Degradation on mechanical properties of virgin and recycled polylactic acid ageing in aqueous environment

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Abstract. A growing demand in polylactic acid (PLA) has increased in recent years due to the increasing of non-degradable plastic wastes. The recycling of PLA waste is seen to be another permissible solution to conserve the resources. This work aims to study the degradation rate of virgin PLA (VPLA) and recycled PLA (RPLA) in terms of the mechanical properties after ageing in different aqueous environment. The samples were immersed in river water (RW) and seawater (SW) for the duration of 150 days. Tensile strength, transverse rupture strength (TRS), impact energy and hardness properties were investigated as a function of immersed time. The results revealed that the loss in the tensile strength accelerated in river water when compared to seawater. There was at least 50% of tensile strength sacrificed in recycled PLA. The TRS had dropped approximately half from its initial value after ageing in river water and about 30% after ageing in seawater. Besides, a huge decrease ranging around 70 - 80% from its initial impact energy was identified. However, the reduction in hardness was relatively low. The findings will help to elucidate the degradation process of PLA and the desired effect on the mechanical performance for further application.

Keywords: virgin polylactic acid, recycled polylactic acid, degradation, ageing, aqueous environment

1. Introduction
The issues towards the environment derived from petroleum-based plastic has brought serious attention around the world. It has been reported that 360 million tonnes of plastic were produced in 2018 and expected to grow to 2000 million tonnes by the year 2050 [1]. A large portion of these plastic will end-up as trash in the landfill and flow through the river and towards the ocean [2]. The demand for biodegradable plastic as single-used packaging material listed under Sustainability Development Goal (SDG) has sparked interests of many researchers to explore new alternative bioplastic material. Among those, polylactic acid (PLA) seen to be the most known renewable plastic with good biodegradability and biocompatibility.

PLA is a synthetic bio-based polyester derived from agriculture product. PLA exhibited excellent characteristics such as zero toxicity, appropriate compossibility, high mechanical strength and thermal stability and ease of fabrication [3]. However, it is said to be suffering on poor thermal stability, brittleness and high production cost, the ever-increasing diversion of starch feedstocks to PLA production is expected to pressure on land use on agriculture and waste management on worn part [4].
The degradation rate of PLA depends on the properties of the final products and disposal environment, but normally required 6 – 24 months to be fully degraded [5]. Recycling of PLA waste could probably help to support waste management challenges.

PLA with the presence of water is susceptible to hydrolytic degradation. Hydrolytic degradation of PLA primary will take place in two stages. At initial stage, random hydrolytic scission of ester bonds proceeds with the diffusion of water into amorphous regions which leads to the reduction of molecular weight. As the degradation continues, the crystallinity of the polymer increased. During second stage, hydrolytic attacks occurs from the edge towards the center of crystalline area with the degradation of the major portions of amorphous area [6]. The PLA degradation rate is strongly dependable on the particle size and shape, medium temperature, humidity and pH, moisture absorption, molecular weight of PLA, crystallinity and surface area [7].

Past studies that are related to hydrolytic degradation of PLA and other polyester polymer are reported as shown below. In a study done by Deroine et al. [8] have investigated the degradation mechanism and kinetics of PLA in distilled water and seawater. The researchers have remarked that the water uptake in each environment is according to Fickian behavior. However, the degradation rate in distilled water was higher when compared to seawater. In another work done by Iniguez-Franco et al., [9] have concluded that hydrolytic degradation of PLA in pure water and ethanol solution. The findings showed PLA experienced a faster hydrolytic degradation in 50% ethanol solution as compared in pure water. Higher percentage of crystallinity was also reported in similar samples. The alteration in molecular weight and crystallinity during hydrolytic degradation were significantly affected the mechanical properties of PLA.

Beltran et al. [10] have studied the effects of different mechanical recycling processes on the hydrolytic degradation of PLA immersed in phosphate buffered solution at the temperature of 37°C and 58°C. It is noted that the water absorption is higher on recycled PLA as compared to neat PLA. The rate of water absorption was also enhanced as the temperature of the solution increased. Consistent conclusions were drawn by Rapacz-Kmita et al. [11] which remarked on the accelerated hydrolytic degradation on PLA immersed in water at temperature 80°C. The hydrolytic degradation above T_g has increased the degree of crystallinity which consequently leads to an increase of rate in degradation of PLA. As the degradation rate increases, the mechanical properties will also reduce.

