BIOPOLYMER NANOCOMPOSITES WITH GRAPHENE FOR 3D PRINTING APPLICATIONS: PROPERTIES AND SAFETY ISSUES

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Abstract

Polylactic acid-based nanocomposites incorporating graphene nanoplatelets were developed and characterized. A significant enhancement of mechanical, thermal and electrical properties were observed by increasing of nanofiller content around the percolation threshold. The 6 wt.% graphene-based nanocomposites are proposed as a promising novel material for 3D printing application by fused deposition modelling. The scratch properties enhancement and multifunctionality at lower filler content makes the nanocomposite films suitable for packaging application. However, the migration of graphene nanoplatelets may raise safety concerns at high temperature treatment of packaged foods, which needs of further investigations.

Keywords: *graphene-PLA nanocomposite, 3D printing, packaging, multifunctionality*

1. INTRODUCTION

Manufunctional nanocomposites based on the polylactic acid biopolymer filled with graphene nanoplatelets are increasingly studied to enhance barrier properties and functionality of food packaging materials [1]. So far, little is known about the effectiveness of the graphene-polymer nanocomposites as a novel material for 3D printing by fused deposition modeling (FDM). The introduction of nanotechnology into this innovative field offers huge potential and opportunities for the manufacturing of 3D designed structures with customizable properties and specific multifunctionality [2]. In particular, the interest in adding nanomaterials into the host matrix aims to improve mechanical, thermal and electrical properties of the resulting structures. In our previous studies on the poly(lactic) acid based nanocomposites filled with graphene and carbon nanotubes for 3D printing application, variety of factors are reported to govern the final nanocomposite properties and due to the complexity of those factors, variety of contradicting properties may be obtained [3,4]. Although the graphene nanoparticles are tightly bound in the matrix polymer, their release through the lifecycle of nanocomposite could be possible [5]. Therefore, the potential hazard associated with the specific applications of graphene-polymer nanocomposites needs of careful investigations. In the present study we address the role of graphene nanoplatelets incorporated in a biodegradable poly(lactic) acid for the enhancement of mechanical, electrical and thermal properties, as well as the safety issues of graphene towards 3D printing and packaging applications.

2. MATERIALS AND METHODS

2.1. Materials

The poly(lactic) acid (PLA) polymer used in this study was Ingeo™ Biopolymer PLA-3D850 (Nature Works) with MFR 7-9 g/10 min (210°C, 2.16kg). Graphene Nanoplatelets (GNPs) with purity 90 wt.%; mean diameter 5 - 7 μm; number of layers < 20 were supplied from Times Nano, China. The melt extrusion processing was used for fabrication of nanocomposites. Masterbatch of 6 wt.% GNPs was prepared by melt mixing of the filler and the polymer in twin screw extruder (COLLIN Teach-Line ZK25T), in the temperature range 170-180 °C and screw speed of 40 rpm. Further on, the masterbatch was diluted with neat PLA by a second run to 1.5% and 3% filler contents. Filament of 1.75 mm diameter for 3D printing (FDM) was produced from the nanocomposite pellets by using a single screw extruder.

The characteristics of the filament were studied. The film samples were prepared from the composite pellets by hot pressing at temperature of 180 ^{o}C and pressure of 1 bar.

2.2. Methods

Tensile mechanical measurements were carried out using the tensile module of the Universal Mechanical Testing Machine (UMT-2, Bruker). The tests were performed at room temperature by using 1kN sensor, with a tensile speed of 1 mm/min. Filament samples, 7 specimens of each composition, with circular cross-section of diameter 1.75 mm and length 50 mm were tested. The tensile mechanical characteristics determined from the test were Young's modulus, ultimate strength and elongation.

Scratch experiments were carried out with the tribology testing module of the UMT–2. The samples were films of thickness 30 μm scratched by force control method applying normal load of 2N and using micro-cutting diamond blade with tip radius of 0.4 mm. Tangential force (Fx) was measured vs. the applied constant normal force Fz and the scratch resistance was determined as Fx/Fz.

The electrical conductivity was measured via volt-ampere (V-A) circuit, using the High Resistance Electrometer Keithley 6517b (Beaverton, OR, USA). The DC conductivity measurements were performed on the filaments. The samples were metallized by a silver paint for obtaining electrical contacts spaced at a distance of 10 mm on the filament. A suitable voltage applied between the electrical contacts, induces a current (I) which in turn determines a voltage drop (V_m) detected between the contacts. The electrical resistance (R_c) of the material and the electrical conductivity of samples were calculated based on Ohm's law. The average results from 3 tests were calculated.

