

INVESTIGATION OF RHEOLOGICAL AND SURFACE PROPERTIES OF POLY(LACTIC)ACID POLYMER / CARBON NANOFILLER NANOCOMPOSITES AND THEIR FUTURE APPLICATIONS

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Abstract. The recent subject of great research challenge and one of the most active area of research for well in materials science include the development of nanofiller reinforced polymer materials for additive manufacturing application. The dispersion of nanofiller in polymer matrix is a critical issue not only for control of processing but also for pre-defined properties. Quantitative analysis of extent of dispersion of nanofiller by measuring the rheological and surface characteristics of polymer nanocomposites has great technical importance for improving processing conditions, as well as for understanding the fundamental characteristics of materials at the nanoscale. The incorporation of nanofiller graphene into polymers is a promising approach to impart certain electrical and magnetic properties, mechanical reinforcement and high thermal conductivity to the resulting material. Rheological and surface properties of the poly(lactic) acid (PLA) based nanocomposites incorporating 0-9 wt.% graphene nanoplates (GNPs) were investigated in the present work and a new strategy to tune such properties of PLA matrix by varying filler content is proposed.

KEYWORDS: RHEOLOGY, SURFACE PROPERTIES, DISPERSION, NANOFILLERS, CARBON NANOTUBES, GRAPHENE, POLY(LACTIC)ACID POLYMER.

1. Introduction

Due to significant features, carbon nanofillers have gained particular attention as polymer reinforcement [1]. Incorporation of carbon nanomaterial in polymer matrix has led to the production of versatile composites with improved mechanical and electrical properties. Polymer/carbon nanofiller nanocomposites have been used in range of technical applications such as sensors, solar cell, electromagnetic interference (EMI) shielding materials, etc. Since the discovery two decades ago, graphene family has drawn remarkable attention because of their unique electrical, thermal, optical, mechanical and flammable properties. They have been widely used to improve polymer properties. These nanofillers produce huge interfacial areas between the polymer and the fillers. Despite the intensive research on graphene nanocomposites, understanding of the importance of the filler-polymer interface is still limited and further investigation of the structure-property relationships is needed. Graphene, a monolayer of sp²-hybridized carbon atoms arranged in a two-dimensional lattice, has attracted tremendous attention in recent years owing to its exceptional thermal, mechanical, and electrical properties [1-3]. It is known to all that the properties of composites depend not only on the strength of the interfaces between nanofillers and matrix but also the dispersion status of nanofillers. High specific surface area and wrinkled surface morphology of nanofillers would lead to a reinforced interface. However, the relationship between dispersion status and enhancement effect of nanofillers was seldom discussed systematically due to the difficulties in its quantitative characterization.

In the present work, we report on rheological and surface properties characterization of Poly (lactic acid) (PLA)-based nanocomposites incorporating graphene nanoplatelets (GNP) with varying filler ratios. The GNP/PLA composite films were investigated by Rheology, Zeta potential and Contact angle measurements. The effect of filler types and filler loading on rheological and surface properties of composite films were studied by investigate the rheological behavior in oscillatory and steady shear flow, and measuring isoelectric point, contact angle and calculate surface free energy of composites films. The aim of the study is to clarify the degree of dispersion of monofiller, GNP at various fillers ratio in PLA matrix, as well as to understand better the interfacial filler-polymer interactions. In this study we present a new strategy to tune the rheological and surface properties of PLA matrix by varying the GNP filler contents.

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), peak melt temperature ~180 °C, glass transition temperature ~ 60 °C, tensile elongation 3.1%. Ingeo™ 3D850 is a grade developed for manufacturing 3D printer filament having some remarkable 3D printing characteristics such as precise detail, good adhesion to build plates, less warping or riling, and low odor. The Graphene Nanoplates (GNPs) adopted as nanofillers were supplied from Times Nano, China, having commercial code (TNGNP) [4]. The specific features of the used carbon nanofiller IS collected in Table 1.

