Analysis of Structure and Functional Group of Filament Product-Based PLA/Nanographite Nanocomposite

Heru Suryanto[1*], Aminnudin Aminnudin[2], Redyarsa Dharma Bintara[2], Abyan Farras Putra[2], Fikri Munif Nashrullah[2], Joseph Selvi Binoj[3], Nithin Panicker[4]

[1]*Center of Excellence for Cellulose Composite (CECCom), Department of Mechanical Engineering, Faculty of Engineering Universitas Negeri Malang, Jl. Semarang 5, Malang 65145, Indonesia.*
[2]*Department of Mechanical Engineering, Faculty of Engineering Universitas Negeri Malang, Jl. Semarang 5, Malang 65145, Indonesia.*
[3]*Institute of Mechanical Engineering, Sayeetha School of Engineering, Saveetha Institute of Medical and Technical Sciences (SIMATS), Tamilnadu, India, 602105.*
[4]*Oak Ridge National Laboratory, Oak Ridge, TN, USA, 37831.*
[*]Corresponding author: suryantoheru@yahoo.com

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ABSTRACT

In many polymer compounds, Polylactic Acid (PLA) is a polyalcohol material that has the most potential material which is potent for biological degradation. They have been applied as filaments in additive manufacturing. The PLA properties can be modified by adding nanomaterials such as graphite nanoplatelets. This study aims to obtain the characteristics of PLA-based filament nanocomposite with nanographite reinforcement. Methods include exploration research to obtain nanocomposite filament with PLA and 1% of nanographite. The mixing process of nanographite in PLA solution with chloroform solvent and then the extrusion process of nanocomposite using a single extruder. The product comparison before and after the extrusion process was analyzed using X-ray diffraction and Fourier Transform infrared. Diffractogram results indicate that the original PLA structure is amorphous, and after mixing using nanographite, peaks of nanographite appeared clearly. After the extrusion process, some peaks at 16.7° and 19.1° disappeared, but only a peak 26.6° appeared in the diffractogram. Extrusion makes the structure change. Functional group analysis confirms that some reactions occurred so that many peaks were removed, and several new peaks were observed. It indicates that the extrusion process of PLA/nanographite results in different structures and functional groups that indicate a change in its properties.

Keywords: Extrusion, FTIR, nanocomposite, nanographite, PLA, XRD

I. Introduction

Plastic is a versatile material with advantages such as relatively high mechanical strength, low density, lightweight, easy processing, and low cost. Due to this, plastics have been used in many industrial fields and thus become a source of large amounts of waste. BPS in 2021 states that Indonesia's plastic waste reaches 66 million tons per year [1], becoming the second largest waste producer in the world and requiring serious handling, such as reprocessing it into products of economic value.

3D-Printing is an additive manufacturing technology that is developing with great potential in various fields. Compared to injection molding, 3D-Printing is predicted to grow from 18% in 2018 to 32% in 2026 [2], worth between USD7-23 billion to USD51.77 billion

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in 2026 with 200 million users [3]. Commonly used polymer 3D-Printing filament materials: ABS, PLA, and PP [4]. However, the price of these filaments is quite expensive, so it needs to be overcome by producing 3D-Printing filaments from plastic waste. However, the use of plastic waste causes the strength to decrease by 11% [5][6], the impact strength decreases by 20.2%[7] and the shear strength increases by 6.8%, frequent blockages in the nozzle, and the hardness decreases by 2.4%[8]. In addition, filaments from plastic waste tend to have rough and curved surfaces [9]. Therefore, the use of plastic waste to produce quality filaments needs to be done with the help of nanomaterials.

