

## Study of the Chemical Endurance of Particulate Reinforced Thermoplastic Composites

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### ABSTRACT

Poly(lactic acid) (PLA) is a biodegradable thermoplastic made from lactic acid monomers obtained through fermented glucose in crops like wheat and corn. PLA has numerous applications, including industrial packaging, biomedical equipment, and membranes, due to its low toxicity, biodegradability, and recycling potential. However, little is known about the short-term aging effects of particulate reinforced PLA composites in complex environments. This study investigates the chemical endurance of various PLA composites before and after exposure to different chemicals and hygrothermal conditions. The results reveal that the fabrication processing method greatly affects the degradation rate. The PLA/Carbon Fiber Powder (CFP) samples had the highest chemical resistance towards degradation in 1% HNO<sub>3</sub> followed by 2% NaOH with a maximum mass increase of 2.8% and 3.9% respectively. The PLA/CFP samples showed lowest chemical resistance under a combination of water and aging temperature, with an average maximum weight gain of 9.64% throughout the three CFP loadings. Continuous test for 15wt% CFP sample under subsequent liquid immersion and hot air exposure had an insignificant mass loss of 0.76% but a very brittle surface with severe micro and macro cracks were present on the sample surface. In conclusion, while PLA/CFP composites demonstrate notable chemical resistance under certain conditions, the short-term aging effects, particularly under hygrothermal conditions, reveal the significance of fabrication processing methods and the potential brittleness induced by continuous exposure to specific environments, emphasizing the need for a comprehensive understanding of material behaviors.

**Keywords:** Thermoplastic, Chemical endurance, Poly(lactic acid)

### 1. INTRODUCTION

Since the early 20th century, plastics have played a crucial role in modern civilization's development, with most products now containing synthetic plastics. Thermoplastic (TP) polymers have gained popularity in industries due to their cost-effectiveness and versatile properties, offering design flexibility through various processing methods like injection moulding and compression moulding.<sup>1</sup> These materials are ideal for crafting compact components such as gears, actuators, and buttons, meeting the demands of advancing technology.

Traditionally, metals were preferred for harsh environments due to their strength and high melting points, but they are expensive and cumbersome to process. Hence, the focus has shifted to developing thermoplastics with improved strength-to-weight ratios for similar challenging applications.<sup>2</sup> However, exposure to harsh conditions such as high temperature, high pressure, corrosive chemicals etc. can lead to aging effects in plastics, altering their chemical structure and mechanical properties, potentially causing failure.<sup>3</sup> These effects depend on material properties, aging time, temperature, and immersion solvent. To mitigate these issues, reinforcement fillers and additives such as carbon and glass fibres are used to enhance resistance to chemicals, temperature, and other factors.

Some researchers attempted to study the chemical degradation filler reinforced polymers. Hidemitsu Hojo et al. showed that glass fibre-reinforced polymer (GFRP) matrices are susceptible to oxidation and hydrolysis in liquid solutions due to ester bonds in the matrix resin.<sup>4</sup> P. Cousin et al. found that carbon fibres exhibit high resistance to chemicals, making them a promising filler for TP composites.<sup>5</sup> A. Boubakri et al. explored the effects of aging duration and temperature on the degradation of immersed TP polyurethane material, observing accelerated degradation at higher temperatures.<sup>6</sup>

With increasing interest in eco-friendly materials, there is a demand for PLA-based TP in applications exposed to chemicals. PLA-based TP are popular in various fields due to their biodegradability, low toxicity, absorption properties, and recyclability.<sup>7</sup> However, there is limited research on the short-term aging effects of particulate-reinforced PLA composites, particularly the specific mechanisms in relation to the characteristics of the reinforcing particles. The understanding of the short-term aging effects enable the development of materials with improved performance and durability in various practical applications. This experimental study aims to investigate the impact of different amounts of carbon fiber powder (CFP) particulate filler (5 wt%, 10 wt%, and 15 wt%) on the chemical endurance of PLA-based TP.

