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Nanoindentation analysis of 3D printed poly(lactic acid)-based composites reinforced with graphene and multiwall carbon nanotubes

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ABSTRACT: Influences of different nanocomposite loadings in poly(lactic acid) (PLA) matrix on resulting hardness and elasticity were examined in nanoindentation experiments. The following study was focused on the nanomechanical properties of PLA reinforced with graphene nanoplatelets (GNPs) and multiwall carbon nanotubes (MWCNTs) by using Berkovich type pyramidal nanoindenter. A masterbatch strategy was developed to disperse GNP and MWCNT into PLA by melt blending. Young's modulus and nanohardness of as-prepared nanocomposites were characterized as a function of the graphene and carbon nanotubes loading. The nanoindentation analysis reveals that these carbon nanofillers improve the mechanical stability of the nanocomposites GNP/PLA, MWCNT/PLA, and GNP/MWCNT/PLA. That improvement of mechanical properties strongly depends on the fillers content. It was found that the best mechanical performance was achieved for the compound having 6 wt % graphene and 6 wt % MWCNTs in the PLA matrix. The received values for nanohardness and Young's modulus are among the highest reported for PLA-based nanocomposites. © 2018 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2018**, *135*, 47260.

KEYWORDS: carbon nanotubes; composites; graphene; nanoindentation; poly(lactic acid); 3D printing

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INTRODUCTION

With the increasing demand for environmentally friendly materials, poly(lactic acid) (PLA) has attracted a lot of interests from both industry and scientists. Derived from renewable resources, PLA possesses nice features including biocompatibility, sustainability, and biodegradability.[1] After graphene was discovered in 2004,[2] this new carbon material has received great attention because of its exceptional mechanical, electrical, and thermal properties.[3] Polymer nanocomposites based on graphene exhibit substantial properties enhancement at much lower filler loadings than polymer composites with conventional nanoscale fillers, such as glass[4] or carbon fibers,[5] which finely results in simple compound processing. Moreover, the multifunctional properties enhancement of graphene containing products could create new applications of biodegradable polymers. The PLA shows a high Young's modulus of around 3–4 GPa and a tensile strength between 50 and 70 MPa.[6] Nanoindentation is widely applied for the determination of mechanical properties[7–10] at micro and nano length scales. In recent article,[11] the nanomechanical properties of three-dimensional (3D)-printed PLA and PLA–graphene composite have been evaluated by nanoindentation tests using Berkovich diamond indenter with tip radius of 100 nm. It has been found lower indenter displacement for the PLA–graphene sample compared to pure PLA at applied load of 500 μN.

In this work, we have used instrumented nanoindentation technique, introduced by Oliver and Pharr,[12,13] for measuring hardness and elastic modulus defined directly from indentation load and displacement curves. Without the need of high-resolution testing equipment, the above method has widely been adopted and applied in the characterization of mechanical behavior of materials at nanometer scales.[14–17] In our previous works,[18,19] it have been investigated the reinforcement effect of multiwall carbon nanotubes (MWCNTs) in polypropylene as well as the mechanical properties of bilayer graphene/poly(methyl methacrylate) thin films.[20] By applying nanoindentation force of 5 mN, it was established 20% improvement of the composite hardness for 0.3 wt % carbon

nanotubes content and almost 50% increasing of rigidity for the composite having 3 wt % carbon nanotubes. In another article,[21] it has been found that in polymer matrix MWCNTs are rather dispersed in small aggregates than in single nanotubes. The presence of aggregates leads to lower specific surface area and hinders the formation of framework structure, which is essential to improve mechanical properties. Thus, the main task of processing is to disperse the aggregates as much as possible. Therefore, uniform dispersion of the nanotubes is required to realize the potential of the nanotubes as reinforcing fillers.[22,23]

The aim and novelty of our present study is to verify the influence of graphene, carbon nanotubes, and synergetic effect of their mixtures inserted in various concentrations into green PLA matrix on the surface mechanical properties, as hardness and elasticity. The nanoindentation tests were made on 3D printed samples, using fused deposition modeling (FDM) technology. 3D printed scaffold structures, produced from PLA, have been studied in advanced medical applications.[24] FDM technology has been applied for printing of cellulose reinforced PLA.[25] Due to layer-by-layer process, the mechanical properties of the printed specimens are strongly influenced by the building direction, extrusion temperature, and height of the layers but less significantly on the infill shape and printing speed.[26,27] In order to achieve good repeatability in terms of the physical properties of the materials, the samples have to be obtained under appropriate process parameters.

