

SPRAYING LAYER-BY-LAYER POLY(VINYL ALCOHOL) – GRAPHENE OXIDE NANOCOMPOSITES

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Abstract

A bottom-up approach for poly(vinyl alcohol) (PVA) - graphene oxide (GO) nanocomposites using a spraying method is presented. Very simple and versatile, spraying allows to build-up uniform multilayered composite films with good structural control of each layer. 150 bilayers were deposited to create a semi-transparent film with improved mechanical properties at a loading of 5.4 wt.% GO. The Young's modulus and strength of these films doubled or nearly doubled which is believed to be due to the nanoscale hierarchical organization of the composite incorporating the 2D nanofiller, and hydrogen bonding between the PVA and the GO sheets.

1 Introduction

Bio-composites such as bones, teeth, or nacre are composed of mineral particles and a protein matrix with superior strength and toughness. For example, nacre is 3000 times tougher than the mineral particle it is based on. Common features in bio-composites are their complex architectures with several orders of hierarchical structure, different hierarchical structures at different length scales, arrangements and orientations, high volume fraction of high aspect ratio particles with the smallest building blocks often being at the nanoscale [1].

Highly organised man-made nanocomposites have been mainly obtained by the layer-by-layer (LbL) approach. This process is a bottom-up approach leading to a hierarchically structured nanocomposite. The most well-known process used is dip coating which consists in dipping repeatedly a substrate into three solutions (polymer, filler, and aqueous media) [2]. Recently, another approach has been developed by Deville *et al.* [3] based on cast freeze-dried nanocomposites which also leads to highly ordered 3D structures [4].

Spraying is a recent, simple, versatile and rapid method for multilayer assemblies. It is a bottom-up approach, which consists of alternatively spraying two solutions (polymer and filler) on various substrates. The main advantage of spraying, besides being a simple method, is the ability to grow layers on large areas or objects with complex shapes like textiles [5].

Two dimensional (2D) particles such as graphene or graphene oxide are very attractive and promising for multifunctional nanocomposites and can out-perform 1D fillers like carbon nanotubes. For mechanical properties, 2D particles have specific advantages over 1D particles because of the larger surface area in contact with the polymer matrix. The ability of graphene oxide (GO) to disperse in aqueous solution as well as its ability to form H-bonding with polar polymers makes it a great candidate for spraying layer-by-layer composites.

In this study, we present a layered nanocomposites obtained by sequential deposition of PVA and GO in solution. A uniform thin film consisting of 150 bi-layers is rapidly obtained over a large area. Each layer is characterised by AFM. The uniform growth is monitored with UV-Vis spectrometer and the mechanical properties of the composites are addressed in function of the filler orientation.

2 Experimental

The poly(vinyl alcohol) was supplied by Sigma Aldrich (Mw ~ 85,000-124,000 g.mol⁻¹, 98-99 % hydrolyzed). The graphene oxide was obtained by Hummer's method and provided by Sichuan University (Chengdu, PR China).

Layer-by-layer nanocomposites were obtained by sequential deposition of PVA and GO in solution on a glass slide covered with a sacrificial layer via the spraying method. The composite film was prepared in three steps: preparation of the mother solution, followed by sequential layer deposition to finally obtain a free standing film.