Sailema-Palate et al. [12] have investigated the degradation of poly(e-caprolactone) (PCL) in different extreme pH levels; pH 1 and pH 13. The results revealed that the water absorption in pH 1 is more dominant and increased hydrolytic rate which leads to intensive mass loss and porosity. Theoretically, as the amount of porosity increases, the mechanical properties will also deteriorate correspondingly. Similar finding was reported by Rajesh et al. [13] which observed a reduction of water absorption for PLA/Jute composite that has undergo alkaline treatment. As known, water absorption in biocomposites is considered as serious problem to be taken into consideration. The water absorption experience by the fibers inside the composite promote unusual swelling and dimensional instability that leads to the decreasing in mechanical strength due to degradation of interface of fibers and matrix.

In a study done by Rowe et al., [14] it was reported that the weight loss is inversely proportional to the initial solution pH which indicated that the degradation rate was lesser in alkaline environment as compared to acidic environment. However, a contradicting result have been debunked by Scaffaro et al. [15] which reported faster degradation kinetic on PLA/graphene nanoplatelets composite and PLA/lignocellulosic composite which are ageing in buffer solution with pH 10.

Although numerous studies on degradation of PLA had been published, very limited work on mechanical properties degradation of RPLA is being explored. With such versatile applications, huge usage of PLA has contributed to the high waste which mainly came from the worn parts. The recycling of PLA waste has been seen as a permissible solution to reduce the quantity of PLA waste in the landfills and those indiscriminately discarded into the environment. However, one of the most important conditioning factors when substituting a RPLA for a VPLA is whether the original characteristics of VPLA are still being preserved. This study aims to investigate the degradation in mechanical properties of VPLA and RPLA in aqueous environment; river water (RW) and seawater (SW). The degradation in
mechanical properties is evaluated by tensile stress, transverse rupture strength (TRS), impact energy and hardness. Both samples; VPLA and RPLA are immersed in river water and seawater for a total duration of 150 days. The fracture morphology was also observed using scanning electron microscope.

2. Methodology

2.1. Material
The VPLA pallets were purchased from a local supplier in an injection moulding grade. The pallets were in cylindrical shape, with an average length and diameter of 3 mm. The RPLA were retrieved from the injection moulding waste. The waste was mostly collected from runners and crushed using a grinding machine. The recycled grounded material was in an angular shape with the average size less than 4 mm.

2.2. Sample preparation
Samples for tensile test, transverse rupture test (TRS), impact test and hardness were manufactured using the reciprocation injection moulding machine. The injection process was done continuously for 150 cycles. 50 samples were randomly selected for each type of mechanical testing. The process was repeated to prepare for the recycled PLA samples.

2.3. Ageing condition
Sample ageing was performed by immersing the samples in river water (RW) and seawater (SW). The river water and seawater were collected from nearby location with a coordinate of latitude 5.4˚N and longitude 100.4˚ E. Both types of water were then poured in containers and placed in the laboratory. The temperature and pH of the baths are maintained and monitored weekly. The temperature and pH for river water are 27°C ± 0.5 and 6 respectively. Meanwhile, the temperature and pH for seawater are being kept at 27°C ± 0.5 and 7.5. The samples were aged continuously for 150 days.

2.4. Mechanical properties testing
The tensile strength was obtained using Universal Testing Machine based on ASTM D638 at room temperature. The gauge distance was 101.5 mm with a moving speed of 1 mm min⁻¹. A sampling rate was 20 pts s⁻¹ and full-scale load range of 50 kN.

The TRS that was obtained using Universal Testing Machine based on ASTM D790 at room temperature. The span was set at 60 mm with a crosshead moving speed of 1 mm min⁻¹. A sampling rate was 20 pts s⁻¹ and full-scale load range of 50 kN were recorded. The impact data was gained through Izod/Charpy Impact Tester according to the ASTM D256 set at room temperature. The hammer impact was fixed at 5.42 J. The mass of the pendulum is 0.906 kg.