EXPERIMENTAL

Nanocomposites Preparation

The PLA polymer used in this study was Ingeo Biopolymer PLA-3D850 (Nature Works) with a melt flow rate of 7–9 g/10 min (210 °C, 2.16 kg). Graphene nanoplatelets (GNPs) with purity >99.5 wt % and average thickness of ~12 nm as well as MWCNTs having purity >95 wt % and diameter >50 nm, were supplied from Times Nano, China. Monofiller nanocomposites of GNP/PLA and MWCNT/PLA, as well as bifiller systems GNP/MWCNT/PLA with ratio 50:50 of GNP to MWCNT as varying the filler contents from 0 to 12 wt % were prepared by melt extrusion. Platelets with geometry 60 × 12 × 2 mm^3 and very low roughness were prepared using FDM technique and layer-to-layer deposition. For production of this set of samples was used German RepRap X400 Pro 3D printer with two printing heads, equipped with Simplify3D slicer. The specimens were obtained in flat build orientation under nozzle temperature 210 °C, layer thickness 0.25 mm, and printing speed of 2600 mm min^{-1}. All samples were stored in a vacuum package.

Characterization Methods

Nanoindentations were performed using universal nanomechanical tester equipped with atomic force microscopy, produced by Bruker Surface Analysis, USA. The hardness and elastic modulus were calculated from the recorded load–displacement curves using Oliver–Pharr method.[12] Mechanical properties were directly determined by indentation load and displacement measurements without need to image the hardness impression. Load was measured as a function of penetration depth. Indenter type Berkovich Diamond with tip radius of 70 nm was used for indentations in force control mode of

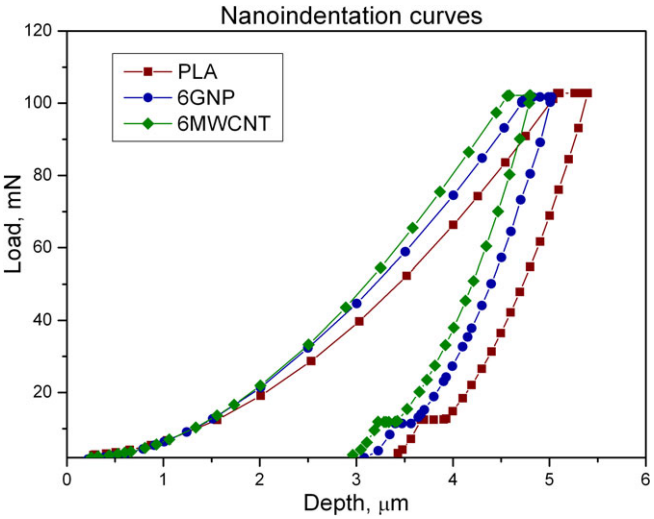

Figure 1. Representative load–displacement curves showing different penetration depth, respectively, at pure PLA, 6 wt % GNP/PLA, and 6 wt % MWCNT/PLA nanocomposites. [Color figure can be viewed at wileyonlinelibrary.com]

100 mN. Each test was repeated 48 times (4 × 12; spacing between indents 80 μm) to have statistical data. No surface smoothing was needed for the 3D printed samples designed for nanoindentation since each printed object adhered well enough to the printer bed and thus has got a sufficient smooth surface. A typical indentation experiment consists of the following steps: (1) approaching the surface, (2) loading to the peak load of 100 mN for 15 s, (3) holding the indenter at peak load for 10 s, (4) unloading from maximum force of 100 mN to 10% for 15 s, (5) holding at 10% of max force for 15 s, and (6) final complete unloading for 1 s (load function 15s-10s-15s trapezoid). The hold step was included to avoid the influence of the creep on the unloading characteristics since the unloading curve was used to obtain the elastic modulus of the material. The elucidation of the nanoindentation hardness and Young's modulus was made through the above-noticed Oliver–Pharr method[28] and every one value in the nanomechanical results was received by means of experimental load–displacement curves (Figure 1). The nanoindentation tests were made at maximum force of 100 mN and retention time of 10 s in order to eliminate the viscoelastic contribution and to validate the Oliver–Pharr model.

The estimation of the nanomechanical properties through nanoindentation, perform an idealized and small volume of the 3D printed structures where the existence of porosity will have insignificant influence on the measurements. The resistance to displacement of GNP/PLA and MWCNT/PLA at fillers loading of 6 wt % comparing to neat PLA (Figure 1) suggests the higher endurance to plastic strain in the reinforced samples.