Poly(vinyl alcohol) was dissolved in deionised water at 90°C and continuously stirred for 4 hrs, to give a solution at 0.5 wt.%. The PVA solution was then cooled down to room temperature. Graphene oxide solution was obtained by dispersing the GO in deionised water at 1mg.mL⁻¹ by a high-power ultrasonication tip (1000 J at 20 %). GO suspension was left aside for at least 12 hrs to let thicker graphite aggregates to precipitate. The glass slides were cleaned with methanol in an ultrasonic bath for 20 min and dried with compressed air. The sacrificial layer was obtained by dissolving polystyrene (PS) in toluene at 90°C and stirred for 3 hrs, to give a 5 wt.% solution. This solution was deposited on the clean glass slide and spin-coated at 2000 rpm for 1 min. The glass slides were functionalized with O₂ plasma for 4 min to functionalize the surface. The PVA solution of 0.5 wt.% was further diluted to obtain 0.05 wt.% and this GO suspension was mixed with ethanol in a ratio of 60:40 (ethanol: water) and subsequently diluted to 0.1 mg.mL⁻¹ (0.01 wt.%). Glass slides covered with the sacrificial layer were fixed on a board with tape. 0.1 g of PVA solution at 0.05 wt.% was used for spraying 56 cm². The airbrush spray gun was kept at 20 cm from the surface and the pressure was fixed at 18 psi. 0.8 g of GO suspension at 0.01 wt.% was used to spray 56 cm². Here the spray gun was kept at 30 cm and the pressure was fixed at 25 psi. The layer-by-layer PVA-GO nanocomposites and PVA films were obtained by sequential deposition of PVA and GO in solution and PVA solution respectively as described in Figure 1. The glass slides were then immersed in toluene solution for 3 hrs. The nanocomposite films were then peeled off from the glass slide. The obtained free standing films were fixed on a metal frame and immersed in toluene solution for 24 hrs, prior to removing completely the sacrificial layer.

UV-Vis spectroscopy was taken using a Perkin Elmer 950. Atomic Force Microscopy was performed using an NT-MDT in tapping mode. Morphological examinations were carried out using a FEI Inspector-F scanning electron microscope (SEM). Tensile tests were performed

using an Instron 5586 at room temperature, equipped with a load cell of 1N at a test speed of 10% of the specimen length.

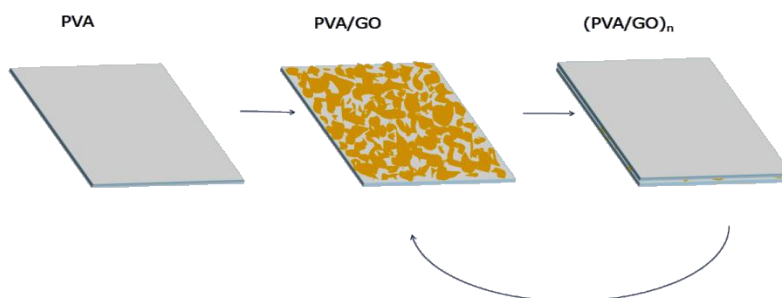


Figure 1: Spraying approach for layer-by-layer assembly where alternatively a solution of PVA/DiWater and GO/DiWater/Ethanol were sprayed on a glass slide coated with a PS sacrificial layer. The free-standing films were obtained by immersing the glass slide in toluene solution to remove the sacrificial layer.

3 Results and Discussion

The current LbL PVA-GO nanocomposites are made by a bottom-up approach where a nanometer-thick layer of GO and a layer of PVA are sequentially sprayed on a glass slide covered with a PS sacrificial layer as described in Figure 1. The GO obtained by Hummers's method [6] has a highly functionalized surface with hydroxyl groups which allows the GO platelets to disperse well in water. Ultrasound sonication was used to disperse the GO in DI water, breaking down the aggregate and thus providing monolayers of graphene oxide with high aspect ratio. However, over-exposure of GO to ultrasound also damages the sheets. UV-Vis spectroscopy was used to monitor the dispersion of the GO in DI water as described by Yu et al. [7]. The maximum exfoliation for GO corresponds to the maximum absorbance in UV-Vis. A threshold in the UV-Vis peak was obtained after 1000 Joules. The supernatant was extracted and the aqueous solution of GO was diluted with a solution of DI water: ethanol to finally obtain an ethanol:DI water ratio of 60:40. The solution of GO in ethanol:DI water was stable even after several months.