The thermal conductivity was tested by Hot Disk 2500 analyzer (Hot Disk Inc., Göteborg, Sweden). The measurements were performed with disk specimens of diameter 16 mm and thickness 3 mm, hot presssed and 3D printed one, at room temperature. Three samples were tested and the average results were calculated for thermal conductivity.

Transmission Electron Microscopy (TEM) at accelerating voltage 200 kV was used for analysis of the

migrated nanoparticles into the food simulants. A micro-quantity of the food simulant after migration test was dropped on standard copper TEM grid covered by membrane from amorphous carbon. Then the grid was dried in dust-free atmosphere at ambient conditions and visualized at different magnifications.

Scanning Electron Microscopy (SEM) Philips 515 at accelerating voltage 25 kV and 5 kV was performed to study the film surface morphology. Before the examination in the microscope, the samples were covered with metal coating for better conductivity of the surface and to avoid the discharge effects. The cut edge of the films was visualized before and after migration test.

3. RESULTS

3.1. Tensile properties

Tensile mechanical characteristics of the filaments are evaluated as varying the graphene content from 1.5 to 6 wt%. The Young's modulus, tensile ultimate strength and elongation are determined and the results are summarized in Table 1. In Figure 1, the percentage of enhancement of tensile characteristics by increasing the filler content is summarised. As seen, the impact of graphene on the tensile Young's modulus is increased gradually with increasing GNP loading, thus 25% increase of the modulus is observed at 6 wt.% GNP content. It should be mentioned the slight increase of the tensile strength and the elongation at 1.5 wt% GNP, while an insufficient decrease of both characteristics are observed at 3 wt% GNPs. This effect is more pronounced at 6 wt.% GNPs, with 5% and 11% decrease of strength and elongation, respectively, which was assigned to the worsen filler dispersion.

The scratch test on the film samples demonstrated a significantly enhanced tangential force (F_x) at the relevant applied normal force (F_z) by addition GNPs in the PLA polymer. Therefore, the GNPs from 1.5 to 6 wt.% content contributed to the reinforcement of the PLA-based nanocomposite and accordingly to gradual enhancement of the scratch resistance of nanocomposite films. The scratch resistance results vs.

GNP content are presented in Table 1. While the gradual enhancement of scratch resistance from 5 to 15% by increasing the filler content from 1.5 to 6 wt.% GNPs is shown in Fig. 1.

Composite	Tensile Modulus, MPa	Tensile Strength, MPa	Elongation, %	Scratch resistance Fx/Fz
PLA	593.6	28.0	8.4	1.45
1.5GNP/PLA	634.4	28.1	8.6	1.53
3GNP/PLA	669.3	27.2	8.2	1.63
6GNP/PLA	738.1	26.5	7.4	1.70

Table 1. Tensile characteristics of GNP/PLA filaments and scratch resistance of pressed films as varying the graphene content from 1.5 to 6 wt.%

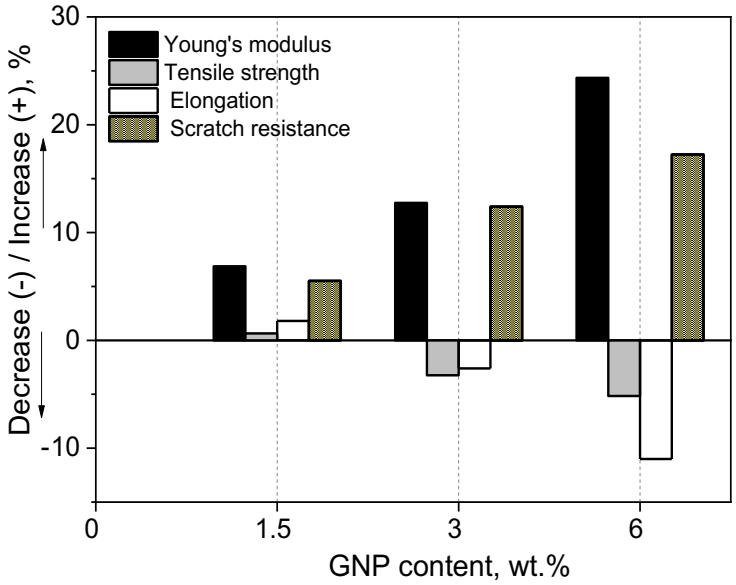

Fig. 1. The percentage (%) improvement of tensile characteristics of GNP/PLA filaments and scratch resistance of films by increasing the GNP content

