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Few-layer graphene aqueous suspensions for polyurethane composite coatings

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ABSTRACT

Graphite nanoplates (GnP) have recently attracted attention as an economically viable alternative for the development of functional and structural nanocomposites. The incorporation of GnP into waterborne polyurethane (WPU) with loadings from 0.1 to 10 wt.% was studied. The mechanical properties of the composite films were assessed by tensile testing showing an increase of the Young's modulus up to 48%. The electrical conductivity increased by 9 orders of magnitude and the water vapor permeability of the composite films decreased 57% for composites containing 5.0 wt.% of GnP.

INTRODUCTION

Graphite nanoplates (GnP), a thin form of graphite flakes with thickness ranging from that of few-layer graphene to approximately 100 nm, have recently attracted attention as an economically viable alternative for the development of functional and structural nanocomposites. [1] Normally these materials are obtained by expansion process, using heat or microwave irradiation, resulting in GnP or expanded graphite (EG) with an interlayer spacing similar or higher than that of graphite (0.335 nm). [2-4] Polyurethane (PU) is a versatile polymer which has been extensively used as paints, adhesives and coatings in a wide variety of applications in the field of construction, textiles, foot wear, furniture, packaging, electronics, automotive and aerospace, among others. [5-8] The synthetic methods for PU production can be differentiated as: solvent free, in organic solvents, and in water. The latter is denominated as waterborne polyurethane (WPU) and has been presented as an eco-friendly alternative to other solvent-borne PU since only water is evolved during the drying stage. [9] WPU typically presents excellent elasticity, abrasion resistance and flexibility. Some of the properties of WPU such as water resistance, thermostability and mechanical properties are inferior to those of solvent-borne PU. [5,9] The incorporation of carbon based reinforcing materials such as carbon black, carbon nanotubes, GnP and graphene (graphene oxide and reduced graphene oxide) in the WPU matrix has been used to improve the mechanical, thermal, electrical and barrier properties of the composites, relative to WPU. [10-15] The present work reports the production of thin films of WPU/GnP with loadings from 0.1 to 10 wt.%. The mechanical properties of the composite films were measured by tensile testing showing an increase of the Young's modulus up to 48%. The electrical properties increased by 9 orders of magnitude and the water vapor permeability of the composite film decreased 57% for 5.0 wt.% of GnP content.

EXPERIMENTAL

Graphite nanoplates (GnP) were obtained from Nacional de Grafite, Brasil (grade Micrograf HC11). According to the manufacturer the GnP Micrograf has a flake size distribution ranging from 3 and 60 µm. Waterborne polyurethane (WPU), grade ICO-THANE 10, was purchased from I-Coats N. V., Belgium.

GnP Micrograf was dispersed in powder form in WPU suspension at loadings from 0.1 to 10 wt.%, using an Ultrasonic processor UP100H from Hielscher, equipped with a sonotrode MS7D during 1h. The mixtures were then sprayed onto a heated polypropylene plate used as a mold (60ºC).

The mechanical property measurements were performed on a universal testing machine Instron 4505 at a crosshead speed of 25 mm/min, according to ASTM D 882. The values reported are the average of the results obtained for 10 specimens tested. The measurements of volume resistivity were carried out on a picoammeter Kethley 6487 with Kethley electrodes 8009. Three nanocomposite films were prepared and analyzed for each composition. For each applied voltage the corresponding current value was the average of 100 measurements. The water vapor transmission (WVT) tests were performed using the desiccant method according to the standard of ASTM E96-66. Scanning electron microscopy (SEM) of the cryo-fractured composite films was performed on a NanoSEM FEI Nova 200 microscope after platinum coating.

RESULTS AND DISCUSSION

The GnP Micrograf (in powder form) was mixed with waterborne polyurethane to produce thin films of WPU/Micrograf at loadings from 0.1wt.% to 10.0 wt.%. The SEM images of the pristine GnP Micrograf are presented in **figure 1**.