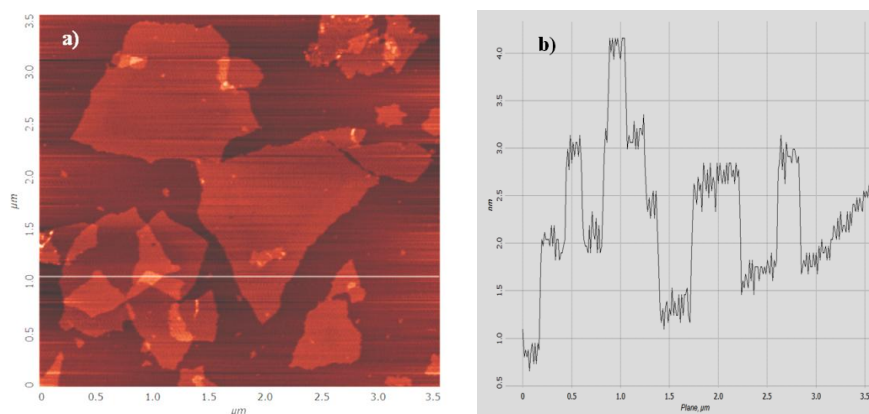


Figure 2: AFM picture in tapping mode of GO sprayed on mica substrate. a) Height image showing the GO platelets topography. b) topography profile along the white line.

In the case of spraying GO platelets, a mixture of ethanol:DI water was used because ethanol has a lower vapour pressure, so it evaporates quicker and prevents the particles from reaggregating. Furthermore, this can facilitate the dissolution of the PVA layers of the

composites. Sprayed on mica, the GO platelets are mainly monolayers with a thickness of 1.3 nm as presented in

Figure 2 and in accordance with the structure of GO [8]. However, the range of diameters of the GO platelets is very wide from 50 nm to 2.5 μm . But in average on 100 particles, the diameter is 400 nm, giving an average aspect ratio of 300. In the case of spraying PVA, the polymer drops need to fully wet the surface to allow them to recombine and form a homogeneous layer. The surface of the spin-coated PS layer was plasma treated to create hydroxyl groups and make the surface more hydrophilic. By modifying, the pressure, the size of the nose and the distance, we were able to form a uniform layer of PVA as presented. The thickness of the layer was measured by scratching the PVA layer onto the glass slide and is in the range of 10-15 nm. UV-Vis absorbance was used to follow the uniformity of the layer growth and the deposition of each PVA-GO bi-layer was monitored by UV-Vis absorbance until 5 bi-layers. The absorbance increased after each bi-layer deposition of PVA-GO and follows a linear increase. We can therefore conclude that a uniform deposition of PVA-GO layer was obtained by the current spraying method.

PVA-GO nanocomposites consisting in 150 bi-layers were rapidly built-up. Scanning electron microscopy provided an average film thickness of around $\sim 1.8 \mu\text{m} \pm 0.2$. Also, as presented in

Figure 3, the cross section of the PVA-GO shows a layered structure. To measure the GO loading in our composite, TGA was used. At 600°C, the loading of GO in the composite is $\sim 3.7 \text{ wt.}\%$. However, as previously reported by Zhou et al. [9], GO is thermally unstable and can undergo different mass loss. In agreement with their TGA data, GO undergoes a loss of 45 wt.% at 600°C. From this the corrected percentage of GO in the LbL films corresponds to a loading of $\sim 5.4 \text{ wt.}\%$.

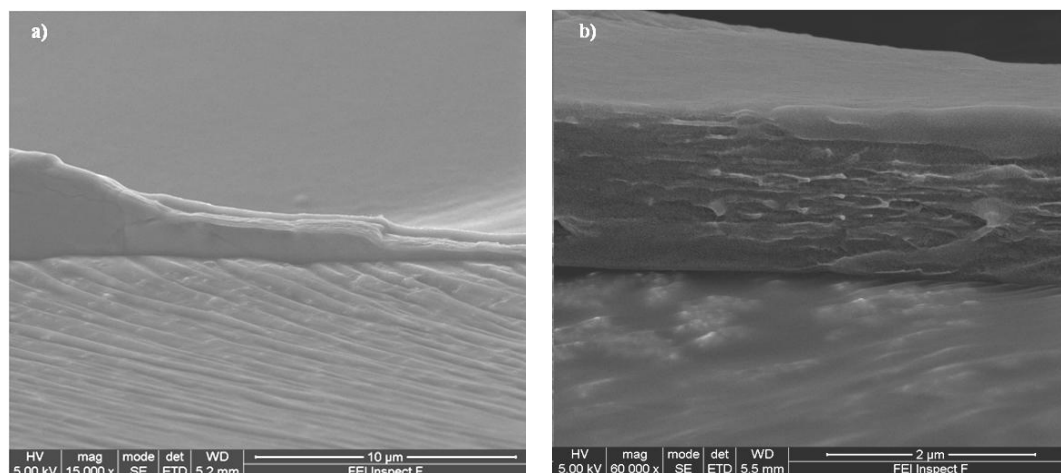


Figure 3: SEM characterisation of 150 bi-layers of PVA-GO nanocomposite free standing film. a) cross-section of the film. b) closer view showing the layered structure.