3.2. Electrical conductivity

The PLA polymer is an electrical insulator having low electrical conductivity in the range 5.10^{-10} S/m. Polymers containing electrically conductive fillers show interesting electrical properties like semiconductors and metals without losing the processability of polymers. Figure 2 represent electrical conductivity vs. GNP content for GNP/PLA nanocomposites. As seen, at 1.5 wt.% GNP the electrical conductivity values are close to that of the neat PLA. Continuous increasing of GNP contents in the range 3÷6 wt% resulted in a sharp increase of dc-conductivity, this assuming the formation of a conductive network of filler in the PLA matrix, associated with percolation threshold. Researchers reported that the critical factors that affect the percolation threshold of conducting polymer composites are the filler contet, aspect ratio and the degree of filler dispersion [3,4]. The electrical percolation threshold (EPT) is the minimum amount of conducting filler allowing to form a continuous path within the insulating polymer matrix resulting in a steep increase of electrical conductivity, that follow a power-law of the type: $\sigma = \sigma_0 (\phi - \phi_C)^t$,

where σ_0 is the conductivity of the filler, ϕ_C is the EPT and t is a critical exponent depending on the morphological arrangement of the filler in the percolating structure.

Based on the power-law equation, the electrical percolation threshold for the GNP/PLA nanocomposites is estimated of 4 wt.% GNP content, as pointed by the arrow in Fig.2. The dc-conductivity at EPT is of 1.10^{-5} S/m, while at the filler content of 6 wt.% GNP, the conductivity showed the value of 0.0133 S/m.

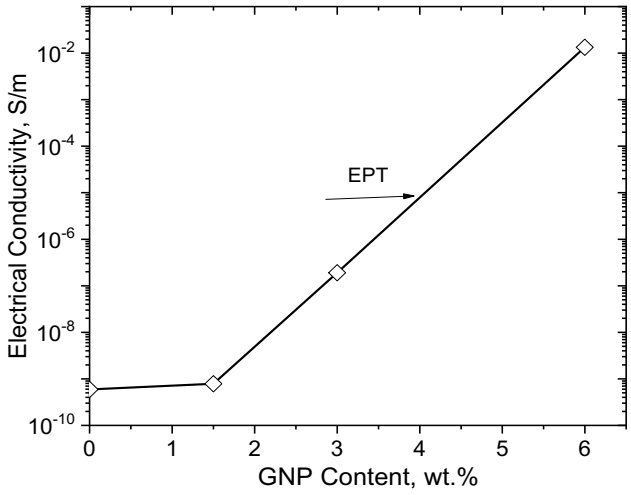

Fig. 2. Electrical conductivity of GNP/PLA nanocomposite filament vs. GNP content. Arrow pointed the electrical percolation threshold (EPT).

3.3. Thermal conductivity

Generally, the thermal conductivity is a measure of the ability of a material to transfer heat. Thermal management is a crucial issue in the electronics industry as electronic devices are more integrated and miniaturized. If the heat is not dissipated promptly, the efficiency and the lifetime of the system could be reduced, or even damaged. Thus, a material with high thermal conductivity is needed to dissipate the heat. Thermal conductivity through a polymer is a complex process, influenced by many parameters like temperature, crystallinity, orientation of the macromolecules, and so on. Polymers are usually thermal insulators having values of thermal conductivity around 0.1-0.2 W/mK. Graphene has very high thermal conductivity in the range of 3000 - 5000 W/mK. Adding graphene to a polymer, enhanced thermal conductivity of polymer composite is expected, which depends significantly on the filler content, degree of dispersion and interfacial interactions [3].