Table 1. Characteristics of GNPs used in PLA nanocomposites

Property	GNPs (TNGNP)
Purity, wt.%	>99,5
Number of layers / Thickness, nm	<20 / 4-20
Diameter/medium size, μm	5-10
Length, μm	-
Outer diameter, nm	-
Aspect ratio	~250
Transition Metal oxide, %	-
Surface area, m ² /g	-

2.2. Methods of preparation of melt extrusion

Nanocomposites were prepared by melt extrusion at 170 – 180 °C, using a tween screw extruder (COLLIN Teach-Line ZK25T) at screw speed 40 rpm. Monofiller (GNP/ PLA) composites, as varying the filler content from 1.5 to 9 wt.% were produced.

2.3. Methods for characterization

2.3.1. Rheological measurements

The rheological measurements were carried out with AR-G2 Rheometer (TA Instruments) using electrical-heated parallel plate geometry (25 mm diameter) and gap size of 500 μm between plates. The test samples for rheological analysis were prepared by pressing of the nanocomposite filaments produced by melt extrusion, at 1 ton and temperature of 200°C to discs with diameter of 25 mm and thickness of 1.5 mm.



Fig.1. Rheometer AR-G2

The viscoelastic flow properties were measured using low amplitude oscillatory flow mode, at a temperature of 200°C. The complex dynamic viscosity η^* , storage modulus G' , and loss modulus G'' were measured versus the angular frequency ω of 1 – 100 rad/s at low strain amplitude of 0.1 %. The linear viscoelastic strain amplitude of 0.1 % was preliminary determined by strain sweep test at angular frequency of 1 Hz. Before starting the rheological experiment, the tested material was heated at 200°C for 15 min. in the gap between the parallel plates, and pre-shear was applied to avoid unwanted errors during the measurement. The TA Advantage Software was used for data analysis and calculation.

2.3.2. Zeta potential

Composites surface zeta potentials are determined by streaming potential measurements that are believed to be surface sensitive [5]. Zeta potential (ζ) analysis was performed as a function of pH to determine the isoelectric point (IEP) of all polymer-filler composites. The isoelectric point of the flat surface of neat PLA and nanocomposites with and without incorporating varying amounts of 1.5 – 9 wt% GNP in PLA matrix have been measured at room temperature by SurPASS electrokinetic analyzer (Anton Paar GmbH, Austria).



Fig.2. The SurPASS 3 surface charge analysis system, Anton Paar

The film sample was cut from prepared in advance pressed films and adjusted to the dimensions of the sample holders and fixed using double-sided adhesive tape. The required pH value in the samples was adjusted by adding an appropriate amount of 0.05 M HCl or 0.05 M NaOH. The zeta potential measurements were carried out in the pH value range of 2 – 6. By equipment we determine the zeta potential at the surface of a macroscopic solid in contact with an aqueous solution. Zeta potential was used to further characterize the nature of the interaction between PLA with GNP, and compare with pure PLA. For each pH, the zeta potential measurement was repeated 4 times and average was taken.

2.3.3. Contact angle

The equipment used for measuring of samples for the Contact angle analysis was A DSA100 – KRÜSS goniometer (Kruss, Hamburg, Germany). The contact angles (CA) of the liquid droplet on the flat surface with and without incorporating varying amounts of GNP in PLA matrix have been measured with two different liquids with varying surface tension at 20 °C to determinate the Surface Free Energy (SFE). The used liquids were deposited onto the film by a sessile drop method [6].



Fig.3. KRÜSS goniometer - DSA100

The fitting used for each drop was determined using the best fit observed, and at least twenty measurements were performed for each sample. Data were collected with Advance-Drop shape software, from KRÜSS. Films were characterized using two liquids - Mili Q water and ethylene glycol, to be able to perform the two-component surface energy characterization. The films were attached to a microscope glass slider with double sided tape for the duration of the analysis. All measurements were made in static contact angle mode.

The SFE values were calculated using Fowkes methodology [7-9]. The values of the contact angles (water and ethylene glycol) were used to calculate the surface energy (γ) using an harmonic mean equation [10]. The solution of the equation also gives the values of dispersion (γ^d) and polar (γ^p) components of surface energy, where γ^p is a polar component due to dipole-dipole interactions and γ^d is dispersed component. The polar component is the sum of polar, hydrogen, inductive, and acid-base interactions, while the dispersive component accounts for van der Waals and other non-site specific interactions [11-14].

