A NOVEL METHOD FOR MODIFICATION OF POLY(LACTIC ACID) FILAMENT BY GRAPHENE OXIDE FOR 3D PRINT

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Abstract

In this study, we introduce a method for modifying poly(lactic acid) (PLA) filament, which is adjustable to enhance the rheological properties and biocompatibility of printed products or impart specific characteristics by bonding nanoparticles onto the surface of graphene oxide. What distinguishes our method is the post-production modification of PLA filament before the printing process. Graphene oxide, being a unique nanomaterial with diverse applications in science and technology, serves as a platform for modification due to the presence of functional groups on its surface that are accessible for binding modifiers or nanoparticles. The persistence of graphene oxide on the surface of printed items even after 3D printing highlights its potential for further modifications. This presence was verified through scanning electron microscopy and Raman spectroscopy.

Keywords: Graphene oxide, additive manufacturing, PLA, 3D printing

1. INTRODUCTION

The poly(lactic acid) (PLA) is aliphatic bio-based thermoplastic made from renewable sources such as sugar cane, corn starch, or sugar beet [1]. The main advantages of PLA are biodegradability, biocompatibility, exceptional mechanical properties, impressive transparency, and good processing ability compared to other biodegradable polymers. PLA is used in various fields such as food packaging, paper coatings, textiles, and medicine [2]. Graphene oxide (GO) is a derivative of graphene, a two-dimensional carbon allotrope consisting of a single layer of carbon atoms arranged in a hexagonal lattice. While graphene is a pure carbon material, GO is graphene that has undergone a chemical treatment, resulting in the introduction of oxygen-containing functional groups on its surface.

The oxygen-containing functional groups on GO can include hydroxyl (-OH), epoxy (-O-), and carboxyl (-COOH) groups, among others. These functional groups make GO hydrophilic (water-attracting) and render it more chemically reactive compared to pristine graphene [3]. Incorporating GO into PLA printed materials yields a range of property enhancements. GO, a two-dimensional material composed of carbon atoms arranged in a hexagonal lattice and adorned with oxygen-based functional groups on its surface, imparts a multitude of benefits when combined with PLA. These advantages encompass heightened thermal stability [4], increased mechanical strength and toughness [5], improved electrical and thermal conductivity [6,7], enhanced flame resistance [8], as well as augmented biocompatibility [9], all contributing to a superior overall material performance. This study unveils new possibilities for crafting intricate structures utilizing 2D materials, a development that holds immense potential for enhancing the mechanical performance of printed structures.

Additionally, these structures could find applications in areas such as pollutant adsorption, antibacterial functionalities (through modification with antibacterial substances), and biocompatibility, facilitated by an easily modifiable filament method.

2. MATERIALS AND METHODS

2.1 Chemicals

Demineralized water was produced using an Aqual 25 reverse osmosis apparatus (Aqual, Česká, Czech Republic) and further treated with Millipore System Inc. (Billerica, MA, USA) to obtain ultrapure water with a corresponding resistivity of 18.20 MΩ·cm (at 25 °C). All experiments used ultrapure water unless otherwise stated. The pH values were evaluated using a pH meter (WTW inoLab, Weilheim, Germany) with a WTW SenTix pH electrode.

2.2 Synthesis of large-area graphene oxide

GO was synthesized by chemical oxidation of 5.0 g graphite flakes (100 mesh, ≥75 % min) (Merck, Darmstadt, Germany) in a mixture of concentrated H_2SO_4 (670 mL, 96.0 wt%, Lach-Ner, Neratovice, Czech Republic) and 30.0 g $KMnO_4$ (Merck, Darmstadt, Germany) according to modified Tour's method [10] to obtain large area sheets of GO. The reaction mixture was stirred vigorously. After 10 days, the oxidation of graphite was terminated by dropwise addition of H_2O_2 (250 mL, 30.0 wt% in H_2O, Lach-Ner, Neratovice, Czech Republic), and the colour of the mixture turned bright yellow, indicating a high oxidation level of graphite. The formed graphite oxide was washed with 1 M HCl (6 L, 37.0 wt% in H_2O, Lach-Ner, Neratovice, Czech Republic) and repeatedly washed with ultrapure water (total volume used 60 L) until a constant pH of 3-4 was achieved.

