

## The Effect of Multi-Extrusion Process of Polylactic Acid on Tensile Strength and Fracture Morphology of Filament Product

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### ABSTRACT

Polylactic acid (PLA) is one of the most used materials in FDM 3D Printing. Large-scale consumption of PLA on an industrial scale could cause environmental and efficiency problems. Thus, PLA waste and industry waste need to be recycled to limit excessive waste. This study aimed to investigate the change in mechanical property, morphology, and structure of mechanically recycled PLA. Recycling was performed 12 times using the extrusion process with an extrusion temperature nozzle of 170°C. The SEM, structural analysis, and amorphous-crystalline analysis used XRD. The results showed a gradual decrease of tensile strength from each recycle with a total of 20% (13.22 MPa). The decrease percentage equalled the number of recycling. After the 9<sup>th</sup> recycle, PLA experienced a drastic tensile strength decrease, in which the 12<sup>th</sup> recycle tensile strength had a 14% (8.17 MPa) reduction. The morphology analysis of the tensile test sample presented significant morphology change, in which morphology defects such as void, flakes, and cracks appeared after the 6<sup>th</sup> recycle. Although, until 12 times extrusion, it did not significantly affect the PLA phase shape. Mechanical recycle using a multi-extrusion process is not recommended exceeding six times.

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**Keywords:** *Extrusion, microstructure, PLA, recycle, tensile strength.*

### I. Introduction

3D printing technology is an innovative and versatile additive manufacturing because it can print various materials such as thermoplastics, ceramics, and metals. This technology grows in various fields, including medical, pharmaceutical, automotive, and aerospace, with a growth rate of 18% in 2018 and predicted to increase to 32% in 2026 [1]. This situation improves manufacturing efficiency while also fulfilling custom products following customer order specifications [2]. The common polymer materials used in 3D printing manufacture are acrylonitrile butadiene styrene, polypropylene, polylactic acid (PLA), and polyethylene [2]. The quality of the filament is crucial so that the manufacturing process is not hampered and to get good manufactured product quality.

PLA is a biopolymer obtained from the lactide ring-opening polymerisation of sugar raw materials fermentation [3] and has the most potential to replace conventional petroleum-based plastics [4]. This polymer has good mechanical and thermal properties and does not harm the environment [5]. PLA can be easily processed using various conventional thermoplastic material processing, such as extrusion [6]. Extrusion is the process of forming a polymer or workpiece by pushing the material in a closed cavity using a screw or cylinder through a die to produce a particular shape [7].



Although PLA has many advantages over conventional plastics, large-scale consumption of PLA on an industrial scale will cause environmental and efficiency problems. [8]. Therefore, the finished biopolymer waste and industrial waste from the product manufacturers need to be recycled to limit excessive waste. Recycling is considered better from an environmental perspective than waste burning to avoid related environmental impacts such as global warming [9].

Biopolymer recycling is a challenge for researchers because the materials are heterogeneous [10]. Methods to recycle biopolymer materials can be classified into mechanical recycling, chemical recycling, and thermal processing [11]. Mechanical recycling is accomplished by melting and re-moulding the biopolymer using multiple extrusion and/or injection cycles. Of the several recycling methods that can be done, mechanical recycling is considered one of the best material recovery methods because it is easy to do, low cost, and has easier parameter control [12].

In recent years, several studies have been conducted to determine the recycling effect of PLA, focusing on changes in its mechanical properties. Anderson [13] used PLA, which was recycled five times and reused for 3D printing, showing a 10% reduction in tensile strain. Chaitanya [14] performed a PLA recycling test for up to eight extrusion cycles in a different study. The tensile strength of recycled PLA decreased by 11.64% after the first recycling and a 20.9% decrease in the second recycling. Additionally, repeated extrusion of PLA causes changes in rheological, thermal, and mechanical properties [14], [15]. Hence, it is essential to investigate the limitation of total PLA recycling cycles so that its waste can still be used in good quality, especially as 3D printing filaments.