3. Results and Discussion:

3.1. Rheological measurements

The effect of graphene on the linear viscoelastic response of the PLA polymer and the composites at 200°C is shown in Figure 4. The frequency dependence of the dynamic complex viscosity η^* is shown in Figure 4 and the storage and loss moduli (G' & G'') versus angular frequency ω is seen on Figure 5 as varying the filler contents from 1.5 to 9 wt% for GNP/PLA nanocomposites.

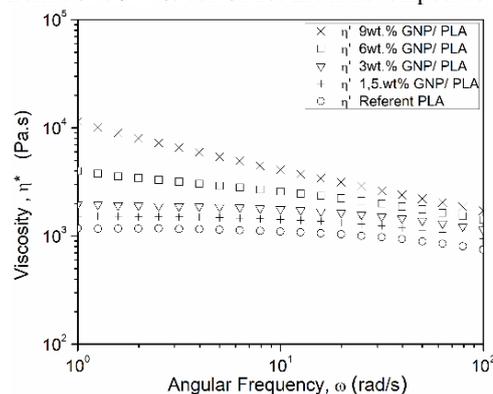


Fig.4. Complex viscosity η^* versus angular frequency of GNP/PLA nanocomposites at 200°C with varying the filler contents from 0 to 9 wt%.

Figure 4 shows, that 1.5 and 3 wt% GNP/PLA composites have a Newtonian plateau in the low frequency range ($\omega < 10$ s⁻¹), similar to the neat PLA, while 6 and 9 wt% GNP/PLA demonstrate pseudo-plastic flow behavior, associated with percolation.

In Figure 5, the viscoelastic moduli G' and G'' versus angular frequency ω are shown. In the terminal region, $\omega \rightarrow 0$, the storage G' and loss G'' modulus of the neat PLA fit with scaling law, $G' \sim \omega^2$ and $G'' \sim \omega^1$. For GNP/PLA composites in Figure 5, the slope of both moduli slightly decreases by increasing the filler contents from 1.5 to 3 wt%, while at 6 and 9 wt% GNPs, the slope of both

dynamic moduli decreases significantly, but the flow behavior is liquid-like, with $G' < G''$.

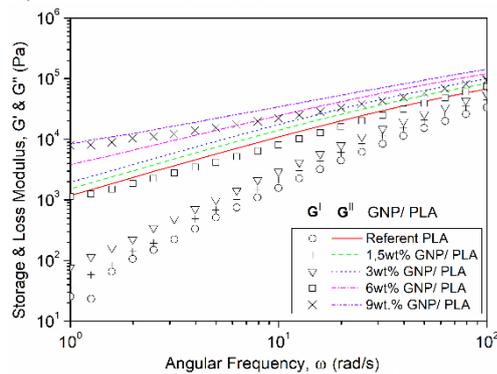


Fig.5. Storage and loss moduli G' and G'' versus angular frequency of GNP/PLA nanocomposites at 200°C with varying the filler contents from 0 to 9 wt%.

It is important to determine the rheological percolation threshold as the viscosity and the properties of nanocomposites are generally enhanced above this critical filler concentration [15]. The rheological percolation threshold is usually associated with the structural liquid-to-solid transition indicating the formation of a percolation network of interconnected nanoparticles, immobilized with matrix polymer [15, 16, 17 – 19]. Different approaches are used in the literature to determine the percolation threshold [15, 18, 20]. In this study we apply the rheological criteria: Cole-Cole plot, in order to verify applicability for the studied GNP/PLA nanocomposites for precise estimation of the rheological percolation threshold.

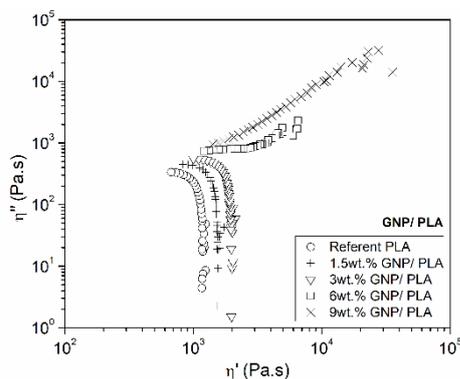


Fig.6. Cole-Cole plot of dynamic viscosity η' versus imaginary viscosity η'' for: GNP/PLA nanocomposite at 200°C with varying the filler contents of 0 – 9 wt%.

