Analysis of the Addition of Nanographite on the Characteristics of Polylactic Acid Filaments Produced by Extrusion Process

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Abstract. PLA-based filaments are often used as a basis for 3D printing, and efforts to improve the properties of PLA filaments are made into nanocomposite filaments. The purpose of this study was to determine the effect of adding nanographite on the surface morphology, the geometry of the filament roundness, and the functional groups present in the PLA/nanographite nanocomposite. The method used experimental research with variations in the addition of nanographite to PLA of 0.5wt%, 1wt%, and 1.5wt%. Nanographite was added into PLA by dissolving using chloroform, while filaments were produced using a single screw extruder. The roundness geometry was observed with an optical camera. The functional groups were analyzed with FTIR, and the morphology of the filament surface was observed with SEM. The results show that the addition of nanographite to PLA results in changes in functional groups, which indicate changes in chemical bonds with changes in peaks in the wavenumber range of 1000 – 2000 cm^{-1}. The addition of nanographite makes the filament's morphology rougher due to agglomeration, which is spread unevenly. Analysis of the roundness of the nanocomposite filament diameters showed a difference in the average filament. The best filament diameter was a 0.5% nanographite sample with a roundness value of 99.02%.

1 Introduction

The development of industrial raw materials is very advanced, including plastic. Plastic is the lightest, cheapest, and most corrosion-resistant material with good thermal and electrical insulating properties. Plastic is one of the most widely used materials in the world, with global production increasing at an average of around 9% per year since 1950 [1]. Industrial plastic is often used as the base material for filament in 3D printers.

3D printer technology is based on creating three-dimensional (3D) structures layer by layer directly from computer-aided design drawings, such as B. Computer Aided Design

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(CAD). 3D printers can create physical objects from geometric representations by adding materials sequentially [2]. Product 3D printing depends on parameters including print speed, print temperature, layer height, and infill line direction [3]. 3D printing technology is truly innovative and has developed into a versatile technology that opens up new possibilities and gives hope to many potential companies looking to increase their production. Traditional thermoplastics, ceramics, graphene-based materials, and metals can be printed with 3D printer technology [2].

PLA-based filament is often used as a basis for 3D printers. Polylactic acid is a renewable FFF polymer with a low cost and low melting point and is widely used. PLA is a biodegradable polymer of lactic acid or D-lactide, produced from the fermentation of starch obtained from natural plant sources such as corn [4]. Composites form two or more components with different physical or chemical properties when combined, producing materials with unique properties different from the components [5]. Several methods to produce filament include developing compound compositions and redesigning to improve and adapt existing products and bring new products to the market sustainably [6]. Filament can be produced using recycled materials to reduce production costs [7] and also added nanomaterial to produce filament composite [3]. Nanographite is a good conductor of heat and electricity, with high stiffness and strength ranging from 15.5 MPa to 89.1 MPa. One of the additives that change the properties of PLA is nanographite because it is cheap and has good thermoelectric properties, so it can be used to improve certain properties such as stiffness, thermal stability, fire resistance, and low permeability [8]. In addition, it can be used as a filler in the production of polymer compounds with competitive multifunctional properties [9]. This study aims to investigate the effect of adding nanographite into PLA on the characteristics of PLA filament.

2 Materials and Methods

2.1 Materials

Nanographite was provided from local supplier (CV. STC, Malang-Indonesia). PLA granules (Doudeke, China) was used to make composite filament. Chloroform ($CHCl_3$) as PLA solvent was supplied from Sigma Aldrich (Singapore).

2.2 Mixing PLA with Nanographite

Nanographite with a concentration of 0.5%, 1%, and 1.5% was dissolved in a beaker glass containing $CHCl_3$ 450 mL with stirred for 15 min. at 500 rpm on a magnetic stirrer at room temperature. The solution was homogenized by a sonicator for 30 min. with a power of 400 Watt. The solution was then added 150 g PLA and stirred at 300 rpm for 90 min. A mixture of PLA with nano graphite was left for a day and then stirred for 15 min. using a mixer. The mixture was poured into the mold and dried by leaving it for 48 h at room temperature. The dried PLA nanographite was crushed to obtain composite pellets.