Interestingly, our LbL PVA-GO film has a very high degree of transparency in the visible light. The photographs in

Figure 4a of PVA-GO films reveals that the transparency of the LbL films is decreasing as the PVA-GO bi-layer number increases. However,

Figure 4b also shows that despite this decrease, the optical transparency of a free standing 150 bi-layers PVA-GO film remains high in the visible range; i.e. the transparency at 550 nm is 85%.

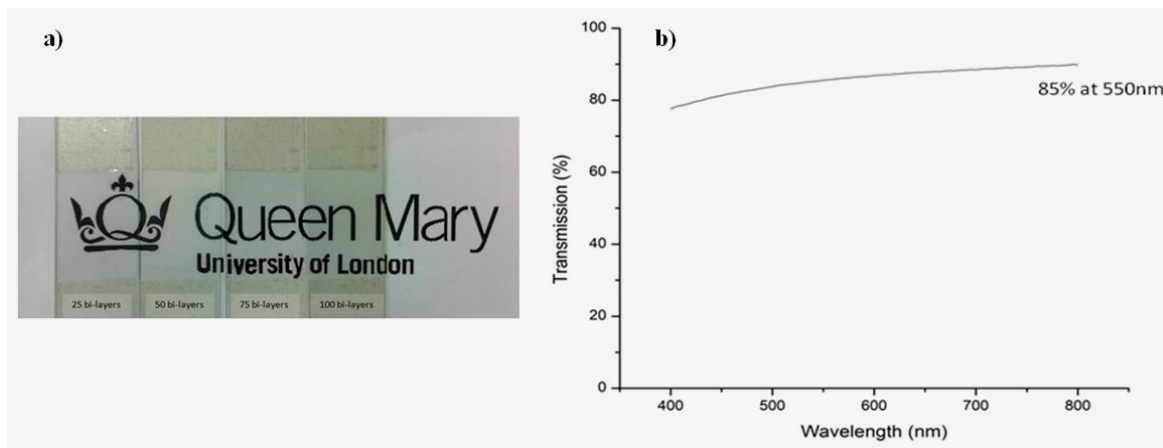


Figure 4: a) Photograph showing the transparency at 25, 50, 75, 100 bi-layers. b) Transmission spectra of 150 bi-layers PVA-GO film.

The mechanical properties of the layered nanocomposite films were studied by tensile testing and presented in

Figure 5 and

Table 1. Young’s modulus of the nanocomposites is doubled, while the ultimate tensile strength (UTS) is improved by 90%. Due to the embrittlement effect, the strain at break is however significantly reduced. The effective modulus of the graphene in the nanocomposites was back-calculated using the Halpin-Tsai model [10] in accordance with [11]. From this the effective contribution of the GO to the composite modulus is around 120 GPa, which is below the intrinsic Young’s modulus of GO at 203 GPa [12], but still indicates a good reinforcing efficiency.