## 2. MATERIAL AND METHODS

The PLA-based TP composites were produced using the solvent casting method.<sup>8</sup> CFP with different mass ratios was incorporated into the PLA. The PLA/CFP composites were subjected to different characterisation tests such as immersion, hygrothermal, gravimetric measurement and scanning electron microscopy (SEM) to study their properties.

### 2.1. Materials

The crystalline PLA pellets were supplied by NatureWorks and dissolved using chloroform (CHCl<sub>3</sub>). Milled CFP was purchased from Easy Composites. Reagents for the immersion tests such as nitric acid (HNO<sub>3</sub>) and sodium hydroxide (NaOH) were used as received. The samples were prepared in the shape of disk with 20 mm in diameter and 2 mm in thickness. A customised mould was fabricated as shown in Figure 1 using aluminium sheets to produce multiple samples. The mould was fastened using six M8 bolts and nuts to provide even distributed clamping force.



**Figure 1.** Customised PLA test sample mould made of aluminium sheet.

### 2.2. Sample Preparation

PLA pellets were dried in oven at 50°C for 6 hours to ensure moisture removal. The dried pellets were then gradually added into the CHCl<sub>3</sub> solvent and mixed using a magnetic stirrer at 350 rpm, with an increasing rate of 50 rpm/min until reaches 1200 rpm over the period of 2 hours at 40°C until a homogenised PLA/CHCl<sub>3</sub> dope solution with 25 wt% of PLA was formed. The solution mixing process for samples incorporated with CFP were done via a solvent-assisted method as suggested by Iona Cosmoiu et al.<sup>9</sup> The filled PLA/CHCl<sub>3</sub> dope solution was transferred into the sample mould using a dropper. Finally, the casted samples were placed under a fume hood for 24 hours to undergo slow evaporation, followed by evaporation in an oven at 50°C for 6 hours. The steps were repeated to produce composite samples of PLA with CFP content of 5 wt%, 10 wt% and 15 wt% respectively.

### 2.3. Immersion and Hygrothermal Test

Immersion tests of the composite samples were performed in HNO<sub>3</sub>, NaOH and deionized water following ASTM standard D543. The immersion tests were measured at the duration of 5, 10 and 15 minutes to study the effect of short-term aging. An additional 'continuous' test was performed at the composite sample with 15 wt% CFP to

study the impact of exposing HNO<sub>3</sub>, NaOH, warm water, and hot air consecutively towards the composite. The sample was sequentially immersed in HNO<sub>3</sub>, NaOH, and water for 5 minutes each and taken out to be weighed. The samples were pat dried using tissue paper in between intervals before the next immersion. Then, the PLA/CFP samples were placed in an oven at 120°C for 5 minutes before being taken out to be weighed again. The weight average of the specimens was recorded and used to calculate the moisture absorption content,  $M_T$  using,

$$M_T(\%) = \frac{W_T - W_0}{W_0} \times 100 \quad (1)$$

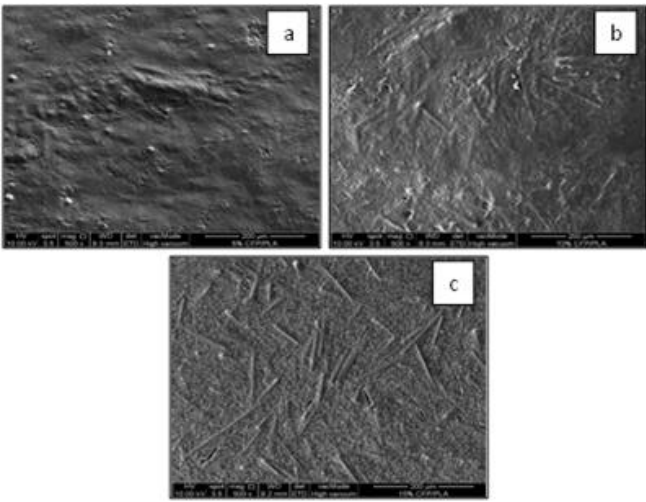
where,  $W_T$  is the sample weight at time,  $t$  and  $W_0$ , is the initial sample weight respectively.