2.3 Extrusion Process

Composite pellets were extruded in a single screw extruder (Wellzoom Extruder, China) at 175 ºC with a screw speed of 2.6 rpm with nozzle diameter of 1.75 mm.

2.4 Functional Group Analysis

The test sample was cut to 10 mm × 10 mm and functional groups of the composite were analyzed by FTIR (Shimadzu IR Prestige-21, Japan). The samples were scanned at a wave number range of 4000 cm^{-1} to 400 cm^{-1} with the rate of 4 cm^{-1}.

2.5 Morphology Observation

Surface morphology analysis of PLA nanographite filaments using SEM with the Hitachi brand type TM4000Plus. This test is carried out in the Lab. Mechanical Engineering, State University of Malang. Sample preparation for SEM testing was carried out by cutting the filament with a dimension length of 10 mm. SEM testing was carried out using 1000 times magnification.

2.6 Roundness analysis

Testing the geometric roundness of the filament diameter using a vernier caliper aims to obtain a filament with the desired size, namely 1.75 mm. Testing was carried out at the UM Mechanical Engineering Nanoresearch Lab by calculating the tolerance for roundness deviation in the filament.

3 Results and Discussion

3.1 Filament Product

The results of PLA nanocomposite extrusion are depicted in Figure 1. The controlled PLA filament was pellucid and had fairly smooth filament surface. Meanwhile, nano graphite in the dissolved PLA in chloroform made them have a dark color and the filament was more brittle.

Fig. 1. Extrusion product: filament of nanocomposite PLA-nanographite.

Nano graphite in PLA filament causes a rough filament surface compared to controlled PLA. This is because, in PLA nano graphite filaments, there is clumping of nanographite, which is not evenly distributed (agglomeration). Nanographite clumping occurs due to the imperfect mixing of the materials with each other and also due to a lack of melting during the extrusion process.

3.2 Morphology of Filament Surface

The surface morphology of the printed filaments observed using SEM is shown in Figure 2. The presence of nano graphite nanoparticles can be seen in Figures 2.b - d. The wavy structure indicates that the extrusion occurs with unstable feed and pressure [10]. Nano graphite particles mixed with polyacid (PLA) form a conductive network. When the nano graphite strengthening increases to the leaching limit, agglomeration occurs, and some graphite layers are large enough to detach from the matrix [11]. Similar to other research results, the addition of nanographite makes the surface structure of the filament rougher due to the clumping of nanographite (agglomeration), which is distributed unevenly so that the filament has a rough texture when viewed with a microscope [12]. Agglomeration is caused by chemical-mechanical processes. Mechanical processing refers to the physical attachment mechanism in a fast single screw crimping process rather than filament pulling and high pressure exiting the nozzle. High rotation speeds increase kinetic energy so that frequent particle collisions occur, which cause the nanographite to interact with each other and form larger agglomerates [13]. In addition, nanographite composites consist of large and small particles. Small particles can be formed during the melt mixing process during extrusion, leading to the fragmentation of large particles [11].

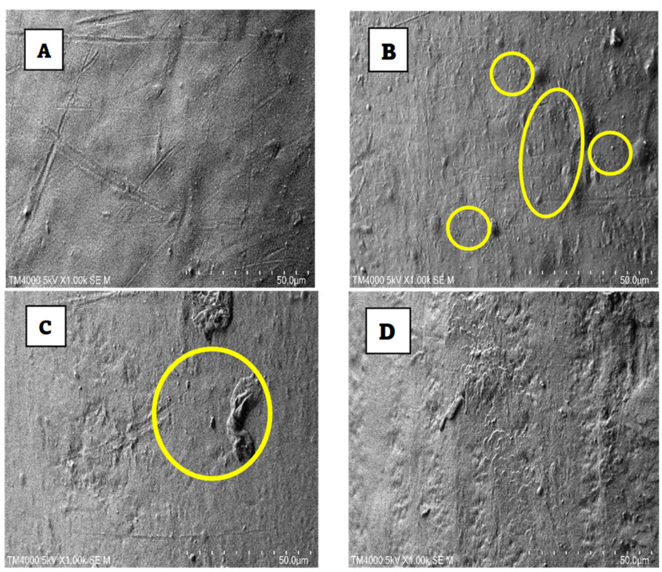

Fig. 2. Morphology of filament PLA (a) PLA control (b) PLA nanograhite 0.5 % (c) PLA nanographite 1% (d) PLA nanographite 1.5 %