The Cole-Cole plot, which presents the frequency dependence of imaginary viscosity η'' versus real viscosity η' is shown on fig.6. The Cole-Cole plot is used to identify the structural changes in the PLA polymer matrix due to the incorporation of GNP filler. The real part and imaginary part of complex viscosity are calculated from the dynamic modulus as follows: $\eta' = G'/\omega$ and $\eta'' = G''/\omega$. As seen, for the GNP/PLA composites at low nanofiller contents 0–3 wt%, the Cole–Cole plot exhibits a semi-circular shape with one arc corresponding to the relaxation of the PLA matrix [21]. While at 6 – 9 wt% GNP/PLA the plots exhibit deviation from the semi-circular shape and shows a linear variation of the storage viscosity versus the loss viscosity. This is a characteristic for a gel-like structure which indicates that maximum particle-particle interaction has occurred, associated with percolation. Therefore, the rheological percolation threshold that may be determined using the Cole-Cole plots is around $\phi_p < 6$ wt% for the GNP/PLA nanocomposites.

3.2. Zeta potential measurements

The quality and stability of nanofiller dispersion in the PLA matrix composites were evaluated by zeta potential measurements; when the material is immersed in a solvent a charge may develop at the

interface creating a potential. Figure 7 presents zeta potential curves of the nanocomposite films as a function of pH for monofiller nanocomposites, compared to the neat PLA. The isoelectric point (IEP) of the films, which is a measure of the surface properties, was observed at pH=2.6 for pure PLA, and it increases gradually to pH=3.6 by increasing the GNP content from 1.5 to 9 wt.%, due to improved conductivity on the surface by the graphene nanofiller. The values of measured IEP and zeta potential $|\zeta|$ for GNP/PLA composites are summarized in Table 2.

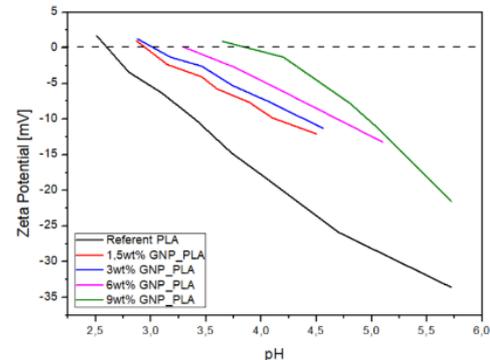


Fig.7. Zeta potential versus pH factor of monofiller, GNP/PLA composites, as varying the graphene content

Table 2. Summarized results for isoelectric point (IEP) and zeta potential $|\zeta|$ of GNP/PLA composites

Sample	Isoelectric point [pH]	Zeta potential $ \zeta $, mV
Pure PLA	2.6	-33.59
1.5wt%GNP/ PLA	2.9	-12.06
3wt%GNP/ PLA	3	-11.28
6wt%GNP/ PLA	3,3	-13.22
9wt%GNP/ PLA	3.6	-21.53