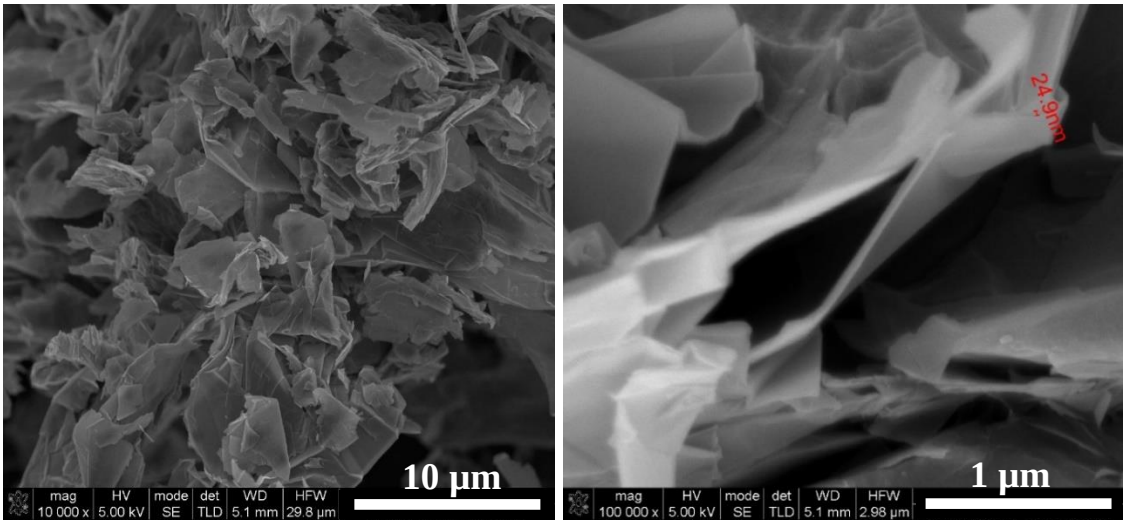

Figure 1. Scanning electron microscopy images of the pristine GnP Micrograf at different magnifications

The mechanical properties of WPU/Micrograf composite films were tested and the results are depicted in the **table I**, and **figure 2b)**. In general, the mechanical properties are enhanced

with the incorporation of the GnP Micrograf. The Young's modulus increased with increasing reinforcement content and the yield strength as well as tensile strength tend to reach their maximum value at 5.0 wt.% of GnP Micrograf. The elongation at break is similar to that of WPU film and above 5.0 wt.% tends to decrease, similar to what is observed for the yield and tensile strength. The stress-strain curves of the WPU film and WPU/Micrograf composite film with 5.0 wt.% of GnP loading are presented in **figure 2a)** and the variation of the Young's Modulus, yield strength as well as tensile strength with the GnP Micrograf loading is presented in **figure 2b)**. **Figure 2b)** illustrates the tendency for mechanical property increase up to a reinforcement load near 4 wt.%, stabilizing or decreasing at higher loads.

Table I. Mechanical properties of the WPU/Micrograf composite films

WPU/Micrograf (wt.%)	Young's Modulus (MPa)	Yield strength (MPa)	Tensile strength (MPa)	Elongation at break (%)
0	524±32	14.5±0.7	18±2	231±37
0.1	587±33	16.7±0.8	19±2	195±35
0.2	581±38	16.2±0.8	20±2	232±46
0.5	619±38	16.3±0.5	21±2	237±43
1.0	619±22	16.3±0.4	22±1	256±13
2.0	615±46	16.7±0.7	22±2	312±34
3.0	688±50	16.3±0.7	22±2	241±39
4.0	767±51	17.0±0.7	23±2	268±32
5.0	769±27	18.2±0.7	22±1	237±16
8.0	780±37	17.5±0.7	16±1	176±37
10.0	779±42	17.4±0.6	15±1	127±41