### 2.4. Microscopy Study

Microscopy study of the samples were conducted using SEM with FEI-Quanta 400F scanning electron microscope. Prior to SEM analysis the samples were coated with platinum powder using Q150R S/ES sputter.

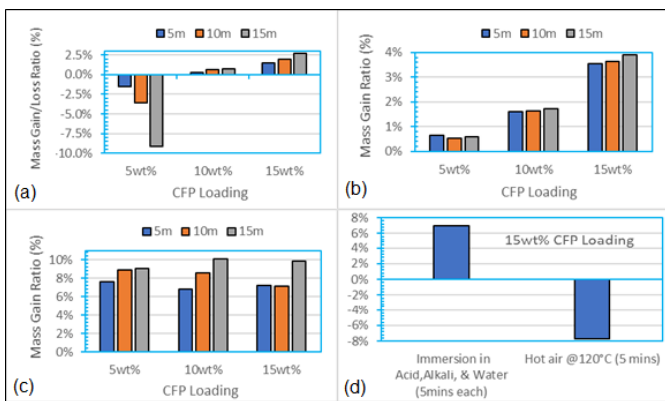
## 3. RESULTS AND DISCUSSION

SEM micrographs of the PLA composite were shown in Figure 2. As shown in Figure 2(a), PLA composite with the lowest CFP showed a relatively smooth surface. Conversely, a rough surface with visible carbon fibre (CF) outline and multiple micropores were observed for 10wt% CFP in Figure 2(b). Similarly, the 15wt% sample displayed a significant CF outline and numerous evenly distributed micropores as shown in Figure 2(c). It was presumed that the formation of micropores resulted from entrapped air and CHCl<sub>3</sub> microbubbles during the solution mixing. As the sample viscosity increases with filler loading, this had induced micropores for more viscous solutions due to the slower kinetics of air/solvent migrating to the surface during the evaporation process.<sup>10</sup> These voids and micropores may promote absorption of reagents/water during immersion test and potentially accelerate TP degradation.



**Figure 2.** SEM micrographs of the PLA composite with (a) 5 wt%, (b) 10 wt%, and (c) 15 wt% CFP before immersion.

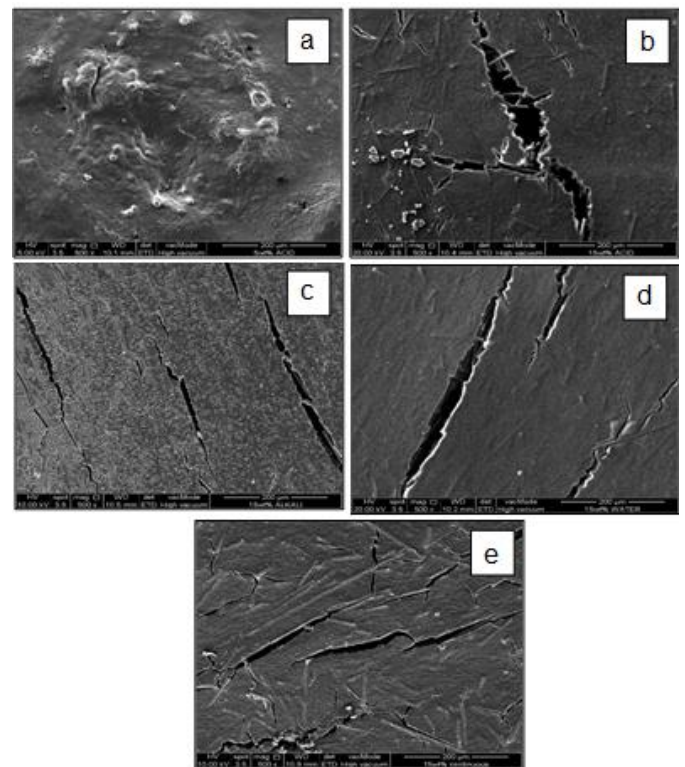
Immersion test results were shown in Figure 3 while selective SEM micrographs were shown in Figure 4. As seen from Figure 3, most of the PLA composites show mass gain, except for composite with 5 wt% CFP loading in HNO<sub>3</sub> and 15 wt% CFP loading when exposed to hot air. Two degradation mechanisms can be identified; heterogeneous and homogeneous degradation. As seen in Figure 4(a), the 5wt% CFP with higher composition of PLA TP underwent heterogeneous degradation and experienced surface erosion (i.e., mass loss). This is because hydrolytic degradation of PLA ester bonds is highly favoured under low pH-values like HNO<sub>3</sub>.<sup>11</sup> A homogenous degradation was observed for higher CFP loading. Due to the short-term immersion duration, only the initial stage of such degradation was observed, that is the absorption of liquid into the resin (i.e., mass gain). It is presumed that with higher CFP loading, the increasing micropores and voids between the matrix and filler will generate potential attack sites for aqueous solutions. As a result, development of macrocracks can be seen in Figure 4(b) where penetration of liquid occurs.