Results indicate that alterations in the pH have a large effect on zeta potential, this referring for agglomerate size. The change in zeta potential was found to alter the stability of the nanoparticle suspension. The suspension stability is dependent upon physical characteristics of both the suspended nanoparticles and their suspension medium. The zeta (ζ)-potential often correlates strongly to dispersion stability with higher magnitude zeta potentials ($|\zeta|$) being more stable due to electrostatic repulsion between particles. Schramm [22] proposed, as a general guide, that at $|\zeta|$ of 0–10 mV the dispersion will be unstable, at 10–30 mV will be slightly to moderately stable; at 30–60 mV will have good stability, and at 60 mV will have excellent stability for electrostatically repelling particles. In our case, with increasing the GNP content the GNP/PLA dispersion system gets more stable. As seen from Table 2, the PLA matrix polymer has the highest value of $|\zeta| \sim 34$ mV. At 9 wt% GNP content, the $|\zeta|$ value sharply grow to ~ 22 mV, so according to [22] we may conclude that such dispersions will be moderately stable. The steadily rising of the absolute value of Zeta potential to 22 mV, as well as the value of the IEP from pH 2.6 for PLA to 3.6 for 9wt% GNP/PLA may be associated with percolation. Our previous studies on rheological behavior [23,24] and electrical properties [24] confirm that the percolation of the GNP/PLA composites is around and above 6 wt% graphene content. From above discussions, we may conclude that the most stable dispersion of GNPs in PLA polymer was achieved above 6wt% GNP content, this related with the formation of a percolated network of well dispersed graphene platelets in the hydrophilic PLA polymer. Therefore, the 9wt.% GNP/PLA composites with Zeta potential of $|\zeta| = 22$ mV have more stable dispersion, due to the percolated network of nanoplatelets, than the 1.5 - 6wt% GNP/PLA composites with values of $|\zeta| = 11-13$ mV, which demonstrate a flocculated, fractal-like structure [23].

3.3. Contact angle measurements

The contact angles (CA) of the liquid droplet on surface of films with and without incorporating varying amounts of GNP in PLA matrix have been measured with two different liquids with varying surface tension. Contact angle measurements investigate surface tension, and they are used to calculate surface free energy (SFE).

Contact angle data for the two test liquids (water and ethylene glycol) apply for monofiller system on base on GNP/PLA are plotted in Figure 8 (a,b). Calculated Surface free energy and its polar and dispersive components are presented on Fig.9. The average values of all surface characteristics for the monofiller GNP/PLA composites are summarized in Table 3.

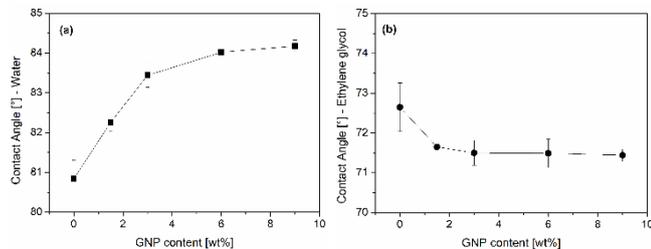


Fig.8. Contact angle vs. GNP content for monofiller GNP/PLA composite, as varying the filler combinations for the two test liquids: (a) water ; (b) ethylene glycol

It can be observed that with increasing the GNP loading slightly higher contact angle values are obtained compared to the neat PLA in the case of water as a liquid. The water contact angle of 9 wt.% PLA/GNP film increased with 3°, if compared to that of pristine PLA films. This may be associated with a small hydrophobic effect of GNP filler. This phenomenon is probably attributed to the hybrid structure of the monofiller nanocomposite, which is related with the interaction between the GNP surfaces and the hydroxyl group of PLA, this leading to a decrease of hydrophilicity of the GNP/PLA composite surfaces. In agreement with Ref. [25], the obtained composites in our study refer to the contact angle values of $0^\circ < \theta < 90^\circ$, where the surface is considered hydrophilic, which corresponds to high wettability. The PLA surface has a lower contact angle of water, therefore exhibit better wettability with water compared to the GNP/PLA surfaces with higher contact angle.

In the case of ethylene glycol liquid, the contact angle is of ~10° lower than that of water; it slightly decreases from 73° to 71°, by addition of only 1.5% GNP, but it goes to plateau with increasing the GNP content to 9 wt.%. Results show that the wettability of GNP/PLA composite surfaces and their lubricant properties to organic liquids will be very good.

The two different liquids (water and ethylene glycol) of known polar and disperse components was used to calculate the surface free energy of GNP/PLA composite films. Table 3 shows the surface free energy for the two liquids used in this study.

Contact angles collected yielded information regarded changes to the energy of the film surfaces before and after reinforced with fillers. The variation of surface free energy against filler's content is given in the Figure 9, showing γ (surface energy) and its polar (γ^d) and dispersive (γ^p) component of the monofiller GNP/PLA composite, compared to the neat PLA.

