because of brush and matrix chain entanglement. Orientation of rGO stacks parallel to the flow direction was observed in injection molded samples as shown in Figure 2d, which reinforces our argument that processing could have led to decreased stack size in modified rGO containing samples.

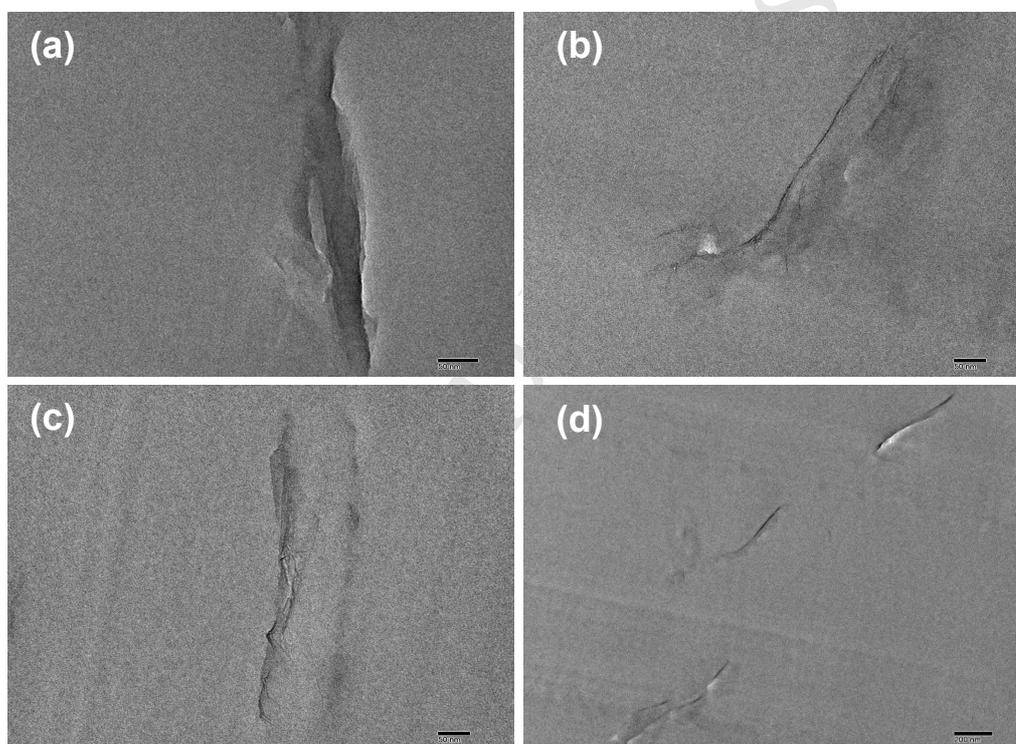


Figure 2. TEM images of (a) PrG(3.0), (b) PrGmid(3.0), and (c,d) PrGend(3.0) nanocomposites. Scale bars are 50 nm except for (d), which is 200 nm.

In addition to direct observation by microscopic techniques, the dispersion of the nanofillers in the PSU matrix has also been evaluated by rheology. Dynamic measurements of rheological properties are an important tool in the characterization of polymer composites since they provide information on the state of dispersion and

on the interaction between the nanofillers and the polymer matrix in molten state. Figure 3 shows the variation of storage modulus (G') as a function of angular frequency measured at 290 °C. The presence of rGO nanosheets induced a moderate effect on the viscoelastic properties at low frequencies, increasing the storage shear modulus even at concentrations as low as 0.1 wt%.