PLA was relatively easy to recycle into filaments than other bioplastics for 3D printing. Recycle was intended to reduce the plastic waste volume that has the potential to cause environmental and efficiency problems. So, this study aimed to characterize the influence of multiple recycling of PLA using extrusion process on microstructure, mechanical performance, and structure.

## II. Material and Methods

### A. Material

The material in this research was PLA filament produced by Sunhokey technology, Guangdong, China. Blue PLA filaments were selected in diameter due to their good thermal performance and environmentally friendly nature [16]. PLA has 1.24 g/cm<sup>3</sup> density, 48.5 MPa tensile strength, 82.7 MPa bending strength, and 150–165°C melting point.

### B. Polylactic Acid Recycling

PLA recycling was conducted by the mechanical process using a double screw polymer extruder, XH-DSE-10 type (Dongguan Xihua, China), equipped with 40 L/D ratios and a 25 mm diameter screw. Before the extrusion process, the PLA filament was cut into 4 mm pellets using a pelletiser machine with a constant speed of 70 rpm. After the pelletising process, the pellets were extruded with a 60 rpm screw speed, a 55 rpm filament puller speed, and a temperature profile set to 175°C, 175°C, 175°C, 180°C, 170°C, 170°C (for the different zones from the hopper to the die-head, respectively) to obtain the samples from the extrusion. Before recycling, the samples were re-pelletised and dried for 2 hours at 35°C, below the glass transition temperature (T<sub>g</sub>), to reduce the water content as much as possible and avoid hydrolytic degradation [16]. The PLA material was then re-extruded under the

same conditions in the first processing step to obtain a recycled PLA sample. The recycling/repeated extrusion process was performed in 5 groups: the first/virgin polylactic acid (VPLA), third recycled polylactic acid (RPLA-3), sixth recycled polylactic acid (RPLA-6), ninth recycled polylactic acid (RPLA-9) and twelve recycled polylactic acid (RPLA-12). The filament product of each group was taken as the test specimens.

### C. Mechanical Properties

Tensile testing was done on reprocessed PLA using a tensile testing machine of type LY-1066A (Dongguan Liyi Environmental Technology, China) to investigate changes in macroscopic mechanical properties according to the ASTM D638 standard [17]. The specimen was a single-filament material with 1.75 ( $\pm 0.5$ ) mm diameter and 200 mm overall length, as shown in Figure 1. The tensile test in static stress was measured at 100 mm/min speed. The analysis was conducted using four samples in each test specimen with the average tensile strength, modulus of elasticity, and elongation as the representative values.

### D. Morphological Analysis

Morphological analysis of the PLA biopolymer tensile test sample was performed using a scanning electron microscope, FEI Inspect-S50 type (FEI, China). Samples from each specimen were prepared by cutting a randomly selected portion of the filament from the tensile test specimen. All specimens were coated in gold-palladium (Au-Pd) on 10 nm thickness before SEM observations to provide good conductivity. Micrographs were taken at 500x magnification, and the accelerating voltage was set at 20 kV.