Efforts to improve the properties of recycled polymers are carried out by adding reinforcing nanomaterials in polymers such as synthetic/natural [10]-[11], graphite [12], graphene [13], and organoclay [14]. Titanium dioxide (TiO_2), as a reinforcement, has a spherical shape, surface chemical properties, and ceramics have been shown to improve the properties of various polymers [15],[16] such as mechanical properties, dimensional and surface stability compared to pure polymers [17]. Nanoclays are elaborating nanocomposites that are light in weight, low in cost, have high strength, abundant availability, high surface area, and reactivity [18]. Nanoclay has a platelet structure similar to graphite [19] known as a solid lubricant [20]. The platelet structure is known to function as a lubricant to improve the rheological properties of the polymer and reduce shear during the extrusion process. The addition of nanoclay to PLA is known to increase the modulus by 10–14% [21] and exhibit more properties at low loading levels [22]-[23]. Some researchers use graphite to strengthen the filament and make the filament conductive [24],[25] also improving its rheological properties, which are used for the production of better electrochemical devices [26]. The main problem in producing good nanocomposites is not only the nanographite exfoliation process but its coalescence and homogeneity, so in this study, we analyze the structure of a functional group of fabricated 3D-printing filaments from PLA with nanographite nanomaterials as reinforcement.

II. Material and Methods

1. Materials

The primary material in this study used Polylactide Acid (PLA) granules obtained through Doudeke (Guangdong, China). Chloroform ($CHCl_3$) was obtained through Sigma Aldrich (USA). Nanographite was obtained from CV. Surya Techno Chemlab (Malang, Indonesia).

2. Mixing PLA/Nanographite

1.5 g of nanographite was dissolved in 450 ml of chloroform using a magnetic stirrer for 15 minutes at a rotation speed of 500 rpm at ambient temperature. The solution was sonicated using an ultrasonic homogenizer for 30 minutes. 150 g of PLA was added to the solution and stirred using a magnetic stirrer at 300 rpm for 90 minutes. The PLA nanographite solution was allowed to stand for 24 hours to dissolve the PLA further. The PLA nanographite solution allowed to sit was stirred using a mixer for 15 minutes. The drying of PLA nanographite was done by pouring the solution into the mold and allowing it to stand for 48 hours at room temperature. The dried PLA nanographite was taken in a mold and cut using a cutting machine to obtain PLA pellets.

3. Extrusion Process

PLA pellets were processed using a single screw extruder (Wellzoom Extruder, China). The extrusion process was carried out at a temperature of 170 °C with a screw speed of 10 rpm. Filament pulling is carried out at a pulling speed of 4.4 rpm [27].

4. XRD Analysis

X-ray diffraction (XRD) analysis was conducted using PanAnalysical Expert pro-diffraction within a diffraction angle of 10-90°.

5. FTIR Analysis

FTIR analysis was performed to analyze the functional groups. The test sample was scanned with a wave range of 4000 cm^{-1} to 400 cm^{-1} at a resolution of 4 cm^{-1} [28]. The test sample was cut to 10mm x 10mm. The device used in this test is the Shimadzu IR Prestige-21, belonging to the Laboratory of Advanced Minerals and Materials, Universitas Negeri Malang (Indonesia).

III. Results and Discussions

The product filament of PLA is shown in Figure 1. The control PLA used as filament has a clear color and smooth surface roughness. Control PLA dissolved in chloroform and mixed with nanographite had a darker color, and the structure of the filament became harder. PLA-nanoraphite nanocomposite has a rougher surface roughness compared to PLA before being combined with nanographite.