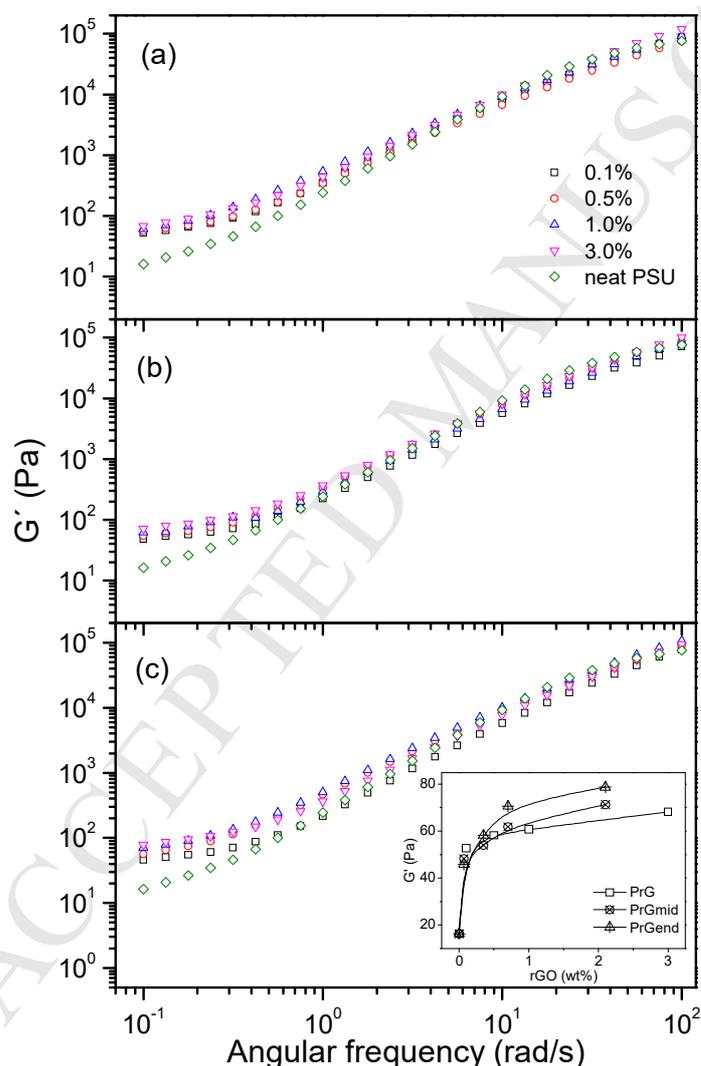


Figure 3. Storage modulus vs. angular frequency for neat PSU and rGO-PSU nanocomposites: (a) PrG, (b) PrGmid, and (c) PrGend. Insert compares the value of G' at 0.1 Hz.

Neat PSU polymer chains are fully relaxed at low frequencies and present initial stages of homopolymer-like terminal flow behavior. However, the dependence of G' on frequency looks almost identical among all rGO/PSU nanocomposites at low frequencies, and the terminal flow behavior is clearly retarded – instead the initial stages of a rubbery plateau can be seen. This effect is indicative of a gradual transition from liquid-like to solid-like viscoelastic behavior, and it may be attributed to the emergence of an rGO network, which acts to restrain the long-range dynamics of the PSU chains. Analogous rheological behavior has been previously reported for other polymer nanocomposite systems [35],[36]. At high frequencies, the influence of the rGO nanosheets on the viscoelastic properties is low and all samples, including neat PSU, look indistinguishable from each other. This behavior suggests that the graphene did not considerably affect the short-range motion of the PSU chains, especially on length scales comparable to the entanglement length.

Although similar observations can be made for PrGmid and PrGend nanocomposites, there are some differences between modified and unmodified nanocomposites. The increment of G' concerning the rGO content at low frequencies is further pronounced for PrGend and PrGmid nanocomposites (insert in Fig. 3c), even considering that the real concentration is lower in both cases (Table 1). This behavior confirms that PSU brushes improve the dispersion of the rGO nanosheets and their interfacial interaction with the polymer matrix [37],[38]. Furthermore, the absence of a clear plateau in the G' value at low frequencies is a clear indication that the system has not reached rheological percolation in any nanocomposite.

3.2 Conductivity and dielectric behavior

Conductivity in a polymer composite is determined by the inter-particle distance between the conducting filler particles, which in turn depends on the dispersion, aspect ratio, and alignment of the nanoparticles. The conductivity of the rGO/PSU nanocomposites was lower than the detection limit of the equipment used, and therefore, the results were difficult to assess. The low conductivity is not surprising;

others also reported low conductivity values for partially reduced GO composites [39],[40]. In addition, isolated local clusters of rGO sheets are effectively embedded in a shell of the electrically insulating PSU with covalently linked hard segments, which was confirmed by microscopy and rheology previously. rGO nanosheets do not interlock, and therefore, the system fails to form electrically conductive pathways and electrically conductive percolated network.

The study of the real and imaginary components of the permittivity was carried out for all samples in order to characterize the state of dispersion. All nanocomposites showed a gradual increase in both the real (dielectric constant, ϵ') and imaginary (dielectric loss, ϵ'') parts of the permittivity with rGO concentration (see Figure S2). The dielectric constant of nanocomposites with unmodified rGO slightly increased with rGO concentration over the entire frequency range (Figure S2a) probably due to high nanofiller surface area, and it was previously reported for other graphene based nanocomposites [7],[37],[41]. More significant enhancement in the dielectric permittivity was detected for polymer-modified graphene nanocomposites (Figure S2b and S2c). A comparison of ϵ' and ϵ'' values of all nanocomposites containing 3 wt% rGO are shown in Figure 4. The dielectric constant of PrGend(3.0) and PrGmid(3.0) at 1 kHz are ~35 and ~25% greater than that of neat PSU, respectively. These increases are significant taking into account the low filler concentration and the relatively low aspect ratio of the rGO. Enhanced dielectric permittivity for PrGend and PrGmid nanocomposites may be attributed again to the better dispersion of the rGO in the PSU matrix.

A gradual decrease in dielectric loss is observed for all samples with frequency because the induced charge is unable to follow the reversing field, which leads to a decay in the electrical oscillations as the frequency is increased [42]. The dielectric loss for PrG nanocomposites was very low due to their poor conductivity (although they were slightly greater than those of the neat PSU matrix). PSU-modified rGO containing nanocomposites (PrGend and PrGmid) showed greater loss factors compared to unmodified nanocomposite (PrG).