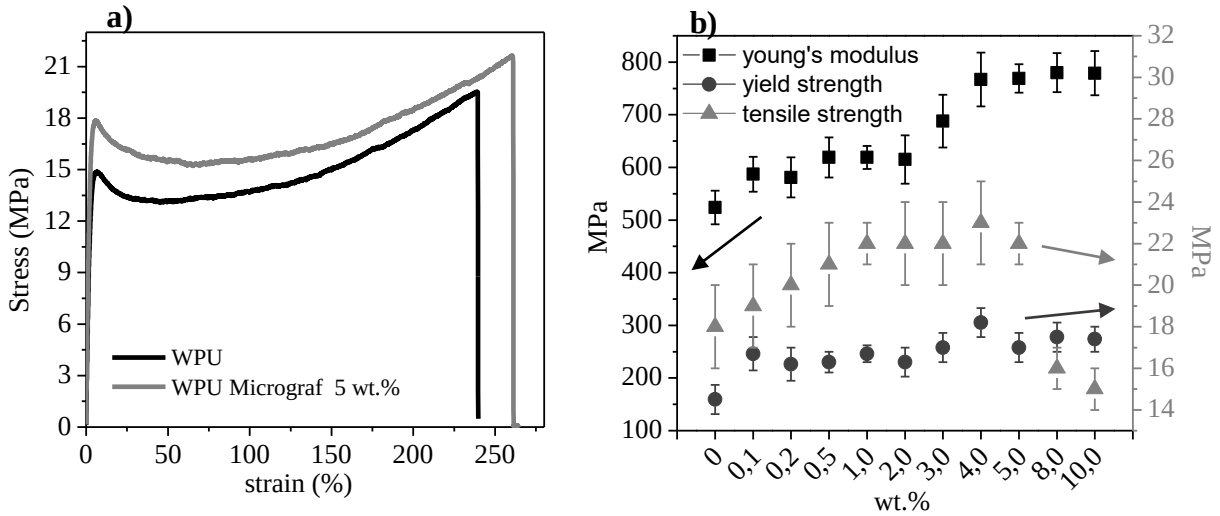

Figure 2. a) Stress-strain curves obtained for films of WPU and WPU/5.0 wt.% GnP Micrograf; b) variation of the Young's Modulus, yield strength and tensile strength with the GnP Micrograf loading.

The mechanical properties are affected by the interfacial adhesion between reinforcement and polymer matrix. **Figure 3 a) and b)** shows the SEM images of the composite film with 5.0 wt.% of GnP. The images illustrate a good WPU/GnP wetting, indicative of good interfacial adhesion between the GnP Micrograf and the WPU matrix, in agreement with the tensile property improvement.

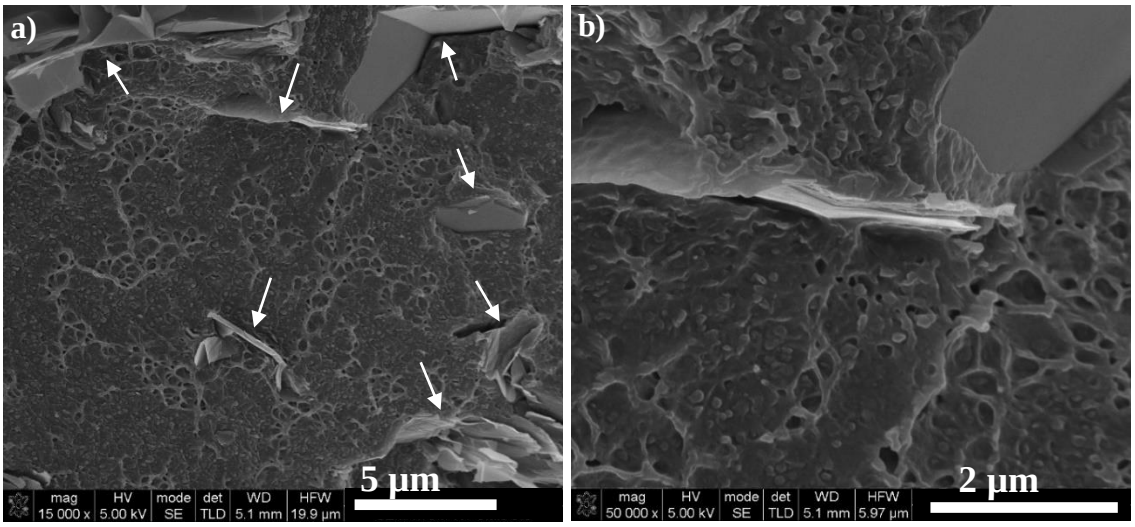

Figure 3. a) and b) scanning electron microscopy images of the WPU/Micrograf composite film with 5.0 wt.% at different magnifications; GnP flakes are identified with white arrows in a).