3.3 Analysis of Filament Functional Group

The results of functional group analysis using FTIR (Fourier Transform Infrared Spectroscopy) are shown in Figure 3. The peak at 3683 cm^{-1} can be highlighted, indicating the presence of a hydroxyl group due to O-H stretching, while the peak at 2993 cm^{-1} indicates the presence of C-H stretching from a symmetrically shaped methyl group. at the peak at 2342 cm^{-1} indicates the presence of a slight stretch of the O=C=O [14]. The presence of C=O bonds of carbonyl and carboxyl groups as well as sharp C-H and C-O carboxyl bending modes, were identified by the presence of peaks at 1773 cm^{-1}, 1462 cm^{-1} and 1146 cm^{-1}, 1234 cm^{-1}, PLA functional groups [15].

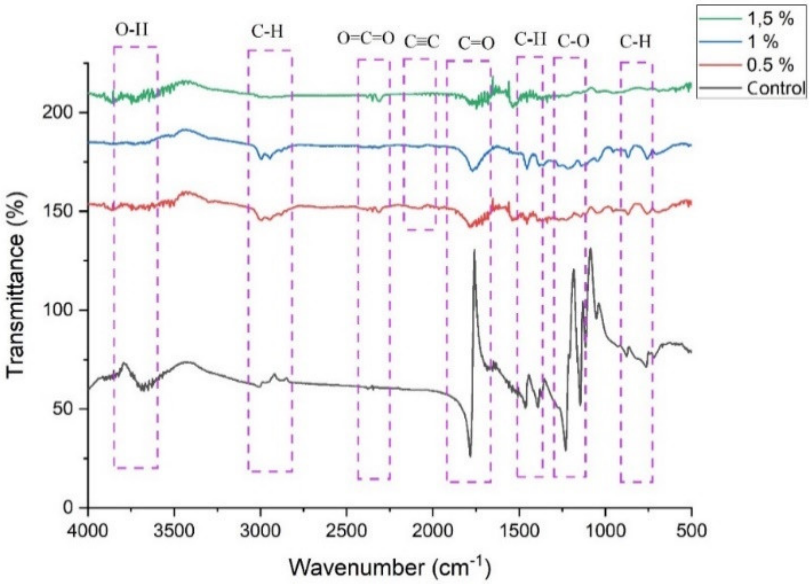

Fig. 3. The FTIR graph of PLA control filament and PLA composite

A decrease in the permeability of the sample filament caused an increase in graphite content in the sample with the tip added. When graphite is added, it can be seen that the C-H bond peak of stretching vibration is 3498 cm^{-1} to 3849 cm^{-1}. Then there is a new peak in the range 2080 cm^{-1} to 2089 cm^{-1}, identified as the C≡C bond [7]. The peak at 1773 cm^{-1} has a higher intensity in all samples, and the peak position changes to a higher frequency in the composite case. Moreover, the C=O stretching intensity decreases with increasing nanographite content, as shown in Figure 4. This phenomenon was similar to the Kaczor report, which is that the changes in intensity (reduction) of these peaks indicate the shortening of the polymer chains and, thus, their degradation [16]. The peaks at 1643 cm^{-1} and 1546 cm^{-1} correspond to the carboxyl and carbonyl groups [17]. This type of bond change and intensity change corresponds to the formation of physical bonds in the compound. Other peaks in the FTIR spectrum of PLA and nanographite composites remained almost unchanged [18].

3.4 Analysis of Filament Roundness

The results of measuring the roundness-diameter of the filament resulting from the extrusion process are shown in Figure 4. The results of measuring the roundness-diameter of the filaments that were made showed that there were differences in the average filaments. The best filament diameter is 1 nanometer for the sample with a difference of 0 mm, while the largest for the nanographite sample is 0.5 μ with a difference of 0.07 mm. So it can be said that the filament has a good round diameter, an average of 1.75−1.77 according to the round diameter tolerance [19]. The industry-wide filament diameter standard is ± 0.05 mm. The best result is the average diameter of the filament in question, which is closest to the target diameter of 1.75 mm at extruder temperature parameters of 175 °C, extruder speed of 2.6 rpm, and filament winding machine of 4.8 rpm. The extruder nozzle size is initially 1.75 mm. However, this diameter produces filaments that are less than 1.75 mm. This will change the nozzle diameter to a larger one, namely 3.00mm.