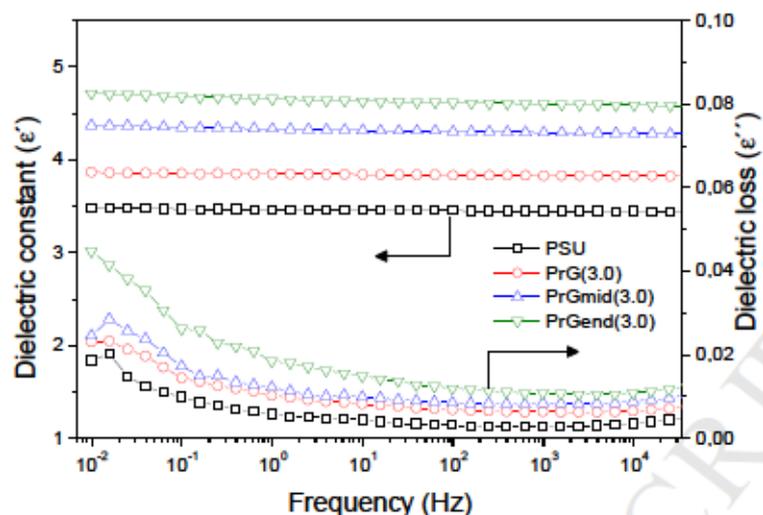


Figure 4. Dielectric spectroscopy measurements of 3 wt% rGO containing nanocomposites and neat PSU at 25 °C.

3.3 Thermal properties

Thermogravimetric analysis for pure PSU and its nanocomposites were very similar showing a single degradation peak, although a moderate improvement in the thermal stability compared with pristine PSU was reached. The temperature corresponding to a 5% weight loss ($T_{5\%}$), regarded as a criterion of stability, is presented in Table 2. $T_{5\%}$ increased gradually with rGO content, showing the increase of thermal stability caused by the nanofiller addition. A rise by about 8, 11, and 13 °C for PrG, PrGmid, and PrGend nanocomposites, respectively, was observed at a 3 wt% apparent rGO concentration. This enhancement in thermal stability may be attributed to the fact that graphene nanosheets delay the release of volatile degradation products and also char formation [43]. Similar results were previously reported for other graphene-based nanocomposites [44],[45]. It is noteworthy that PrGend and PrGmid nanocomposites exhibited an improved thermal stability compared to PrG nanocomposites even though they have in fact a lower content of rGO nanosheets. These results are in accordance with the better rGO dispersion which was observed by SEM and TEM in the modified samples.

DMTA curves are shown in Figure S3. The glass transition temperature (T_g) was obtained at the α relaxation peak of the $\tan \delta$ vs. temperature curve. DMTA also allows to obtain the storage modulus, which will be discussed later on. T_g in

polymers depends on multiple structural parameters such as the flexibility and molecular weight of the chain, branching/crosslinking, and intermolecular forces among other factors. A polymer chain grafted to a solid surface shows a relaxation behavior quite different from that of free chains. Polymer brushes may influence the T_g of the composite through chain entanglement with the polymer matrix chains. The T_g s of the nanocomposites are reported in Table 2, and Figure 5 shows the relative change in T_g with respect to the T_g of neat PSU.

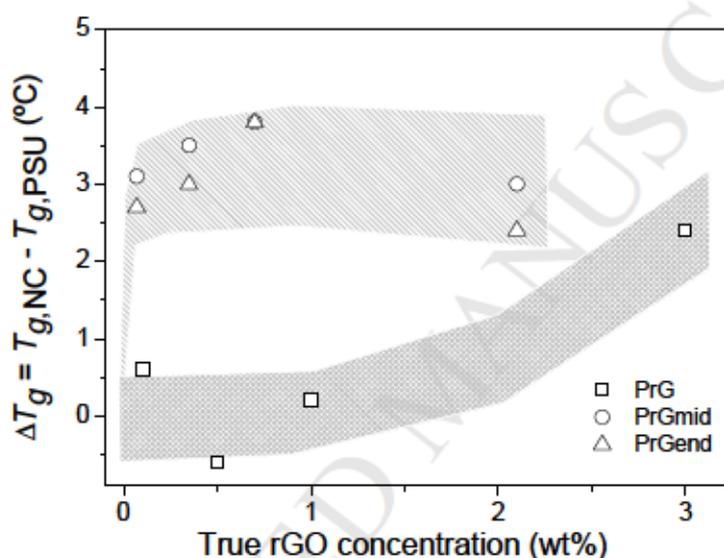


Figure 5. Change in the glass transition temperatures of rGO/PSU nanocomposites. Shaded areas are included as eye guides.