In Figure 3, the thermal conductivity of GNP/PLA nanocomposite vs. GNP content is presented. Two types of samples were tested, 3D printed and hot-pressed. The results show that the thermal conductivity increases almost linearly with increasing of the filler content, where the hot-pressed samples demonstrate higher conductivity than the 3D printed one. Thus, at maximum filler content of 6 wt.% GNPs, the thermal conductivity is around 0.6 W/mK for the hot-pressed samples, while the value of 0.46 W/mK is observed for the 3D printed samples. The neat PLA shows thermal conductivity of 0.20 W/mK for the hot-pressed samples and 0.19 W/mK for the 3D printed one.

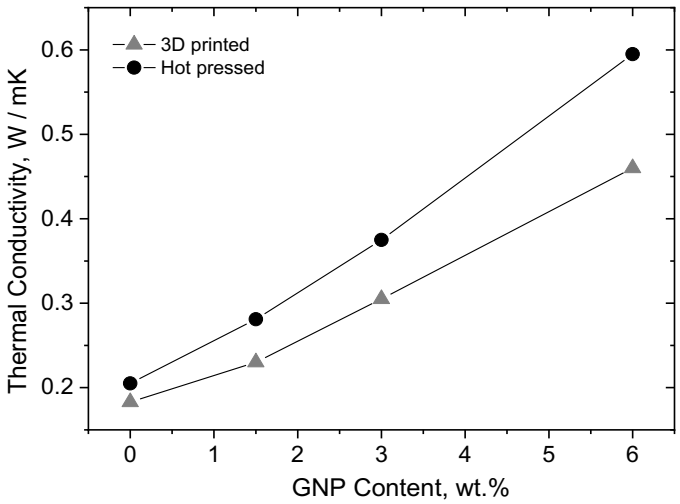

Fig. 3. Thermal conductivity of GNP/PLA nanocomposites vs. GNP content, comparing the 3D printed and hot-pressed samples.

Thus, at 6 wt.% GNP content, the thermal conductivity enhancement is of 200 % for the hot pressed samples and about 150% for the 3D printed samples, compared to the neat PLA. This can be attributed to the high thermal conductivity of the graphene when compared to the pristine polymeric matrix and the networks created by contact between the graphite layers above the percolation threshold (EPT). A better contact and alignment of GNP nanoplatelets during the hot pressing obviously assist the phonon scattering, leading to higher values of thermal conductivity, compared to the 3D printed one. The obtained results open new fields of potential applications for graphene-enabled thermal management, including electronics, which could greatly benefit from the ability of graphene to dissipate heat and optimize electronic devices. Therefore, graphene-polymer composites with strongly enhanced thermal conductivity hold enormous potential for electronics applications.

4. DISCUSSION

4.1. GNP/PLA filament for 3D printers (FDM)

The PLA-based nanocomposites of 6 wt% GNPs content may be proposed as a novel multifunctional filament for 3D printing application, due to the significant mechanical reinforcement, combined with enhanced thermal and electrical conductivity. In order to achieve a good accuracy for the printing objects, the printing of the neat PLA and the nanocomposite filaments was accomplished at appropriate conditions and the printing speed was increased in correlation with the flow index of the printed material. The CAD models are firstly elaborated and then the lightweight porous structures are fabricated by layer-to-layer deposition using Fused Deposition Modeling 3D printer X400 PRO German RepRap (see in Fig. 5). It was found, that the 6 wt.% GNP/PLA composites filament is easily printed using the preliminary optimized printing conditions: nuzzle temperature 200°C, extrusion speed 100 mm/s, layer height 0.2 mm and 100% infill, in a rectangular direction of one layer to another. Extrusion nozzle with diameter of 0.4 mm is used. Fig. 5 shows the 6 wt.% GNP/PLA filament and the 3D printed example porous structures with lightweight, thermal and electrical conductivity suitable for electronics application.

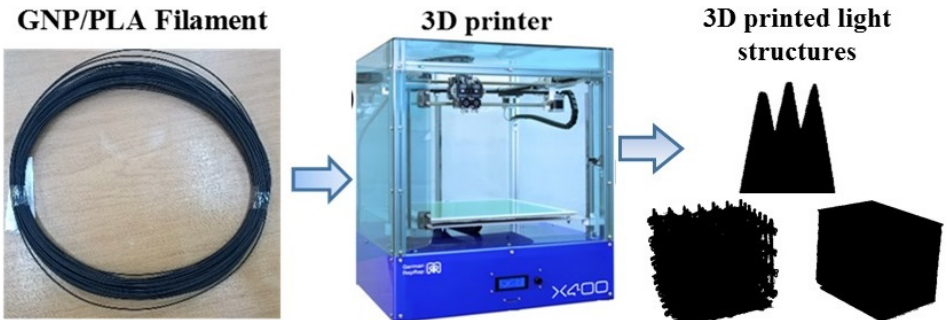

Fig. 5. 3D printed lightweight structures with 6 wt.% GNP/PLA filament using 3D printer (FDM)