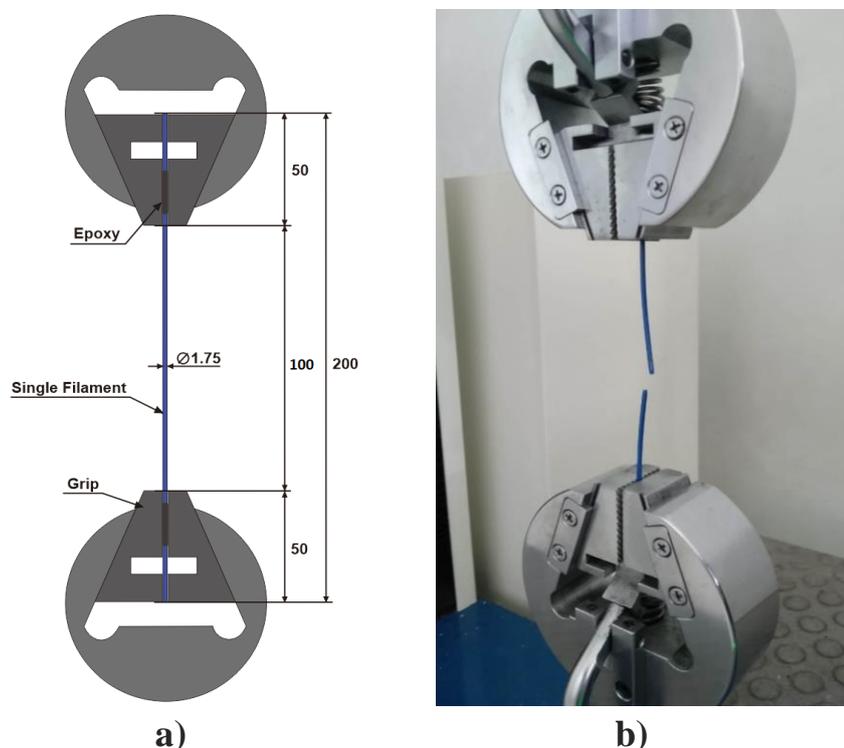


Fig. 1. Tensile test of filament. a) specimen sample and b) testing on tensile testing machine

### E. X-ray diffraction (XRD)

X-ray diffraction (XRD) instrument X'Pert Pro PANalytical Diffractometer (Panalytical, Almelo, The Netherlands) with  $\text{CuK}\alpha$  radiation ( $\lambda = 1.54$  ) was used to analyse the phase change of PLA biopolymer by comparing the virgin sample with recycled samples. Tests were performed on powders made from extruded samples. The diffraction intensity of  $\text{CuK}\alpha$  radiation was recorded between  $10^\circ$  to  $90^\circ$  ( $2\theta$  angle range) at 40 kV and 35 mA.

## III. Results and Discussions

### A. Mechanical Properties

The tensile stress-strain curves of the tensile test specimens extruded using the virgin PLA and 12<sup>th</sup> recycled PLA (RPLA-12) produced by the extrusion process are shown in Figure 2 to show the changes in the recycling process. The curves for the remaining samples (not shown here) fall between the curves drawn in this figure. The curve represents the decrease in tensile strength of PLA, which was recycled 12 times using the extrusion process.