Neat PSU presented a T_g at ~ 195 °C and after the addition of rGO slight but significant changes in T_g were observed. Most of the prepared nanocomposites showed T_g values above that of PSU, which may be a consequence of an increased restriction to chain mobility resulting from the hydrogen bond interactions between the PSU chains and the oxidized functional groups on the rGO nanosheets surface. These results are in agreement with previously reported polymer/graphene nanosheets systems [35],[46],[47]. Furthermore, the DMTA measurements revealed a more pronounced increase in the T_g of the nanocomposites prepared with polymer-modified graphenes (PrGend and PrGmid) at very low graphene concentrations; up

to ~ 4 °C increase in T_g at 1 wt% apparent rGO concentration (~ 0.7 wt% true rGO concentration) relative to neat PSU. It should also be noted that a ΔT_g of 3 °C was observed with only 0.07 wt% true rGO loading. By contrast, PrG nanocomposites prepared with unmodified rGO only showed significant ΔT_g increases at 3 wt% rGO concentration. These results may be attributed not only to a better dispersion of the modified rGO but also to the presence of entanglements between matrix and rGO tethered chains at the interphase.

3.4 Mechanical properties

The mechanical performance of polymer matrix nanocomposites depends not only on the dispersion state and the characteristics of the nanofiller (such as size, aspect ratio, strength, and modulus) but also on the influence of the nanoreinforcement on the matrix properties such as crystallinity. In addition, the filler/matrix interfacial interactions are especially important as they influence the efficiency of interfacial stress transfer.

There is some controversy in the literature about the impact of graphene on mechanical properties because they are strongly dependent on the state of dispersion and the characteristics of the graphene used [25],[48]. In most studies, rGO/PSU nanocomposites have been prepared by solution casting [49],[50], and the reported Young's modulus in these studies is very low – not comparable with those obtained in the current study.

Typical stress-strain curves of rGO/PSU nanocomposites obtained from tensile tests are shown in Figure 6. Table 2 summarizes the main parameters obtained in these tests along with thermal properties and the storage modulus (E') as determined via DMTA at room temperature, which shows a similar behavior to tensile test results. The presence of rGO caused a noticeable impact on the mechanical behavior by mainly influencing the matrix toughness of the polymer-modified graphene samples. The addition of unmodified rGO into PSU matrix (PrG nanocomposites) improved the tensile modulus up to $\sim 12\%$ compared with that of

neat PSU. This enhancement is accompanied by an important decrease in the failure strain at rGO concentrations greater than 0.5 wt%. In fact, these PrG samples failed prior to yielding. Although this might be due to the presence of defects in the specimens, it reveals that they have become brittle. A strong rGO/PSU interface not only allows the stress transfer but also hinders the sliding of the PSU chains, preventing deformation. This tendency is common in graphene nanocomposites because the rigid nanofiller makes the material more brittle [51].