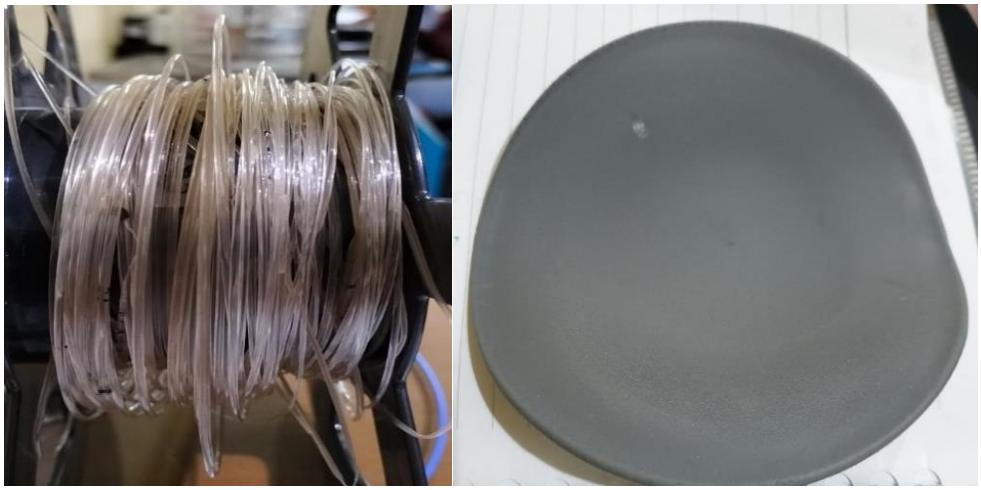

Fig. 1. Results of mixing of nanographite into PLA with chloroform solvent

A. Structure of Nanocomposite Filament

The results of XRD testing of control PLA, PLA with nanographite before extruder, and PLA with nanographite with extruder are shown in Figure 2. XRD data processing using Origin software. Based on the data processing, the crystal structure of the control PLA showed an amorphous structure [29]. Figure 2 shows the appearance of crystals formed in the PLA-nanographite before the extruder at 16.7°, 19.1°, and 26.6°. PLA-nanographite after extruder showed a loss of peaks at 16.7° and 19.1°, and decreased at the peak of 26.6°.

PLA with chloroform solvent showed diffraction peaks at 17° and 19° [30]. PLA with chloroform solvent made PLA-nanographite without extrusion have a crystalline structure because of the solvent nature of Chloroform, which interacts with the polymer chain, making the polymer-solvent interaction stronger and forming a crystal structure. Crystallinity in PLA is also affected by the boiling point of the solvent. Solvents with high boiling points require more time to evaporate, thereby facilitating crystal growth, while solvents with low bp limit crystallization time. Chloroform has a higher boiling point than methylene chloride and takes more time to evaporate, thus causing more crystallization at room temperature drying before the extruder.

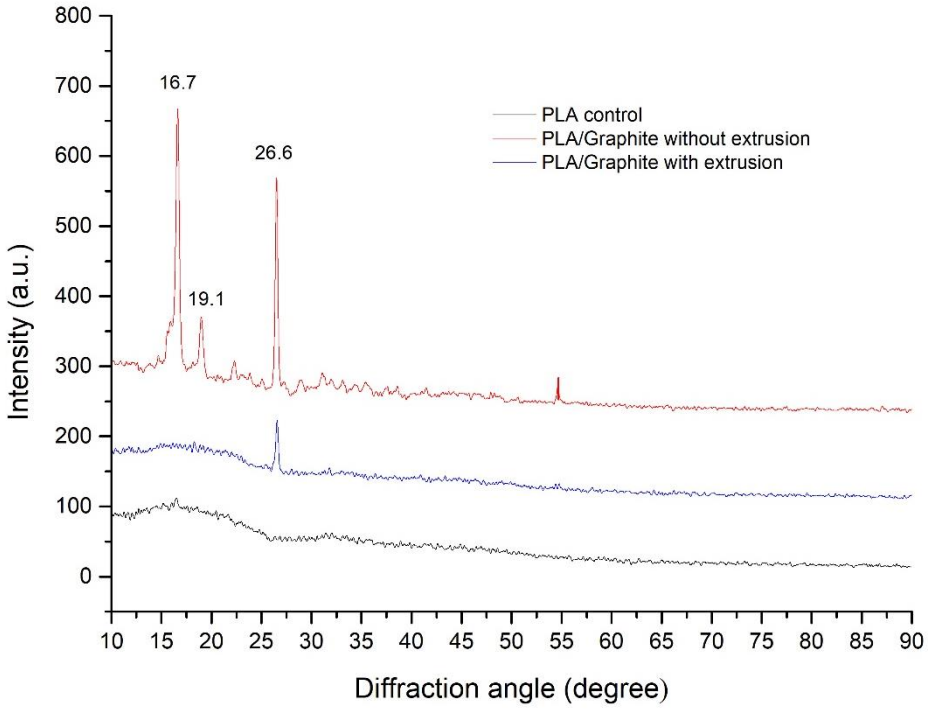

Fig. 2. Diffractogram of XRD in PLA control, PLA-nanographite without extrusion, and PLA-nanographite with extrusion

A decrease in peak intensity was caused by cooling the PLA-nanographite too quickly after the PLA-nanographite came out of the extruder nozzle so that the crystallinity structure had not yet had time to form [31]. Another cause of the loss of peaks and a decrease in crystallinity is the extrusion process being too fast so that the crystallinity of the PLA-nanographite after the extruder becomes amorphous. According to Liu et al. [30], producing higher crystallinity requires a long holding temperature.