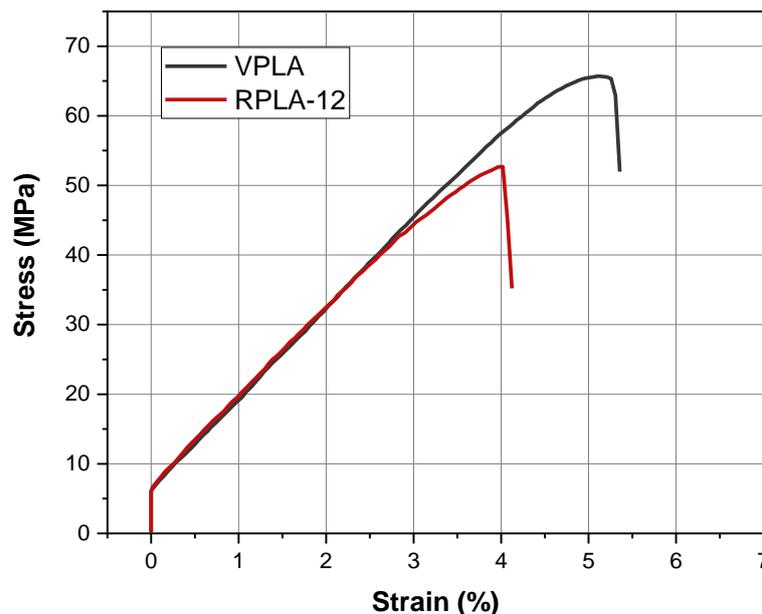


Fig. 2. Stress-strain curves of VPLA and RPLA-12

The PLA tensile test results with different recycling amounts are shown in Figure 3. The tensile strengths from VPLA to RPLA-12 are 65.35 MPa, 63.35 MPa, 62.15 MPa, 60.3 MPa, and 52.13 MPa. The tensile strength of PLA gradually decreased as the amount of recycling was increased by the extrusion process. The decrease in tensile strength in the whole recycling process was 13.22 MPa or 20%. The percentage decrease in tensile strength increased with the increase in recycling, in which the 3<sup>rd</sup> recycling (RPLA-3) decreased by 3% (2 MPa). After the twelfth recycling (RPLA-12), the PLA experienced a drastic reduction in tensile strength with a percentage of 14% (8.17 MPa). RPLA-12 showed a significant decrease in tensile strength and elastic modulus. The decrease in PLA filament tensile strength was caused by the recycling cycle and control parameters such as screw

speed, barrel temperatures, pelletising speed, and other parameters such as water cooler temperature, heating process duration, humidity, etc.

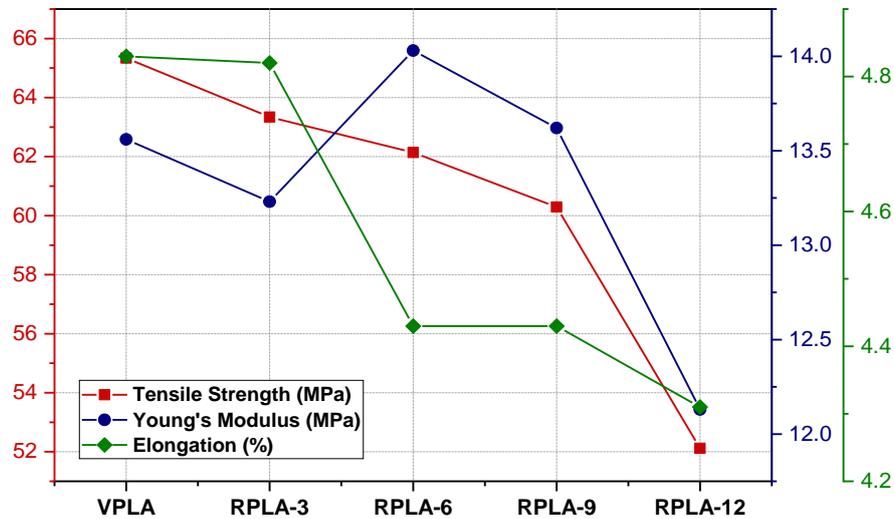


Fig. 3. Mechanical properties of virgin and recycled PLA

Several studies about mechanical recycling on other polymers investigate their mechanical properties, as shown in Table 1. In general, the mechanical recycling of bio-based polymers will cause biodegradation and a decrease in tensile strength.

**Table 1.** Mechanical properties of recycled polymers

Polymer	Tensile strength (MPa)		Young's modulus (MPa)		Source
	Virgin	3 <sup>rd</sup> recycle	Virgin	3 <sup>rd</sup> recycle	
PLA (polylactic acid)	65.3	63.3	13.5	13.2	
PLLA (poly L-lactic acid)	64.1	57.4	2600	2600	[18]
P3HB (poly 3-hydroxybutyrate)	32.1	13.4	-	-	[19]
Bio-PET (bio-polyethylene terephthalate)	23.7	29	1405	1783	[20]
HDPE (high-density polyethylene)	23.4	25.8	240	290	[21]

The main factor that causes a decrease in the tensile strength of PLA filaments is the thermo-mechanical degradation during the extrusion process. There is a heating process using a heating barrel until the material reaches its melting point in the filament extrusion process. Thermal degradation occurs during the extrusion process at high temperatures when the polymer changes from a solid to a liquid. The thermal degradation of biopolymers mechanism is chain scission and depolymerisation reactions (unzipping). It causes polymer chains to degrade to monomers, dimers, or oligomers [22]. Random degradation reactions involve hydrolysis with the water amount, oxidative degradation, cis-elimination, and inter- and intramolecular transesterification reactions [23]. At high temperatures (above the

melting point), PLA can be degraded through inter- and intramolecular ester exchange, cis-elimination, and radical and concerted non-radical reactions, resulting in the formation of CO, CO<sub>2</sub>, acetaldehyde and methyl ketene [24].