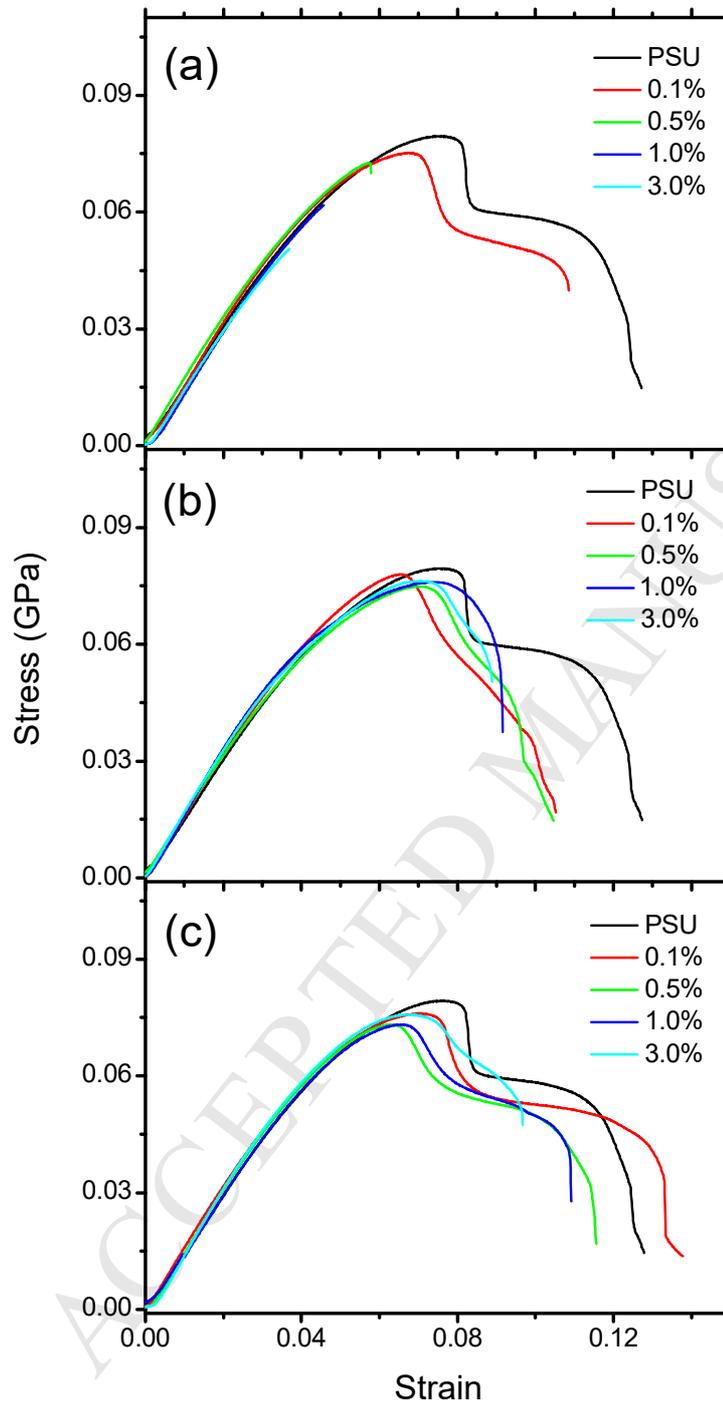


Figure 6. Typical stress-strain curves obtained for (a) PrG, (b) PrGmid, and (c) PrGend nanocomposites. Results for PSU are also included for comparison.

Table 2. Mechanical parameters of PSU and nanocomposites.

Sample	T_g (°C) ¹	$T_{5\%}$ (°C) ²	E'_{DMTA} (GPa)	$E_{Tensile\ Test}$ (GPa)	$\sigma_y/\sigma_{y,PSU}$	$\epsilon_r/\epsilon_{r,PSU}$
PSU	195.4	506	1.99	2.05 ± 0.04	1.00 ± 0.03	1.00 ± 0.12
PrG(0.1)	196.0	508	1.93	2.05 ± 0.13	0.94 ± 0.05	0.84 ± 0.20
PrG(0.5)	194.8	509	1.97	2.12 ± 0.11	– ³	– ³
PrG(1.0)	195.6	513	1.99	2.17 ± 0.04	– ³	– ³
PrG(3.0)	197.8	514	2.19	2.29 ± 0.08	– ³	– ³
PrGmid(0.1)	198.5	509	1.90	2.11 ± 0.04	0.96 ± 0.04	0.85 ± 0.14
PrGmid(0.5)	198.9	510	2.07	2.14 ± 0.07	0.98 ± 0.03	0.80 ± 0.10
PrGmid(1.0)	199.2	510	2.20	2.21 ± 0.09	0.95 ± 0.04	0.73 ± 0.09
PrGmid(3.0)	198.4	517	2.23	2.38 ± 0.08	0.97 ± 0.04	0.69 ± 0.09
PrGend(0.1)	198.1	508	1.99	2.18 ± 0.11	0.96 ± 0.03	0.96 ± 0.15
PrGend(0.5)	198.4	510	2.14	2.19 ± 0.11	0.92 ± 0.04	0.88 ± 0.14
PrGend(1.0)	199.2	513	2.24	2.21 ± 0.04	0.91 ± 0.05	0.74 ± 0.09
PrGend(3.0)	197.8	519	2.34	2.40 ± 0.03	0.96 ± 0.03	0.71 ± 0.09

¹The glass transition temperature as determined by DMTA as the maximum of $\tan \delta$. ²Temperature at which 5% weight loss occurs as determined by TGA. ³Most of the specimens failed prior to yielding.

Grafting of PSU polymer brushes to rGO resulted in a better dispersion of the nanofillers in the PSU matrix, and as a result, mechanical properties were different than those of PrG nanocomposites. Better dispersion explains the further increase observed in the Young's modulus of these samples – up to 16 and 17% for PrGmid(3.0) and PrGend(3.0), respectively. Furthermore, it is remarkable that the PSU-modified rGO nanocomposites also showed a substantial recovery of their toughness as compared to PrG samples (Figure 6). PSU-modified rGO nanocomposites exhibited an important plastic deformation with strain at break values well above 0.1. The increase in the deformability of the nanocomposites with respect to PrG samples may be a consequence of the better sliding capacity of the matrix polymer chains on the surface of the graphenes modified with the

homopolymer brushes. These results indicate that the PrGend and PrGmid composites exhibited good mechanical behavior that is substantially different from those of unmodified rGO nanocomposites, and would justify their use in practical applications.

Graphene and its derivatives show large surface area, and a strong nanofiller/matrix interphase is fundamental to ensure a good interaction between matrix polymer chains and nanoparticles [52]. This work, as expected, confirms the strong interactions between the residual oxidized functional groups on rGO and the polar groups of the PSU backbone. Even so, the additional increase in the modulus of elasticity and toughness recovery in PrGmid and PrGend samples needs to be explained, especially considering that decorating rGO with PSU brushes should decrease the accessibility of the rGO surface by the matrix polymer chains.