Roundness analysis using ImageJ software shows that the nanocomposite filament has roundness equivalent to the control filament. Still, with the addition of 0.5% nanographite, the filament has the best roundness, with roundness reaching 99.02% compared to the control filament (98.1%). Adding 1% and 1.5% nanographite resulted in a decrease in product roundness, namely 98.09% and 98.9%. The standard diameter for filament throughout the industry is ± 0.05 mm with a roundness presentation. Roundness, based on technical data sheets of various filament productions, it appears that ≥ 95% is an acceptable and measured value. The roundness test standard is a measurement standard used to assess the roundness or roundness of a component or object. It is often used in manufacturing processes to determine geometric errors and ensure component quality [20].

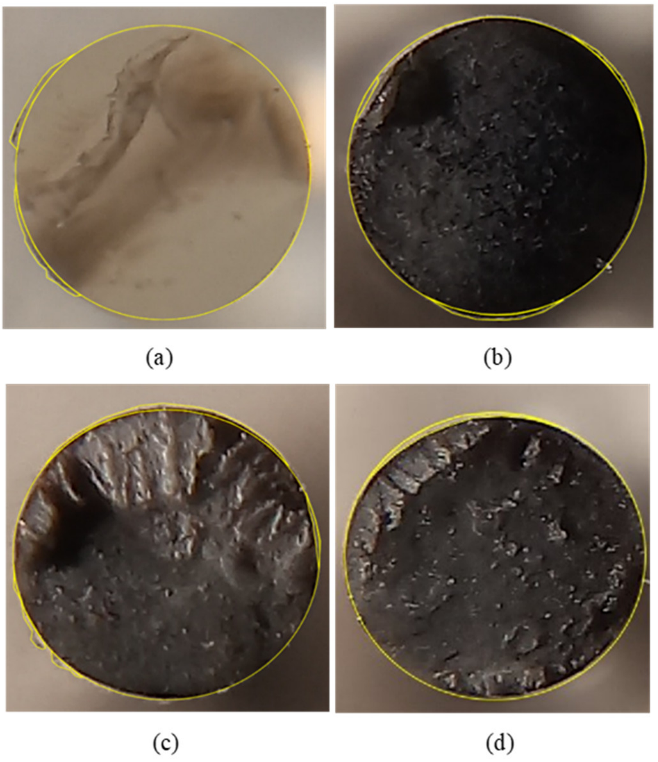

Fig. 4. Diameter measurement of (a) Control PLA filament (b) 0.5% PLA nanographite filament (c) PLA nanographite filament 1% (d) PLA nanographite filament 1.5%

4 Conclusion

The addition of nanographite makes the surface structure of the filament rougher due to the clumping of nanographite (agglomeration), which is distributed unevenly so that the filament has a rough texture when viewed with a microscope. The addition of nanographite affects the surface texture of the filament, which becomes rougher due to the clumping of nanographite, which is not distributed evenly, so it is a research limitation that if more nanographite is added more than 1.5% of the PLA mass, the texture of the filament will become rougher. The addition of nanographite, when tested by FTIR, showed a new peak in the 2000 range, indicating C≡C. This type of bond change and intensity change corresponds to the formation of chemical bonds in compounds. Other peaks in the FTIR spectrum of PLA and nanographite composites remained almost unchanged. The results of measurements of the roundness of the filament diameter that have been carried out show differences in the average filament; the best filament diameter is the 0.5% nanographite sample with a roundness value of 99.02%. For further research, it is necessary to learn about the method of mixing nanographite so that it is more soluble with polylactid acid, although nanographite is good for strength properties, but in the filament texture there is still agglomeration, so it is not perfect. As for the roundness test, it is better to use a more accurate test with ASTM standards so that a more precise roundness value is obtained. For FTIR testing of chemical compounds, nanographite added to PLA has shown an increase in physical strength so that it can be said that nanographite is successful as a reinforcement.

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