The dispersion and microstructure of PLA-based nanocomposites were studied using a transmission electron microscope. The transmission electron microscopy (TEM) analysis was performed by using a FEI TECNAI G12 Spirit-Twin (LaB6 source) equipped with a FEI Eagle-4k charged coupling device camera, operating with an acceleration voltage of 120 kV. Before investigation, sections of the samples were cut at room temperature on a Leica EM UC6/FC6 ultramicrotome and placed on 400 mesh copper grids.

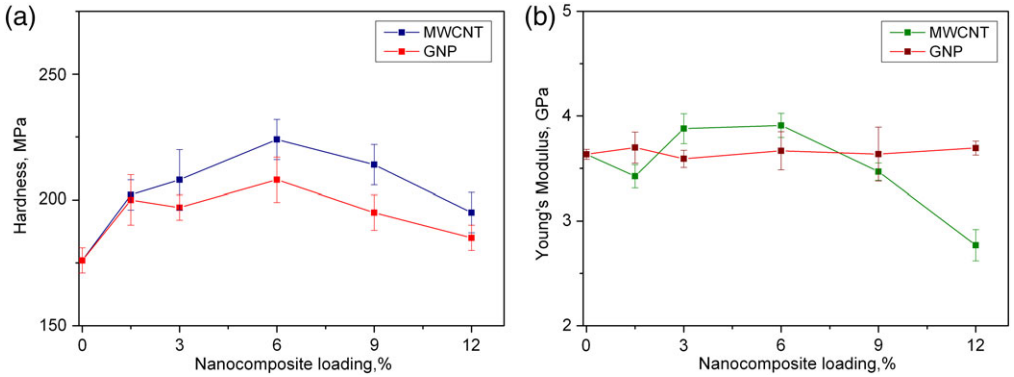

Figure 2. Mean values of (a) hardness and (b) Young's modulus of elasticity versus monofiller content. [Color figure can be viewed at wileyonlinelibrary.com]

A scanning electron microscope (SEM) was used for morphology observations. The SEM analysis was performed using a SEM FEI Quanta 200 FEG, Hillsboro, OR. Before examination, the samples were coated with Au/Pd alloy using an E5 150 SEM coating unit, Polaron Equipment Ltd., Doylestown, PA.

RESULTS AND DISCUSSION

Nanomechanical Properties

The average values of hardness and Young's modulus depending on nanofiller concentration obtained from nanoindentation tests over single filled MWCNT/PLA and GNP/PLA composites are presented in Figure 2(a,b).

The results for hardness and elasticity have standard deviations that are higher in the case of the reinforced materials than the neat PLA. The level of dispersion of the experimental results is significant for the sensibility of the indenter to the inhomogeneity of the composite structure, produced by the presence of MWCNT or GNP, comparing to the pristine biopolymer. The experimental errors are within the range ±5 to ±12 MPa for the hardness and ±0.048 to ±0.257 GPa for Young's modulus. It can be observed that 6 wt % addition of MWCNT or GNP in the PLA matrix is giving best results for nanomechanical properties. The lower values for 9 and 12 wt % mono-filled nanocomposites could be explained with the formation of aggregates in the PLA structure, resulting in worst carbon nanofiller dispersion and therefore having lower hardness and elasticity. The exception in this trend is Young's modulus of elasticity of GNP/PLA nanocomposites that is almost identical for all graphene-loaded samples. It could be due to higher exfoliation degree of GNPs in the PLA matrix.

Figure 3 presents two pillar graphs containing mechanical properties data of nine melt blended, extruded as filaments and 3D-printed nanocomposite systems, all have been compared to 3D-printed PLA as reference. The nanocomposites consist of two carbon nanofillers dispersed in the polymeric base, having different ratios at every compound. By means of precise nanoindentation tests, it was found that the sample possessing 6 wt % GNP combined with 6 wt % MWCNT in the PLA structure has better hardness and elasticity than the other samples with 12 wt % nanocomposite loading as well as regarding the whole series of nanocomposites. It should be remarked the excellent experimental values for the sample having 6 wt % GNP and 3 wt % MWCNT and especially its high Young's modulus. The nanocomposite systems holding equal fillings of 1.5 and 3 wt % GNP and MWCNT also have impressive mechanical properties – above 30% improvement of hardness and above 20% improvement of elasticity compared to pure PLA. Among the nanocomposites at loading of 6 wt %, the sample 1.5 wt % GNP/4.5 wt % MWCNT/PLA shows best hardness that could be explained with good dispersion of the carbon nanotubes as well as the GNPs in the PLA matrix bringing rigidity to the structure. This suggestion was confirmed by TEM micrographs represented in Figure 4.