The well-established Halpin-Tsai model adapted for nanoplatelets has been used to predict the modulus of rGO/PSU nanocomposites [44]. The theoretical modulus is given by Eqs. 1–5 for randomly (E_c) and unidirectional ($E_{||}$) oriented graphene sheets embedded in a polymer matrix. E_g and E_m are the Young's modulus of the graphene and the matrix, respectively; V_c is the volume fraction of rGO; and α_g , l_g , and t_g are the aspect ratio, length, and thickness of the rGO nanosheets, respectively. The aspect ratio (α_g) of rGO was estimated to be 32 from TEM images. A Young's modulus value of 250 GPa was used for rGO in the calculations [47]. The density of PSU and rGO are taken to be 1.24 and 2.2 g/cm³, respectively.

$$E_c = E_m \left[\frac{3}{8} \frac{1 + \eta_L \xi V_c}{1 - \eta_L V_c} + \frac{5}{8} \frac{1 + 2\eta_T V_c}{1 - \eta_T V_c} \right] \quad (1)$$

$$E_{||} = E_m \left[\frac{1 + \eta_L \xi V_c}{1 - \eta_L V_c} \right] \quad (2)$$

where

$$\eta_L = \frac{\left(\frac{E_g}{E_m}\right)^{-1}}{\left(\frac{E_g}{E_m}\right) + \xi} \quad (3)$$

$$\eta_T = \frac{\left(\frac{E_g}{E_m}\right)^{-1}}{\left(\frac{E_g}{E_m}\right) + 2} \quad (4)$$

$$\xi = \frac{2\alpha_g}{3} = \frac{2l_g}{3t_g} \quad (5)$$

The results of the Halpin-Tsai model calculations are shown in Figure 7. Experimental data obtained for the PrG nanocomposites follow the theoretical results of randomly oriented nanoplatelets. It should be noted that the average thickness of nanoreinforcement was roughly estimated to be ~12 nm by TEM analysis, although unmodified graphene stacks were poorly dispersed so they exhibited a large aggregation showing a greater average thickness (Figure 2a).

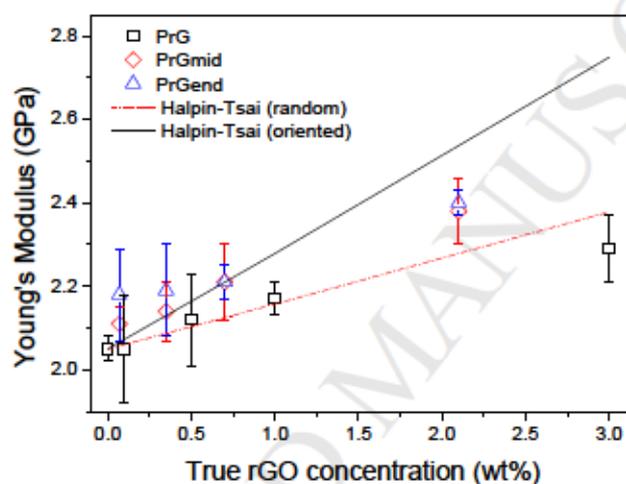


Figure 7. Comparison of the experimental Young's moduli of rGO-PSU nanocomposites to random and unidirectional graphene sheet orientation within the PSU matrix as calculated from Halpin-Tsai equations.

However, more interesting results were obtained for the nanocomposites prepared with polymer-modified graphene, taking into account that the theoretical framework of the Halpin-Tsai model assumes that each component of the composite acts independent of the other. There seems to be a better agreement between the experimental data and the theoretical prediction assuming the rGOs are aligned unidirectionally. This is consistent with our previous observation of the preferred orientation of the graphene sheets as a result of the injection molding process (Figure 2d). At the highest rGO concentration of 3 wt%, the experimental moduli of PSU-modified rGO nanocomposites are lower than the theoretical prediction, which

is probably due to aggregation. On the other hand, at low rGO concentrations, the experimental moduli of both PrGmid and PrGend nanocomposites are greater than the theoretical prediction. This may be caused by the entanglement of grafted and matrix polymer chains, which should favor stress transfer. These results indicate that an extended interphase strongly affects the mechanical behavior of the polymer matrix.

Nanoindentation is another testing method that was used for measuring the mechanical properties such as hardness and modulus at the submicron scale. This technique is sensitive to nanofiller concentration and its dispersion state, as well as to the interfacial adhesion between the nanoparticles and the host polymer matrix [53],[54]. In the current study, nanoindentation was employed on PrG and PrGend nanocomposites only.

Representative loading-unloading curves for neat PSU, PrG(3.0) and PrGend(3.0) nanocomposites are shown in Figure S4. Force vs. displacement curves shifted to lower displacement values with increasing rGO concentration, indicating that the nanocomposite resilience to indentation gradually increased with nanofiller content [55].