2.3 Scanning electron microscopy (SEM)

The morphology of GO sample was examined by SEM on a Tescan MAIA 3 equipped with an FEG (Tescan Ltd., Brno, Czech Republic). The best images were obtained using the In-lens SE detector at working distances between 2.88-5.04 mm and at a 5 kV acceleration voltage. Images were obtained at 2,000-100,000-fold magnification covering the sample area (the side of square 2.08-104.00 µm). Full-frame capture was performed in UH resolution mode, and it took approximately 0.5 minutes with a ~1 µs/pixel dwell time. The spot size was set at 2.4 nm.

2.4 Attenuated Total Reflectance Fourier transform infrared (ATR FTIR) spectroscopy.

FTIR spectra were collected using an INVENIO R FTIR spectrometer equipped with a single-reflection diamond ATR accessory - A225/Q Platinum ATR module (Bruker Optic Inc., Billerica, MA, USA). A fixed load was applied to the small amount of sample to ensure full contact of the solid with the diamond ATR. Solid samples were directly analysed in lyophilized form. Before each measurement, background spectra were collected. Spectra were recorded at 25 °C from 4000 to 400 cm−1 at a resolution of 2 cm−1. Each spectrum was acquired by merging 128 interferograms. Bruker OPUS 8.1 (Bruker Optic Inc., Billerica, MA, USA) software was used for IR spectra recording, and JDXview v0.2 software was used for further spectral evaluation.

2.5 Raman spectroscopy

A Renishaw InVia Raman microscope (Gloucestershire, UK) was used to collect the Raman spectra. A laser beam with a wavelength of 633 nm was used to excite the molecules, and 0.75 mW of laser energy (5% of 15 mW) was used. The sample surfaces were investigated via a 50 × L objective. The time per spectrum was 5 s, and 32 repeats of spectra were collected and further analysed in Renishaw WiRE software version 5.2.

2.6 Filament modification

PLA Economy white filament was purchased in colorFabb (Belfeld, Netherland) with width 1.75 mm. The non-diluted dispersions of graphene oxide was applied using airbrush (PME: Enfield, England, UK) The length of 15 meters of filament (the amount corresponds to 4 squares with a side of 10 cm and thickness 1 mm plus reserve of filament) which corresponds to the weight ~45 g was sprayed 5 times by 4 mL of non-diluted graphene oxide. After each round of spraying the filament was irradiated by infrared lamp to speed up drying of filament.

2.7 3D printing

3D printer Original Prusa i3 MK3S+ (Prusa Research, Prague, Czech Republic) worked under following set up: 0.8 mm nozzle, print bed temperature 200 °C, temperature of printing area 60 °C, and speed 100 %.

3. RESULTS

The GO for modification of PLA filament was synthesized by the permanganate method modified by Offerman. This method produces single-layer GO with large sheets and high yield. The morphology of GO sheets was confirmed using SEM (**Figure 1A**). The SEM image shows sheets with an area in dozens of micrometers. FTIR spectroscopy was used to confirm and identify the oxygen rich functional groups typical for GO. The GO spectrum exhibits distinctive bands indicative of various chemical groups, including C-O (observed at 1050 cm^{-1}) corresponding to alcohols and C-O (observed at 1250 cm^{-1}) corresponding to carboxylic acids, C=C (present at 1631 cm^{-1}). Additionally, a typical broad peak observed at 3322 cm^{-1} corresponds to vibrations associated with O-H bonds.