The Rockwell hardness is determined using Rockwell Tester in R scale. The samples were placed on a steel anvil and brought into contact with indenting ball of a diameter size 12.7 mm. A maximum of 60 kgf is loaded onto the sample for 15 seconds. After 15 seconds, the load is then removed and the indented surface is measured.

2.5. Fracture morphology
The fracture morphology of the VPLA and RPLA before and after ageing in river water and seawater environment were observed using scanning electron microscopy (SEM) with a constant acceleration voltage of 15 kV.

3. Results and Discussion

3.1. Tensile strength
The results of tensile test on VPLA and RPLA before and after ageing in river water and seawater are presented in Figure 1. The results depict an obvious drop in tensile strength after 150 days immersed in river water and seawater. For VPLA, the tensile strength has dropped 43.7% in river water whereas in
seawater the tensile strength has dropped approximately 31.9%. On the other hand, for RPLA, it can be observed that the tensile strength had drastically dropped in both aqueous environments, which is 75.8% in river water and 49.5% in seawater. As known, in aqueous environment, hydrolysis degradation will take place. The hydrolytic degradation process of polyester is based on a hydrolytic cleavage of ester bonds attached on the backbone of the polymer chains. When the water molecules attack the ester bonds in the polymer chains, the average length of degraded chains becomes shorter [12]. Consequently, reducing the ability of the polymer to resist the applied load and force is also decreased. Thus, reducing the tensile strength.

In other note, the findings indicated that the degradation in tensile stress is more accelerated in river water rather than in seawater. This could be due the difference in pH for both environments. As reported by Rowe et al. [14], the degradation rate is lesser in alkaline environment as compared to acidic environment. Since the seawater is more towards alkaline, the ability of water absorption is lower and thus, reducing the hydrolytic degradation of PLA.

The results also revealed that the tensile strength decreased on RPLA is higher when compared to VPLA. This behaviour can be influenced due to the thermal degradation of the recycling PLA during injection of moulding processing which generates shorter polymer chains. These shorter chains have enhanced mobility, facilitating the relaxation and swelling processes and thus increases the water absorption [10].

![Figure 1. Comparison of tensile strength for VPLA and RPLA ageing in river water (RW) and seawater (SW).](image)

3.2. Transverse rupture strength (TRS)

Figure 2 demonstrated the comparison of TRS for VPLA and RPLA after being immersed in river water and seawater for a duration of 150 days. As shown, the TRS value had decreased in both aqueous environments. However, the reduction in TRS in river water was more accelerated. Similar findings were observed for VPLA and RPLA. After being exposed to river water, the TRS for VPLA and RPLA has dropped to 43.7% and 45.4% respectively. On the other hand, for the immersion in seawater, the TRS for VPLA and RPLA had dropped 31.9% and 31.3%. Similarly, the results showed higher degradation rate in river water when compared to seawater. The findings are in agreement with previous work done by Deroine et al. [8] which reported higher degradation rate of PLA in distilled water as compared to seawater. The presence of high mineral salt in seawater could hinder the water absorption, consequently delaying the degradation process. When comparison between VPLA and RPLA are made, it is noticeable that decreasing in TRS in both environments were almost similar. Although RPLA was believed to have undergo excessive molecular chain scission from reprocessing and hydrolytic
degradation which had led to the shorter molecular chain, but no significant differences were observed on TRS values.

Figure 2. Comparison of TRS for VPLA and RPLA ageing in river water (RW) and seawater (SW).

3.3. Impact energy
Figure 3 is a portrayal of comparison in the change in terms of impact energy for VPLA and RPLA after being immersed in river water and seawater for a total duration of 150 days. As illustrated in Figure 3, it can be obviously seen that the impact energy had reduced drastically. Meanwhile, in river water, the impact energy had reduced to 78.9% for VPLA and 86.7% for RPLA. Similarly, in seawater, the impact energy for VPLA and RPLA had reduced to 80% and 71.9% respectively. When PLA was in contact with water, the water absorption would lead to structural change including swelling and increases the mobility of the polymer chains. As the creation of free volume due to swelling allows more water molecules to diffuse in and get absorbed in the PLA matrix. This accelerated the hydrolysis rate and deterioration of the molecular chains [9]. Consequently, resulting in the stiffness of the material [16]. The outcome had revealed that no significant differences in impact energy reduction after ageing for 150 days in river water and seawater.