The load-displacement curves provide information about the viscoelastic, elastic, and plastic deformation behavior. The stiffness of the materials, evidenced by the increasing slope at the beginning of the unloading curve, raised with the increase in the rGO concentration. The curves allow the determination of the elastic reduced modulus (E_r) and hardness (H), following the Oliver and Pharr method [56]. Hardness was obtained from the quotient between the force applied at the maximum penetration depth and the residual projected contact area between indenter and sample (A_c), following the usual procedure [53]. The reduced elastic modulus (E_r) was obtained from equation 6, where S is the contact stiffness, i.e. the initial slope of the unloading curve, considering $\beta = 1.08$ for a Berkovich indenter [57]. The elastic modulus was then calculated using the equation 7 from the reduced modulus and

the indenter modulus (E_i), and the Poisson's ratio (ν) of the sample (a value of 0.34 was used for PSU) and that of the indenter.

$$E_r = \frac{S}{2\beta} \frac{\sqrt{\pi}}{\sqrt{A_c}} \quad (6)$$

$$\frac{1}{E_r} = \frac{(1-\nu_{sample}^2)}{E_{sample}} + \frac{(1-\nu_i^2)}{E_i} \quad (7)$$

Following this procedure, it was found that the reduced modulus values obtained from nanoindentation were greater than those obtained from DMTA or tensile tests [53]. Unlike other techniques, in nanoindentation, the volume of deformation is changing during the experiment and the material is subjected to compression. Nevertheless, the tendency in the mechanical behavior was the same; an increase in the mechanical performance due to the rGO modification with PSU brushes and, in general, with the increase in rGO concentration.

Normalized values of hardness and modulus with respect to neat PSU are presented in Figure 8. As expected, an increase in the rGO loading led to an enhancement in both modulus and hardness. The maximum increase for PrG nanocomposites was 32% for the modulus and 37% for the hardness. A significant additional increment at all compositions was observed when PSU grafted graphene was used. There was a notable increase in the modulus and hardness, around 37% and 43%, respectively, for PrGend(3.0) with respect to neat PSU, taking also into account that modified samples actually have less graphene content in the nanocomposites. This increment was large enough to demonstrate that the addition of modified rGO has a significant effect on the load transfer efficiency at the rGO-matrix interphase.

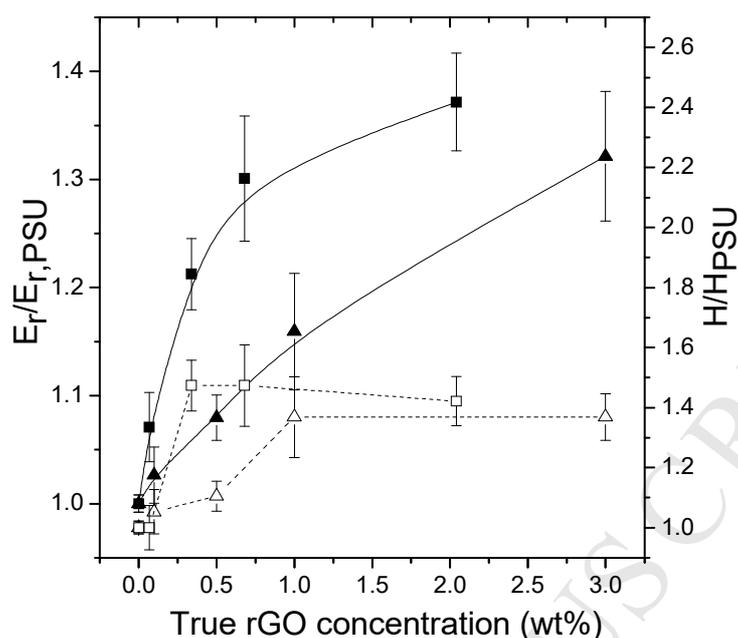


Figure 8. Elastic modulus (solid symbols) and hardness (open symbols) of PrG (triangles) and PrGend (squares) nanocomposites as a function of true rGO concentration obtained via Oliver and Pharr method.

3.5 Interphase model hypothesis and discussion

It is clear that in order to explain the observed changes presented in the previous sections, the interactions between the grafted PSU and the matrix PSU chains must be analyzed. Given that there is an optimal chemical compatibility between the PSU chains grafted on the rGO surface and the matrix PSU chains due to their similar chemical identity, the interactions between them should mainly depend on the degree of polymerization of the grafted polymer (N), the degree of polymerization of the matrix chains (P), and the grafting density (σ). In brief, polymer brushes grafted onto surfaces are considered either in mushroom, dry brush, or wet brush conformation, depending on the interpenetration with the matrix chains.