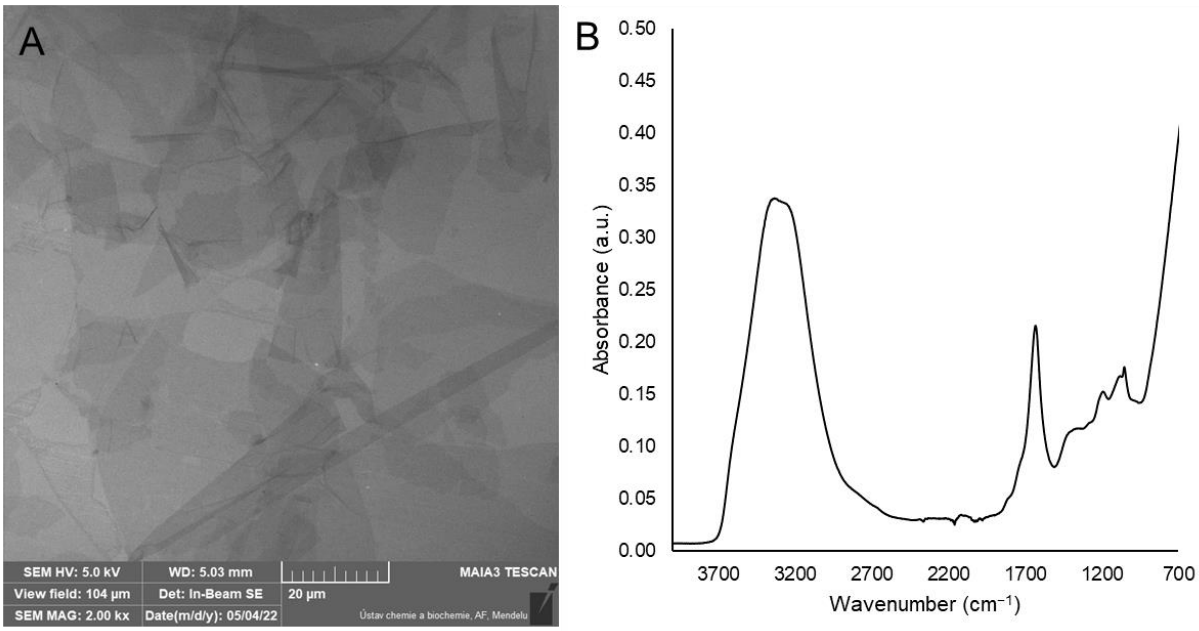

Figure 1 Scanning electron microscopy (SEM) image of sheets of synthesized graphene oxide (A) and FTIR spectra the graphene oxide.

As described in the Materials and Methods section the commercial PLA filament was uniformly sprayed with the dispersion of GO before 3D printing. The hypothesis that GO can persist on the surface of printed items even after 3D printing was studied using SEM. **Figure 2A** shows the surface of a non modified PLA-printed surface visualized with secondary electrons. **Figure 2B** shows the same surface visualized with backscattered electrons. The surface of printed PLA is clear without any modification only with small ruptures. SEM images

of PLA modified with GO clearly show the presence of GO sheets on the surface of printed PLA filament, which was visualized with secondary electrons (**Figure 2C**) and backscattered electrons (**Figure 2D**). The modifier and 3D printed object were analysed by Raman spectroscopy. The typical D and G Raman bands were detected at 1334 cm^{-1} and 1606 cm^{-1} for GO and 1331 cm^{-1} and 1599 cm^{-1} for 3D printed object modified with GO, which confirm presence of GO on the surface..