Besides material heating, the extrusion process also involves mechanical stress generated by the screw rotation to press the material through the die to produce the desired shape. Mechanical stresses such as shear forces, stresses, and compressions during the extrusion process resulted in polymer degradation [25]. Shear forces, stresses, and compressions can cause biopolymer mechanical degradation. Molecular damage is the phenomenon that occurs when mechanical stress occurs in polymer processing. Mechanical degradation reduces the molecular mass of the polymer. Although mechanical factors are not dominant during biodegradation, they can trigger or accelerate it.

Temperature, oxygen, humidity, mechanical stress, and light lead to thermo-mechanical biopolymer degradation, either individually or together [26]. Thermo-mechanical degradation involves oxidation, hydrolysis, and chain-cutting reactions that cause a decrease in molar mass and affect morphological properties in terms of amorphous-crystalline ratio, chirality, or steric rearrangement [27]. The temperature in PLA processing should not be too high to avoid thermal degradation through non-radical reactions that could cause a significant decrease in molar mass which has an essential effect on PLA performance.

In Figure 3, the value of the elastic modulus (Young modulus) fluctuates following previous studies with similar PLA values [28] [29]. Meanwhile, elongation shows a decrease due to recycling. Thus, the decrease in the PLA bioplastics tensile strength was caused by the lack of the material's ability to accept progressive deformation. In the first extrusion process, the PLA could maintain a maximum elongation before experienced 4.83% breaking. However, after twelve recycling processes, the material tolerated elongation of only 4.31%. The decrease in elasticity properties of the recycled PLA material caused the material's ability to absorb energy (tensile energy absorption) to drop drastically [18].

### *B. Morphology Observation*

The PLA biopolymer morphology results from the SEM testing with 500x magnifications are shown in Figure 4. The SEM testing was done on the fracture surface of the tensile test sample. Observations showed that the difference in the total PLA biopolymer recycling cycles exhibited different morphology and characteristics in the tensile test sample fracture. The identification in the virgin PLA sample (Figure 4a) shows a fracture surface that is much flatter and smoother than the recycled PLA. Fault topography in PLA that was not recycled does not show any morphological defects found in a previous study where PLA showed a similar morphology [12]. After the 3rd recycling (RPLA-3), the PLA does not show any significant morphological changes other than that the specimen surface looked rougher and drier than virgin PLA. The 6<sup>th</sup> recycled PLA/RPLA-6 micrograph (Figure 4c) shows a damaged surface characterised by the appearance of voids and scales. In addition, the surface appears rough and is more susceptible to mechanical scratches. This condition is attributed to the crystalline increase in PLA and the change in the glass transition temperature ( $T_g$ ) that causing air trap in the heating process. In Figure 4, visual observation presents that the specimens' surfaces are gradually getting more brittle as a result of successive recycling processes. The morphological defects on the recycled PLA surface increased significantly after the fourth recycling. RPLA-9 micrograph shows a hardened surface with cracks, scaly, and heterogeneous in which the melting particles made it inefficient compared to VPLA. Recycling causes hydrolysis and increases the melt flow rate

(MFR) [30]. This factor may have contributed to the surface imperfections in the recycled samples. Therefore, PLA biopolymers should not be recycled after the sixth recycling. Then, the RPLA-12 micrograph (Figure 4e) shows that the surface had the roughest pattern, indicating a brittle phenomenon with irregular morphology. It shows that PLA recycling causes hardened surfaces, holes and cracks, discolouration, and heterogeneity in which molten particles appeared and made it inefficient compared to VPLA [12].