**Figure 3.** Mass gain in PLA/CFP samples under (a) 1% HNO<sub>3</sub>, (b) 2% NaOH, (c) deionized water, and (d) continuous exposure for 15 wt% PLA/CFP.

As for immersion in NaOH, the highest mass gain reported was 3.9% for 15wt% CFP under 15 minutes. It is presumed that, since the pKa of lactic acid is 3.84, solutions with pH>4 will have dissociated forms of lactic acid, therefore accelerating the rate of hydrolysis via random ester cleavage.<sup>12</sup> The hydrolytic effects of extreme pH alkali solutions are like that of highly acidic solutions. Thus, referring to Figure 4(c) several unidirectional macrocracks were observed due to homogeneous degradation, hence triggering more entry points for liquid sorption and the increasing mass gain with each CFP loading.

Highest mass gain was observed for immersion under deionized water at 70°C. It is believed that under longer durations beyond this saturation point, the second degradation stage will occur where the dissolution of resin into the liquid will result in weight loss increase. The combination of water and aging temperature had accelerated the degradation process for all CFP loadings. Consequently, water penetrates the composite sample and causes chain scission of the ester bonds.<sup>6</sup> These chain scissions will then create new and wider diffusion routes via cracks and voids as shown in Figure 4(d).



**Figure 4.** SEM micrographs of the PLA composite (a) 5 wt%-1% acid, (b) 15 wt%-1% acid, (c) 15wt%-2% alkali, (d) 15wt%-deionized water, and (e) 15wt% continuous after 15 minutes of immersion test.

The continuous immersion test had no significant difference in degradation effects for the mass gain/loss in 15 wt% CFP sample. There was only a 0.75% total weight loss throughout the entire continuous test. However, the SEM surface morphology in Figure 4(e) displayed visible CF outline with severe micro and macro cracks present on the sample surface. This indicates a very brittle surface with

severe degradation due to the subsequent liquid immersion and hot air exposure.<sup>13</sup>

#### 4. CONCLUSION

The investigation focused on how varying particulate filler amounts affect the chemical endurance of reinforced PLA thermoplastic, yielding several key findings. The degradation rate was impacted by the fabrication process, with more voids and micropores promoting increased absorption of reagents/water during immersion tests, accelerating TP composite degradation. All immersion tests resulted in visible macrocracks on the sample surface, except for the 5wt% CFP under 1% HNO<sub>3</sub>, which experienced surface erosion. Higher CFP loading reduced the chemical resistance of PLA/CFP samples in both HNO<sub>3</sub> and NaOH immersion tests. The samples exhibited the highest chemical resistance in 1% HNO<sub>3</sub>, followed by 2% NaOH. However, when subjected to water and aging temperature in combination, the samples showed the lowest chemical resistance. Continuous testing involving liquid immersion and hot air exposure led to a brittle surface with severe micro and macro cracks, accompanied by a negligible mass loss.

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