The coefficient of moisture permeability P(H_2O) decreased with the increase of the GnP Micrograf content (**figure 4**). The composite films with 0.5 wt.% of incorporation showed a decrease of 40 % for P(H_2O) while with 2.0 wt.% and 5.0 wt.% of GnP incorporation the P(H_2O) decrease was 49% and 57%, respectively. The effectiveness of the WPU/Micrograf composites as moisture barrier was demonstrated, presenting a superior performance when compared with results reported in the literature, namely for GO/WPU 0.5wt.% composite, that showed a decrease of 25 % for P(H_2O) [13] and 2D layered molybdenum disulfide (MoS_2)/ WPU 0.5 wt.% composite in which P(H_2O) decreased 6%. [16]. 409

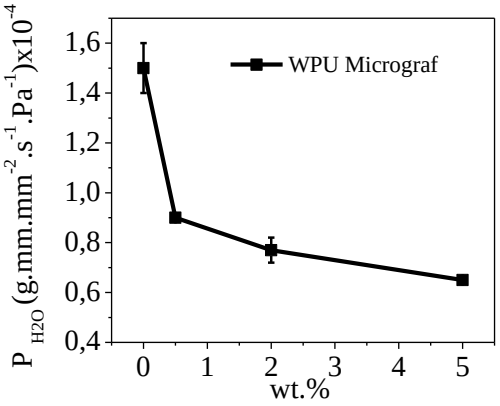

Figure 4. Coefficient of moisture permeability of the WPU/Micrograf composite films

The electrical conductivity of the composite films were masured (**figure 5a**). The electrical conductivity increases with the increase of the GnP Micrograf content and the electrical percolation threshold was found to be between 4.0 and 5.0 wt.% Micrograf. The WPU/Micrograf composite film with 10.0 wt.% of GnP incorporation showed an increase of approximately 9 orders of magnitude relative to WPU. The electrical conductivity of the former was tested (**figure 5b**) by application of 18 volts through a ribbon of the composite film which, above percolation, was able to keep the LED lamps on.

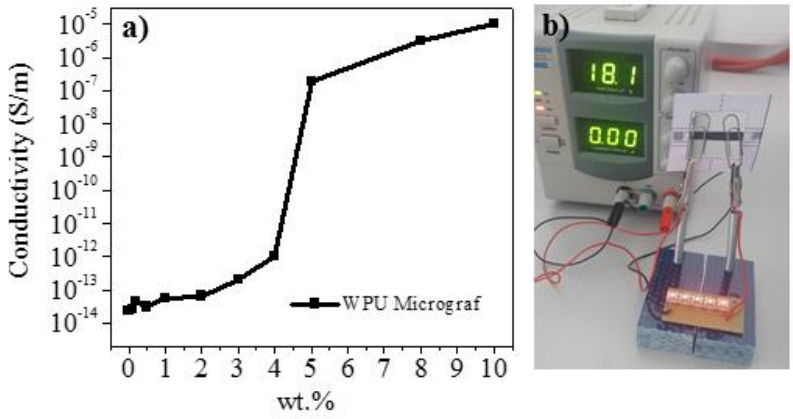

Figure 5. a) Electrical conductivity of the WPU/Micrograf composite films; b) demonstration of the electrical conductivity of the WPU/Micrograf composite film with 10.0 wt.% GnP.

CONCLUSIONS

In summary, WPU/Micrograf composites were produced at loading levels ranging from 0.1 to 10.0 wt%. The composite films presented improved mechanical properties as the reinforcement content was increased, showing an increase of the Young's modulus up to 48%. The SEM images showed good interfacial adhesion between the GnP Micrograf reinforcement and the WPU matrix. The electrical conductivity and barrier properties of WPU/Micrograf composite films increased with GnP Micrograf content, showing and increase of 9 orders of magnitude of the electrical conductivity and 57% of P(H_2O) decrease, respectively.

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