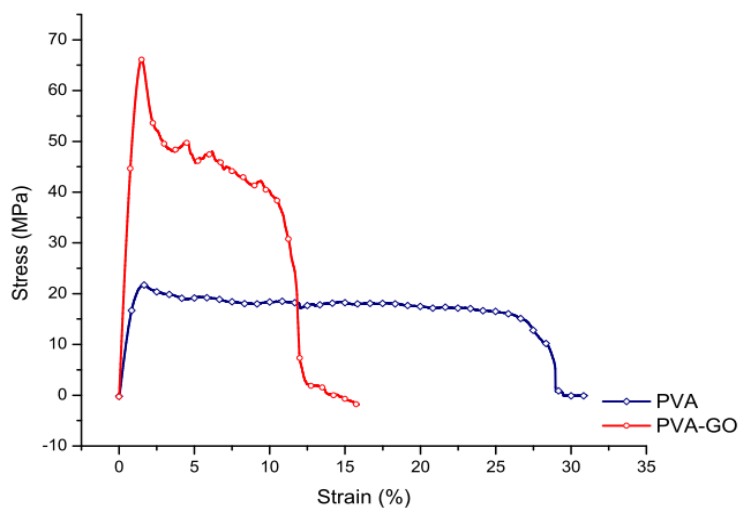


Figure 5: Strain-stress curve of 150 bi-layers GO nanocomposite (round) and 150 layer of PVA (diamond).

Table 1: Summary of mechanical properties. The values are means \pm standard deviation. The data are obtained on a minimum of three samples. The effective contribution of GO to the composite property was back-calculated using the Halpin-Tsai’s model and is denoted as E_{GO} .

Sample	E_{GO} (GPa) back-calc.	E (GPa)	UTS (MPa)	Strain (%)
PVA	-	2.9 ± 0.7	33 ± 13	19 ± 9

PVA-GO (5.4 wt.%)	120	5.9 ± 1.0	62 ± 18	8 ± 2
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The contribution of the graphene oxide in our LbL nanocomposites was compared to the literature for reduced graphene and graphene oxide and plotted in function of graphene loading (Figure 6). The blue shaded line corresponds to the intrinsic modulus of reduced graphene and graphene oxide and the red line is a guide line to the data. As expected and similar to most CNT based nanocomposites, the contribution of any graphene-like particle is higher at low volume fractions as it prevents the formation of agglomerates (which effectively lowers their aspect ratio). Hierarchical composites, as in layer-by-layer nanocomposites, are a way to effectively improve their mechanical properties by increasing their volume fraction and preventing agglomeration.

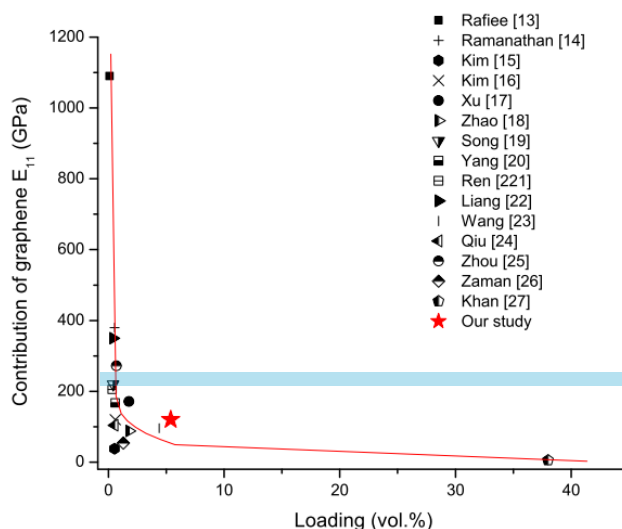


Figure 6: Comparison of the effective contribution of graphene to the composite modulus for nanocomposites taken from the literature in function of their loading. The red star corresponds to the contribution of our LbL PVA/GO, indicating high graphene efficiency. The shaded blue line corresponds to the intrinsic modulus of reduced graphene oxide and graphene oxide with the red line being a guide line.

4 Conclusions

A hierarchical nanocomposite film based on 150 bi-layers of PVA-GO was rapidly build-up by a sequential spraying method. Spraying is a new bottom-up approach which allows for a good control of the structure of each individual layer on a larger scale. The LbL PVA-GO film was 1.8 nm thick with a highly lamellar structure, consisting of ~5.4 wt.% GO. The LbL composite is transparent in the visible light with a transparency of 85 % at 550 nm. Young's modulus and tensile strength of these multilayer films were doubled or nearly doubled. The improvement in mechanical properties is believed to be due to the good stress transfer between the PVA and GO driven by hydrogen bonding, and demonstrates the potential of 2D nanofillers having a larger surface area in contact with a polymer matrix than 1D fillers.

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