Figure 3. Comparison of Impact Energy for VPLA and RPLA ageing in river water (RW) and seawater (SW).
3.4. Hardness
The effect of ageing in aqueous environment on the hardness of VPLA and RPLA is revealed in Figure 4. As shown in the Figure, the mechanical properties degradation in term of hardness in both environment, river water and seawater were minimum for both VPLA and RPLA. After ageing in river water, the hardness drop was 7.5% for VPLA and 20% for RPLA. Meanwhile in seawater, the reduction in hardness properties for VPLA and RPLA were 7.6% and 12.8% respectively. The decreasing in hardness properties could be explain and correlated with tensile strength. The decreasing in tensile strength would reduce the ability of the polymer to withstand an applied load without failing and consequently reducing the ability to resist the deformation. However, the contradicting outcomes have been reported by Beltran et al. [10] which observed slight increment in hardness, approximately after ageing in aqueous solution with pH 7.4 at temperature 58°C. The researchers have reported the increment in of 5% for VPLA and 16.5% for RPLA.

![Figure 4. Comparison of hardness for VPLA and RPLA ageing in river water (RW) and seawater (SW).](image)

3.5. Fracture morphology
The fracture morphology of VPLA and RPLA before and after ageing in river water and seawater were shown in Figure 5. At initial stage, the fractured area was rough and homogenous which showed signs of brittle fractures (Fig. 5a and 5b). After 150 days of being immersed in seawater, no significant differences were observed on the SEM images as illustrated in Figure 5c and Figure 5b. No microscopic abnormalities such as cracks, voids and pores had appeared on the area. On other note, no physical change and/or mass loss were noticed through visual observation on the physical samples which proved that no surface erosion had taken place and the mechanical properties degradation were believed due to the bulk degradation [6].

In contrast, after ageing for 150 days in the river water, the image of fracture area had revealed changes in fracture texture. The gullies were starting to be detected. The existence of the gullies became more obvious on RPLA as shown in Figure 5f. However, no physical change and/or mass loss were seen. This observation is correlated with drastic dropped in tensile strength which exhibited 75.8% of decrease. As previously reported, these gullies will act as stress concentration and core of crack growth which finally will lead to relatively low retention ability in mechanical properties [17].
4. Conclusion
This paper had focused on the mechanical properties degradation of virgin and recycled PLA set in two different aqueous environment: river water and seawater. The samples were continuously immersed in the environment for a total duration of 150 days. Based on the results obtained, it can be concluded that the monitoring of tensile strength has showed in both samples, VPLA and RPLA exhibited decreasing pattern in tensile strength after being immersed in river water and seawater. The tensile strength degradation is higher in river water compared to seawater. It is also noted that the RPLA underwent higher tensile strength degradation as compared to VPLA in both degradation environment. The analysis in TRS has pointed to similar findings. The TRS degradation is more accelerated in river water than in seawater. The RPLA was noted to experience a higher TRS degradation when compared with VPLA after going through 150 days ageing in both environment. The decreasing of TRS in river water for VPLA and RPLA are 43.7% and 45.4% respectively. Whereas for seawater ageing, the TRS for VPLA and RPLA had decrease to 31.9% and 31.3% correspondingly. Also, the evolution of the impact energy showed that the impact energy decreased as the samples underwent ageing in river water and seawater environment. After a duration of 150 days of ageing in river water and seawater environment, the impact energy for VPLA and RPLA showed decay more than three third of the initial impact energy. The impact energy degradation for VPLA and RPLA ageing under river water were 78.9% and 86.7% respectively. Whereas in seawater, the impact energy had reduced 80% for VPLA and 71.9% for RPLA. The study towards the hardness degradation after a duration of 150 days ageing in river water and seawater showed...
slight decreases for both VPLA and RPLA. After a duration of 150 days ageing in seawater, no alteration on the surfaces and fracture morphology were observed on the samples for both virgin and recycled PLA. However, gullies were starting to be seen on RPLA samples which were ageing in river water.

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