Good improvement of hardness and elasticity up to 50% could be seen in Figure 5 for the bifiller nanocomposite systems at 3, 6,

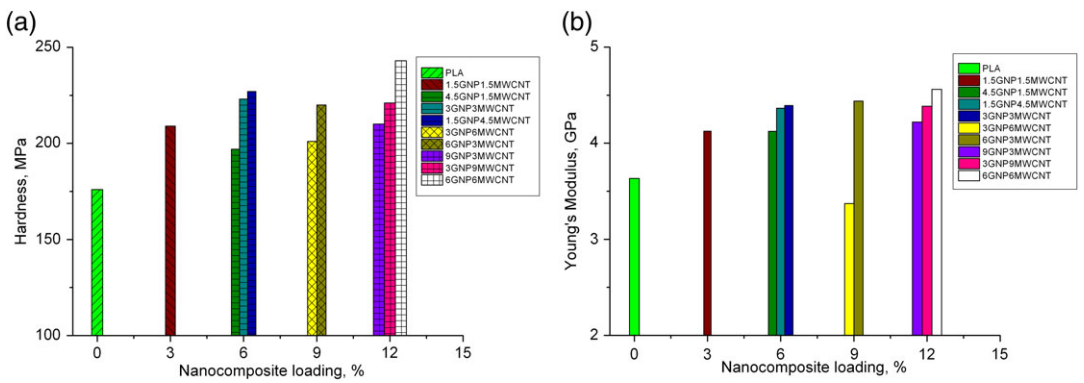

Figure 3. (a) Hardness and (b) Young's modulus of bifiller GNP/MWCNT/PLA systems as varying both fillers content and ratio. [Color figure can be viewed at wileyonlinelibrary.com]

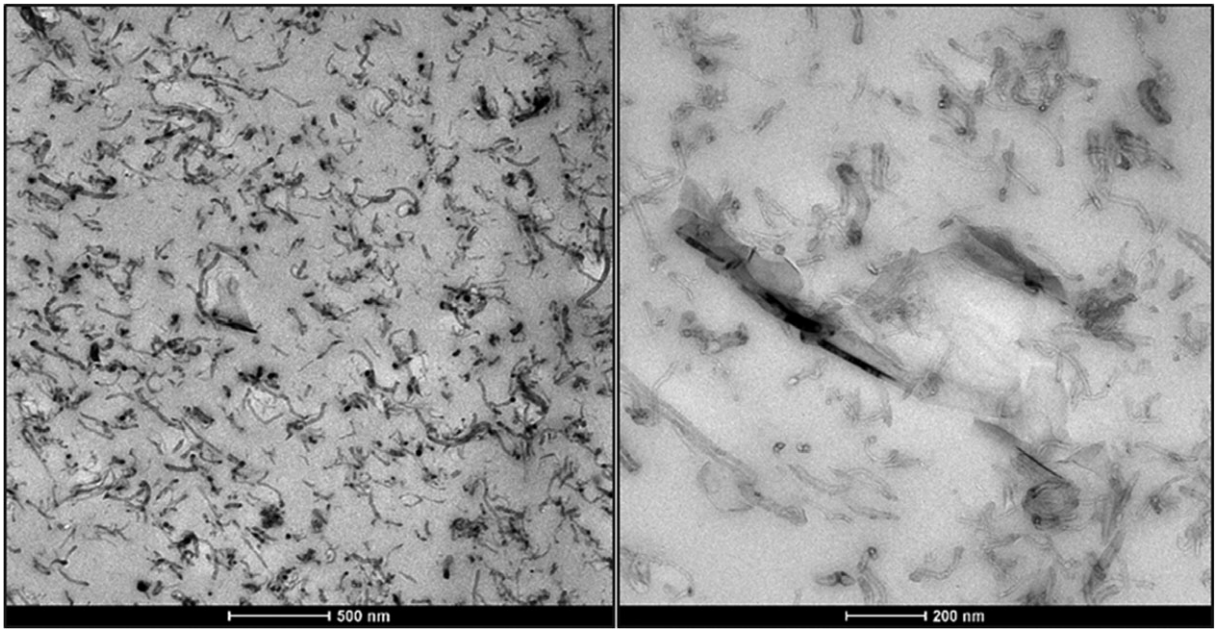

Figure 4. TEM images of nanocomposite 1.5 wt % GNP/4.5 wt % MWCNT/PLA.