B. Functional Group of Nanocomposite Filament

Processing of the Fourier Transform Infra Red (FTIR) test results to determine the content of PLA, chloroform, and nanographite. The FTIR analysis results are a spectrum with a wavelength to assess the PLA, chloroform, and nanographite content through the FTIR reference data. Since the drying process was only carried out under atmospheric conditions, an FTIR analysis was carried out to determine the presence or absence of chloroform residue. The FTIR spectra of PLA and microcomposite are presented in Figure 3.

Figure 2 indicates that the peak at 1780 cm^{-1}. Its wavenumber corresponds to the vibration of the C=O bond of the carbonyl group. The peak at 1415 cm^{-1} corresponds to the C–H strain of CH_3. Peaks of 1068 and 1369 cm^{-1} correspond to the C−O−C bond strain of the alkoxy, indicating the epoxy function of Graphene [32]. The most typical absorption of the C-O ester strain is 1187 cm^{-1}. The peaks at 1546 and 1643 cm^{-1} are related to the characteristic carbonyl and carboxyl functions. In addition, the addition of graphene to oxygen-containing groups increases the miscibility and dispersion of graphene in the matrix through hydrogen bonding/electrostatic interactions [33].

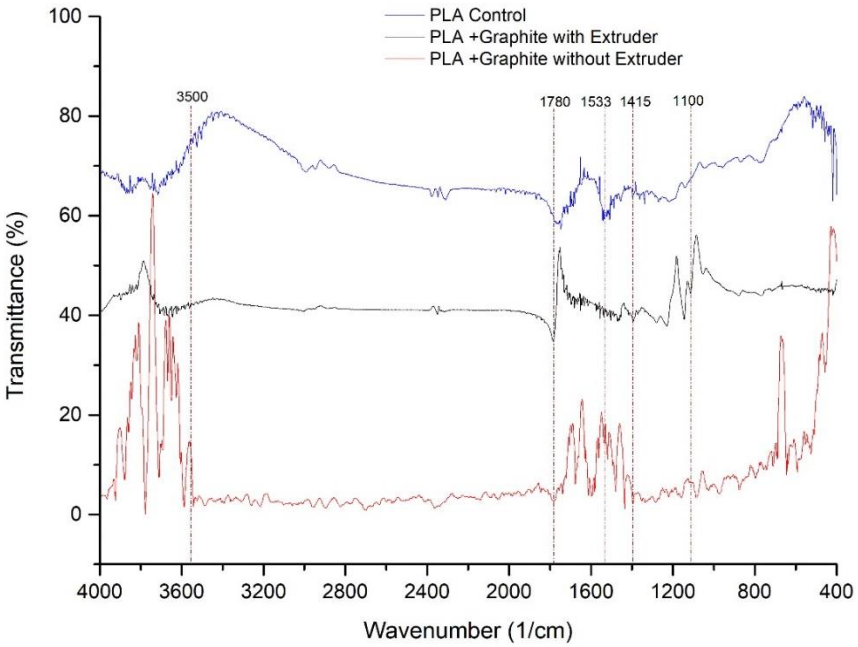

Fig. 3. FTIR of PLA control, PLA-nanographite without extrusion, and PLA-nanographite with extrusion

IV. Conclusions

PLA control has an amorphous crystalline structure. The addition of nanographite to the control plate caused the emergence of new peaks at 16.7°, 19.1°, and 26.6° caused by the drying method of PLA, which had been dissolved with chloroform as solvent and mixed with nanographite, which required slow and long drying time. Long cooling time will increase the crystallinity of the material. PLA-nanographite after extruder removed 2 peaks at 16.7°, and 19.1° and decreased peaks at 26.6°. The addition of nanographite into PLA raises some new functional group peaks. The addition of nanographite to oxygen-containing groups increases the miscibility and dispersion of nanographite in the matrix through hydrogen bonding/electrostatic interactions.

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