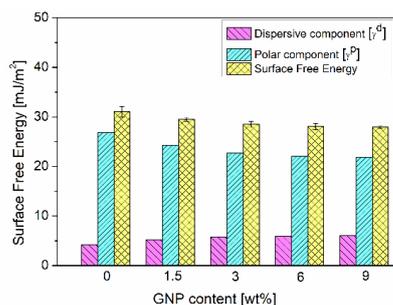


Fig.9. Calculated surface free energy from contact angle test for the mono-filler GNP/PLA composite, as varying the filler content.

Looking at the data (Fig.9 and table 3), we can note that there is a small decrease of surface energy, γ , by increasing the GNP content, which is more pronounced at 1.5wt% GNP. The decrease in γ is mainly caused by a slight reduction in the polar component which involves a strongly polarized interaction of hydrogen bonds, indicating for less polar groups at the surface of the film. This may be associated with a slight increase of the interfacial polymer-filler interactions, by increasing the GNP content. Dispersive component is slightly increasing, which indicate for a small increase in particle-particle interactions with an increase in the GNP content to 9wt%.

Table.3. The contact angle (at 20°C) and surface energies sample components of mono-filler composites GNP/ PLA

Sample	Contact Angle, [°]		Surface energy, [mJ/m ²]		
	Mili Q water	Ethylene glycol	γ	γ^d	γ^p
Neat PLA	80.8±0.5	72.7±0.6	31.1±1.1	4.2	26.9
1.5wt% GNP/PLA	82.3±0.2	71.7±0.1	29.5±0.4	5.2	24.3
3wt% GNP/ PLA	83.4±0.3	71.5±0.3	28.5±0.6	5.7	22.8
6wt% GNP/ PLA	84.0±0.2	71.5±0.6	28.1±0.7	6.0	22.1
9wt% GNP/ PLA	84.1±0.2	71.4±0.2	27.9±0.3	6.1	21.9

It may be concluded that, due to non-polar behavior of filler and polar behavior of polymer the wettability with water of the GNP/PLA composite surfaces slightly decreases by increasing the GNP content from 1.5 to 9wt%. This may be associated with the decrease of polar component of the surface energy, which is connected with dipole-dipole forces leading to an increase of interfacial polymer-filler interactions. On another hand, the dispersive components correspond to the Van der Waals forces. The results show that the dispersive component is slightly increasing, therefore stronger Van der Waals interactions between nanoplatelets are expected by increasing the GNP content.

4. Future application of resulted nanocomposites

The field of nanoscience has blossomed over the last two decades and the importance of nanotechnology increase in areas such as computing, sensors, biomedical and many other applications. In this regard the discovery of graphene [26] and graphene-based polymer nanocomposites is an important addition in area of nanoscience. The superior properties of graphene compared to polymers are reflected in graphene-based polymer composites. Graphene-based polymer composites show superior mechanical, thermal, gas barrier, electrical and flame retardant properties, compared to the neat polymer [27–31]. Our study adds new knowledge about tunable physicochemical properties of the nanocomposites by varying the GNP content and distribution of graphene layers in the polymer matrix, as well as interfacial bonding between the graphene layers and polymer matrix. These properties open new opportunities to revolutionize a variety of practical applications, e.g. multifunctional composites, detectors, smart wearables, paints and printing. Carbon nanofillers have great advantages as additives in polymers for application in Additive Manufacturing (3D printing). It should be highlighted that 3D printing is not only an innovative processing technology, but it is the future of the manufacturing industries. Therefore, unlimited needs exist for novel materials suitable for 3D printing for variety of applications that require improved mechanical performances, conductivity and other functional properties of the final products.

5. Conclusion

Graphene-based polymer nanocomposites are one of the most auspicious developments in the field of material science. The composites based on PLA filled with 0 to 9 wt% GNP filler content prepared by melt extrusion are studied herewith. Rheological and surface properties are obtained as varying the filler content. Rheological percolation threshold for GNP/PLA was estimated around 6 wt% GNP. The wettability with water and the surface

energy of the GNP/PLA surfaces decreases by increasing the GNP content from 1.5 to 9wt%. The obtained effects are associated with a decrease of hydrophobicity and an increase of interfacial polymer-filler interactions. This is proposed as a new strategy to tune the rheological and surface properties of PLA matrix by varying GNP filler contents.

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