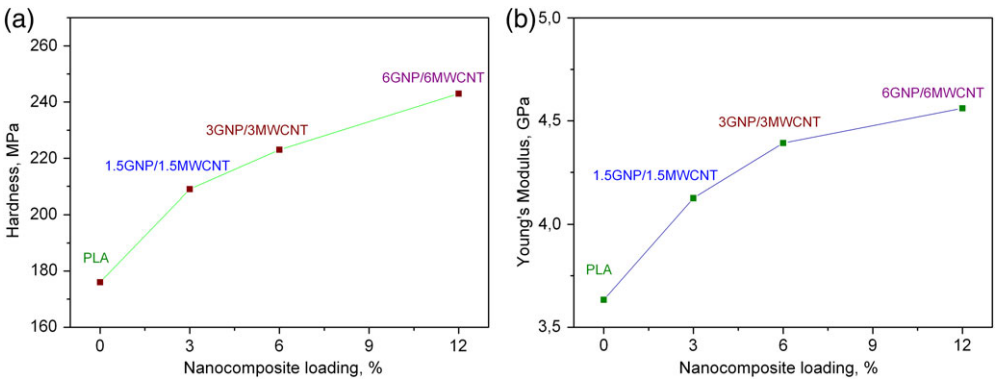

Figure 5. (a) Hardness and (b) Young's modulus of bifiller GNP/MWCNT/PLA systems with 50:50 loading ratio of both nanofillers. [Color figure can be viewed at wileyonlinelibrary.com]

and 12 wt % total carbon fillers content, incorporating equal loadings of GNP and MWCNT in the PLA matrix. The nanocomposite having in its structure by 6 wt % of each nanofiller (12 wt % overall loading) exhibits the best mechanical properties compared to pure PLA. In Figure 5(a,b), there is significant growth of Young's modulus and rigidity, starting from neat PLA and reaching up to the highest nanocomposite loading. Two selected SEM images of the mixed nanocomposite 6 wt % GNP/6

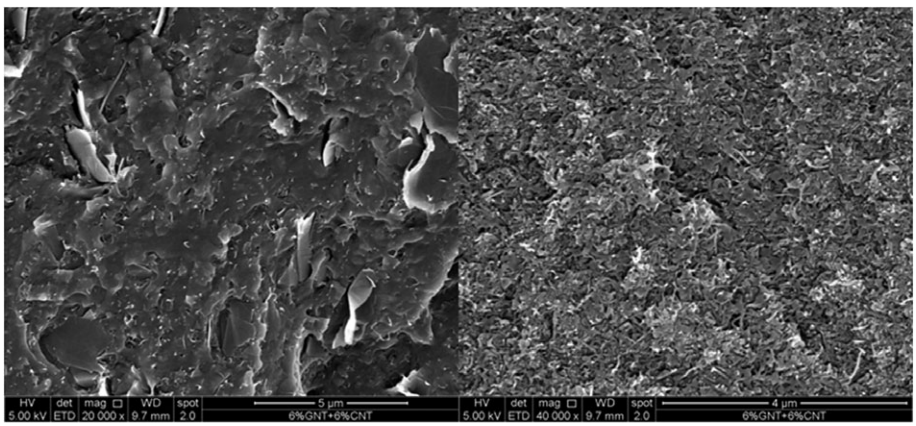

Figure 6. SEM images of nanocomposite 6 wt % GNP/6 wt % MWCNT/PLA.

wt % MWCNT/PLA disclose high degree of structure porosity and good uniform insertion of carbon nanofillers in the PLA matrix (Figure 6).

Apparently, the combination of the two nanofillers (MWCNT and GNP) in the PLA matrix leads to creation of contact network between MWCNT and GNP aggregates (with different size distributions) and also to well-dispersed carbon nanofillers. That is a fact providing the opportunity of unique synergetic effect for improvement of nanomechanical properties of the bimodified composites as proofed by using of the TEM and SEM techniques.

CONCLUSIONS

The nanoindentation tests were made on 3D printed exceptionally smooth samples as an important precondition for reliable results. It is reasonable to conclude that the significant improvement of mechanical properties for PLA-based nanocomposites is attributed to the reinforcement effect of carbon fillers intercalated homogeneously in PLA matrix. It could be noticed that the equal loadings in nanocomposite compounds have given good and stable contribution to the nanomechanical properties of PLA. The TEM micrographs of the nanocomposite 1.5 wt % GNP/4.5 wt % MWCNT/PLA support its excellent mechanical properties, showing that the carbon nanofillers were uniformly dispersed in the PLA matrix and no obvious aggregation was observed.

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