4.2. Safety concerns for GNP/PLA films for packaging

The incorporation of 1.5-3 wt% GNPs in poly(lactic) acid films is a promising approach for active and smart packaging applications leading to several benefits, such as improved mechanical, thermal, barrier and antimicrobial properties. Graphene nanoparticles fall under the definition of a nanomaterial, (EU) No. 696/2011, so the migration of graphene into foodstuff is an important aspect for food packaging application. It is generally believed that due to the fixed or embedded nature in the polymer, the nanoparticles larger than 3 - 4 nm will not migrate from film into food, thus not pose risk to the consumer. However, the chemical stability of the matrix polymers (e.g. partial dissolution or degradation) during the various treatment conditions of the packaged food may assist to the release of graphene nanoparticles from nanocomposite film into surrounding media.

In our previous study [5] we have observed that graphene platelets of mean diameter 100 - 1000 nm indeed migrate from PLA composite film into food simulants (10% and 95% ethanol, and 3% acetic acid) at high temperature treatment (4h at 90ºC) of the films, due to partial hydrolytic dissolution of the matrix polymer. Small amounts of migrants (0.028-0.053 mg/cm2) have been found to release from the nanocomposite films, which is much lower than the overall migration limit for food contact material (0.10 mg/cm^2).

In the present study, we report on new results for the migration of GNPs from PLA composite films into three food simulants, 10% ethanol, 3% acetic acid and 50% ethanol. The food simulants represent the aqueous, acidic and fatty foods, as well as alcoholic drinks and milk. Our study demonstrates that nanoparticle migrants from GNP/PLA film are not detected after the standard migration test for 10 days at 40ºC. However, after the high temperature migration test at 90ºC for 4 hours, the GNP particle migrants are already visible in the food simulants, although rarely. In Fig. 6, the TEM images show that the GNPs migrate mostly as aggregates of mean size around 800-1000 nm, obviously in that size they have been dispersed in the nanocomposite matrix polymer.

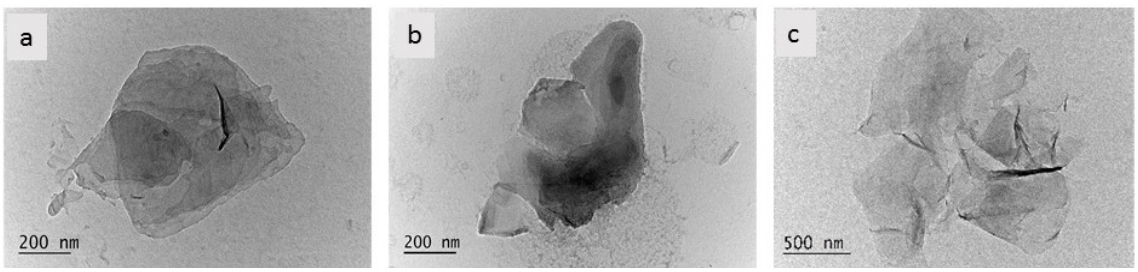

Fig. 6. TEM micrographs of the migrated GNP patricles observed after the migration test of 4h at 90ºC and subsequent drying of the food simulants: (a) 10% ethanol, (c) 3% acetic acid and (d) 50% ethanol.

In Fig. 7, the SEM images show the film cut edges (cross section) before and after the migration test of 4 h at 90°C in the three food simulants. It is seen in Fig. 7 (a) that before the migration test the film cross section is compact and has a homogeneous surface. However, after the migration test, the cross section looks swelled and the extracted substances are visible on the surfaces (Fig. 7 b-d). At higher magnification in Fig. 7(c), the film cross section looks loose and incompact. Hence, we assume that the single GNP agglomerates may be extracted also from the film cut edges after swelling by the food simulant and partial dissolution of the PLA matrix. The results confirm our previous study [5] where extracted GNP particles and even local destruction of the film surface were visible after the migration test at 90 °C for 4 hours.