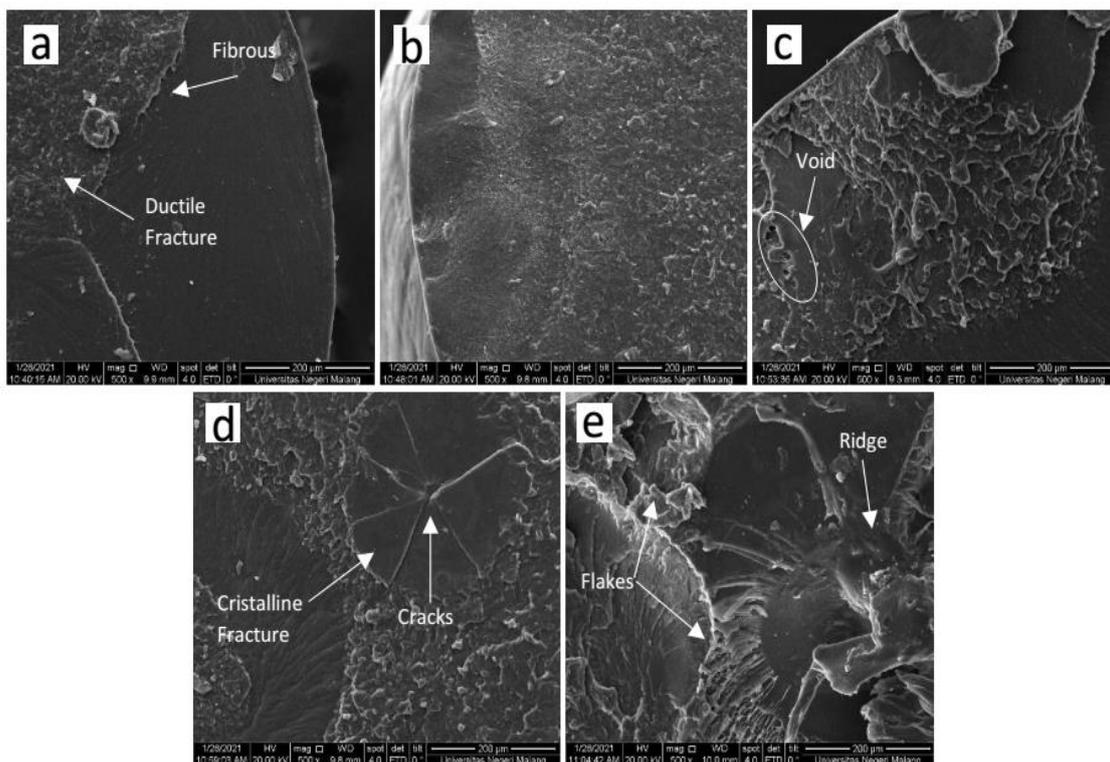


Fig. 4. SEM images of the tensile fracture of (a) VPLA, (b) RPLA-3, (c) RPLA-6, (d) RPLA-9, and (e) RPLA-12

Figure 4 observation exhibits that the fracture morphology has significant differences. The fracture morphology is getting worse following the increasing number of PLA polymer recycling processes characterised by morphological defects. This condition can be directly related to the degradation of the PLA matrix [30]. Morphological defects are possible because repeated recycling causes hydrolytic degradation, which reduces the molecular mass and causes the material's ability to absorb energy (tensile energy absorption) to drop dramatically, as evident by the decrease in the value of Young modulus [28], [31]. In addition, morphological defects may arise due to the structural alignment and new conformation of PLA. The chain cutting effect caused by thermo-mechanical degradation can be monitored by techniques such as differential scanning calorimetry (DSC) in terms of amorphous-to-crystalline ratio and thermal transition [32].

### C. X-Ray Diffraction Analysis

X-ray diffraction analysis was used to identify the crystal structure, including the PLA polymer phase state. Polymers may contain crystalline regions that randomly mix with amorphous regions. PLA has two possible phases: semi-crystalline and amorphous phases [33]. What distinguishes between polymers with semi-crystalline and amorphous phases is that semi-crystalline polymers exhibit relatively broad diffraction peaks and crystalline peaks. In contrast, amorphous polymers have broad X-ray diffractograms, which are difficult to determine by any crystalline model [34].