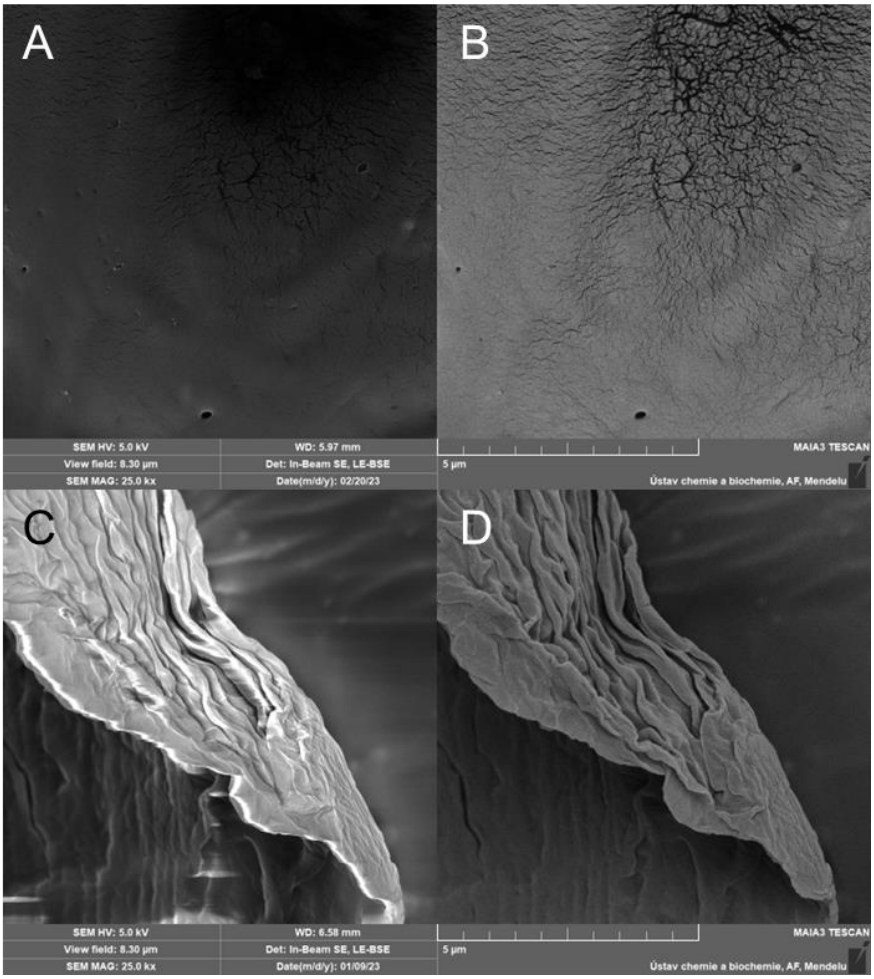

Figure 2 SEM image of the surface of printed poly(lactic acid) (PLA) visualized by secondary electrons (SE) and backscattered electrons (BSE) (B). SEM image of printed PLA surface modified with graphene oxide visualized by SE (C) and BSE (D).

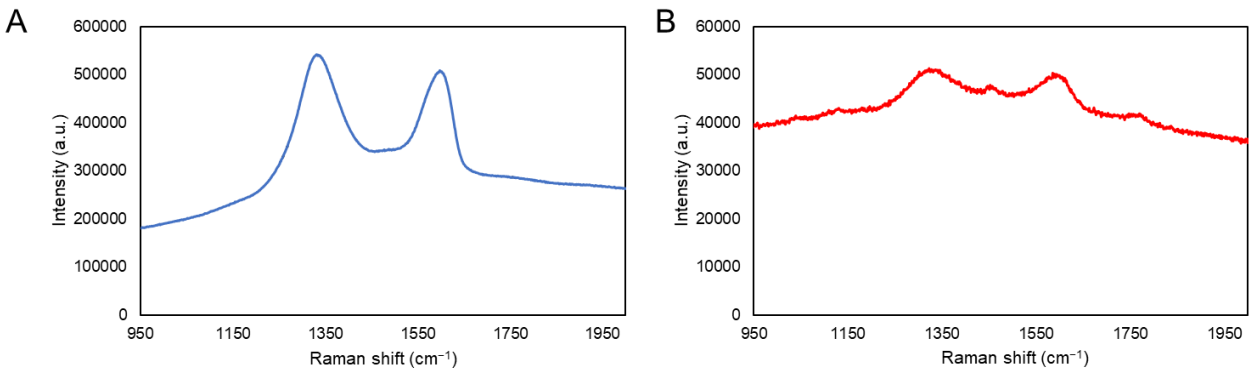

Figure 3 Raman spectra of graphene oxide as a modifier (A) and printed 3D object from PLA modified by graphene oxide (B).

4. CONCLUSION

The commercial PLA filament was successfully modified with as-synthesized GO and printed on the 3D printer. According to the hypothesis, the GO persists on the surface of printed objects even after 3D printing. GO on the surface of printed objects can bestow its properties to the PLA from which the objects are made.

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