Several works predicted the structure and behavior of grafted polymer chains [58],[59],[60],[61]. Low grafting densities lead to mushroom regime, in which the grafted chains remain isolated and do not interact with each other. On the contrary, if the grafting density is higher, the distance between adjacent tethered chains is close

enough that grafted chains can overlap with each other, and therefore, they assume a semi-dilute polymer brush (SDPB) regime. This behavior is usually considered when the grafted interchain distance is less than the radius of gyration (R_g) of the unperturbed polymer in solution. In the brush conformation, the grafted chains can penetrate into the matrix (complete wetting region) or they can be expelled from the interphase (autophobic or allophobic dewetting). Therefore, it is important to know if the system has reached the crossover point between a mushroom and brush conformation. The R_g of the PSU polymer used for grafting in this work is estimated following Ioan [62]; assuming a characteristic ratio (C_∞) of 2 for the polymer [63]. R_g was determined to be 4.2 nm from $R_g = (1/\sqrt{6}) C_\infty n l^2$. The average distance between grafted chains (d) may be obtained from grafting density (σ) via $d = 1/\sqrt{\sigma}$ [64]. However, due to possible stacking of pristine rGO layers, an accurate determination of the grafting density cannot be made. A rough estimation of the grafting density considering layer stacking gives 0.080 chains/nm² for PrGend and 0.14 chains/nm² for PrGmid nanocomposites, which implies an average distance between grafted chains of ~3.5 and ~2.7 nm, respectively. These values suggest that the grafting density is large enough to consider that the brushes adopt a SDPB regime. At the same time, the grafting density is low enough to avoid autophobic dewetting – grafted and matrix polymer chains are well mixed at the interphase. We also have to consider that the processing conditions involved high shear melt mixing, which favors interpenetration of grafted and matrix chains, and leads to extended conformations compared to unperturbed coil, and therefore, expanding the influence of the grafted polymer through the matrix. In the brush or semidilute regime, the interactions between grafted chains forces them to spread away from the surface, with the corresponding penalty of free energy and entropy reduction. Swelling of the grafted polymer by the matrix chains is favored by an increase in entropy, but it also results in a larger stretching of the grafted chains. As a consequence, the extension of the graft chain, and therefore, the thickness of the interphase, results from a balance of these factors. Figure 9 is an attempt to represent the interphase in the

nanocomposites. Grafting of PSU increases the interphase effect not only by chain entanglement but also extending the interphase volume. The higher chain length and lower grafting density of PrG end respect to PrG mid composites explains their better overall behavior.

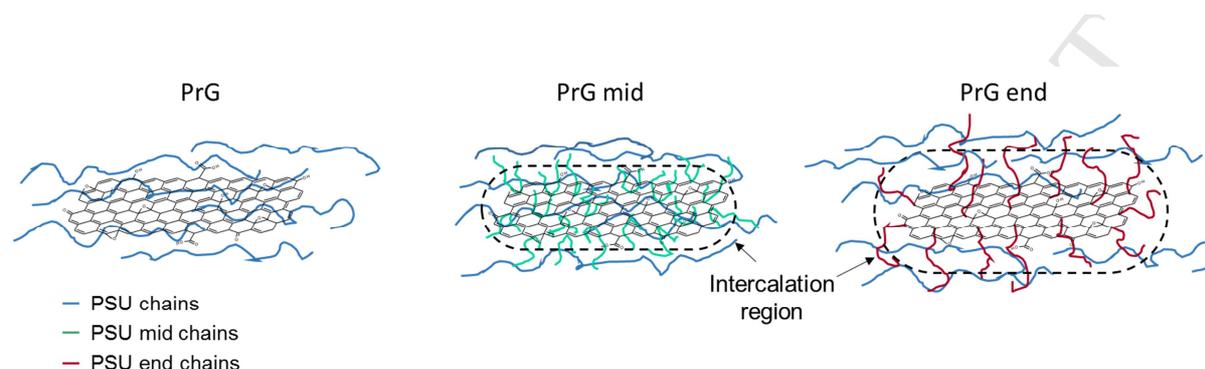


Figure 9. Interphase model proposed for rGO/PSU nanocomposites.

More research would be necessary to confirm these assessments. The visualization of the interface presented in Figure 9 may explain not only the enhancement in interfacial charge transfer, with the consequent improvement in the overall mechanical properties, but also the observed increase in T_g and the rise of sliding capacity when the material is subjected to deformation.

4 Conclusions

In the current study, rGO/PSU nanocomposites, in which graphene was covalently modified by PSU brushes, were prepared. The rGO functionalization increased the compatibility with the homopolymer PSU matrix, allowing the preparation of nanocomposites with an industrially scalable, solvent-free, extrusion-injection method. The unique processing method presented led to improved nanofiller dispersion, and improvements in both thermal and mechanical behavior with respect to unmodified rGO/PSU nanocomposites. The enhancement of mechanical properties were interpreted in terms of an extended influence of the rGO through chain entanglements between grafted and matrix PSU chains. It is noteworthy that not only the mechanical performance of polymer-modified rGO nanocomposites was

improved, but also the toughness and the thermal stability of these materials were increased. This functionalization strategy may widen the potential applications of rGO/PSU nanocomposites.

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