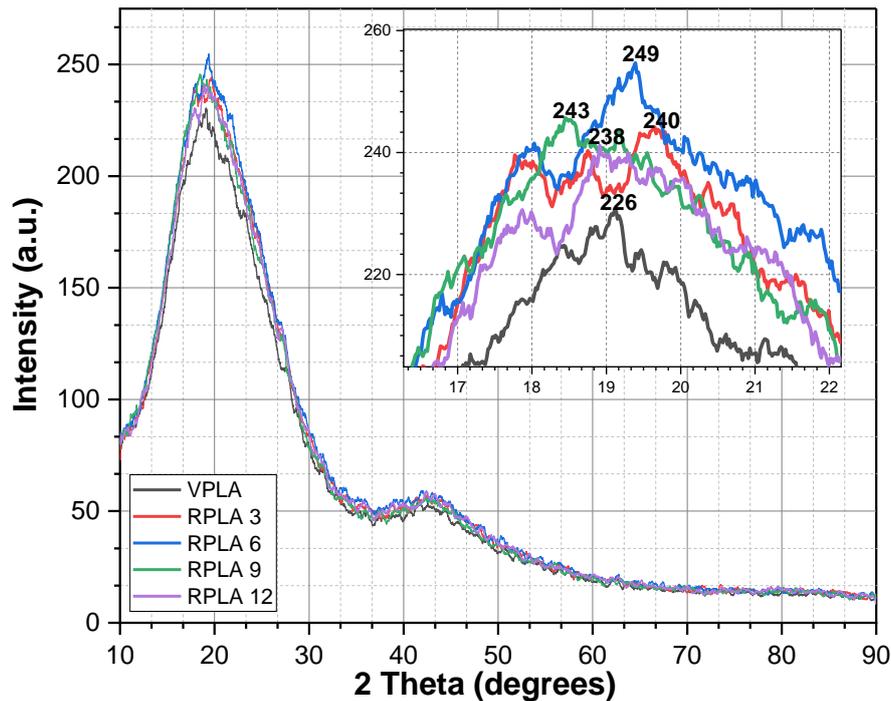


Fig. 5. Diffractogram of the virgin and recycled PLA

Figure 5 shows the diffractogram of PLA samples with recycling amount variations in the data range between  $10.01^{\circ}$ – $89.99^{\circ}$  with a scanning step of  $0.02^{\circ}$ . The results show several diffraction peaks with not many different intensities in the two ranges between  $13.07^{\circ}$  and  $28.75^{\circ}$ . PLA has a shape and exhibits a 10/3 helical conformation packed into an orthorhombic (or pseudo-orthorhombic) unit cell. To date, PLA is known to have four distinct crystalline forms:  $\alpha$ ,  $\beta$ ,  $\gamma$ , and  $\epsilon$  forms and two irregular modifications of the  $\alpha$  forms, namely  $\alpha'$  and  $\alpha''$  forms [35]. The intensity relationship curve for  $2\theta$  obtained a broad diffraction peak and did not have a defined and sharp peak from the test results. It indicated that the resulting PLA tended to be amorphous. Another study that used DSC found that the PLA remained dominant in having an amorphous phase regardless of the number of reprocessing cycles [36] [12].

### IV. Conclusions

This experimental study observed the performance of PLA, which was recycled 12 times using the extrusion process. The tensile test results showed a gradual decrease at each recycling, with a total of 20% (13.22 MPa). The percentage decrease in tensile strength increased with the increase in the number of recycling. After the ninth recycling, PLA experienced a drastic decrease in tensile strength, decreasing 14% (8.17 MPa). The fracture

morphology analysis that was observed using the SEM showed significant morphological changes. The fracture morphology was getting worse following the increasing number of recycling which was indicated by morphological defects in voids, flakes, and crystallisation. Thus, the amount of recycling did not have much effect on the PLA phase shape. Based on these findings, mechanical recycling using a multi-extrusion process exceeding six cycles is not recommended.

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