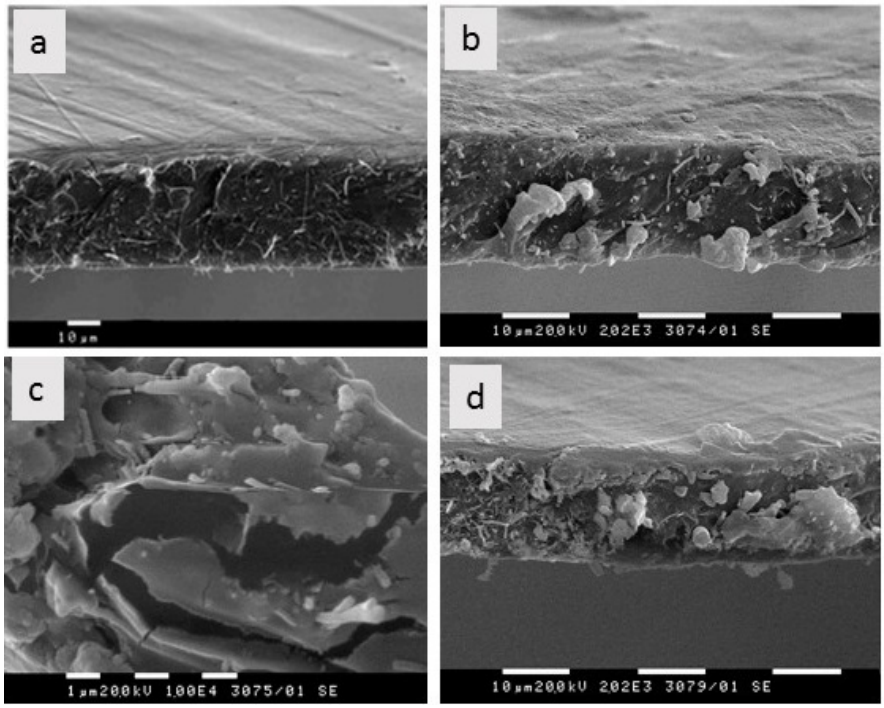

Fig. 7. SEM micrographs of the film cross sections, before (a) and after (b-d) the migration test at 90°C for 4 hours in the food simulants: (b) 10% ethanol, (c) 3% acetic acid and (d) 50% ethanol.

Nevertheless, that the migrated GNPs aggregates are mostly of large size, safety concerns may arise when the GNP/PLA nanocomposite films are widely used as food contact materials. Researchers agree that the shape, high surface area, surface chemistry and purity of graphene may lead to unknown toxicological effects and uncertainties on consumer safety. Concerning the risk from migration of graphene from packaged film into food or drink, little information is currently available concerning the uptake of nanoparticles following oral exposure by ingestion directly from food and drink. Therefore, the risk from the long-term exposure of consumer to graphene via high temperature processed packaged food needs to be carefully studied case by case.

CONCLUSIONS

Polylactic acid nanocomposites incorporating 1.5-6 wt.% graphene nanoplatelets are developed and their tensile properties, electrical and thermal conductivity are characterized. The tensile Young's modulus of the filament samples is increased gradually with increasing GNP loading, with 25% increase at 6 wt.% GNP content. The tensile strength and the elongation are insufficiently affected at 1.5 - 3 wt% GNP content, while more pronounced is the effect at 6 wt.% GNPs, with 5% and 11% decrease of strength and elongation, respectively, which was assigned to the worsen filler dispersion.

The electrical percolation threshold for the GNP/PLA nanocomposite filaments is estimated of 4 wt.% GNP content with conductivity of 1.10^{-5} S/m, while at 6 wt.% GNPs the conductivity value is of 0.0133 S/m. The thermal conductivity enhancement at 6 wt.% GNP content is of 200 % for the hot pressed samples and of 150% for the 3D printed samples, compared to the neat PLA, due to better contact and alignment of GNP nanoplatelets during the hot pressing.

The obtained results open new frontiers of potential applications of 6 wt.% GNP/PLA nanocomposites as novel filaments for printed electronics. While the 1.5-3 wt% GNP/PLA nanocomposite films are suitable for active and smart packaging applications. However, the risk from migration of graphene particles from packaged films needs to be carefully studied case by case

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