1. Introduction

One of the criteria that limit metallic implants in osteosynthesis is the problem of biodegradation. Adequate biodegradation rate has been identified as the solution to stress shielding or off-loading. Gradual healing of fractured bone requires a balance of load between the partially healed bone and partially biodegraded implant (Chandra & Pandey, 2020). Biodegradability is also in demand in areas such as drug delivery systems, degradable sutures, surgical void fillers, etc., (Lyu & Untereker, 2009).

Some biopolymers have been listed as being suitable in these areas, especially as scaffolds for bone fracture fixation (Aworinde, Adeosun, Oyawale, Akinlabi, & Emagbetere, 2018). Apart from biodegradability, a biopolymer that would be used as a bone implant is also expected to possess an apatite-forming ability (AFA) through which the implant would be able to bond to the living bone (Kazek-Kesik et al., 2020; Kokubo & Yamaguchi, 2016; Sadeghzade, Emadi, Tavangarian, & Doostmohammadi, 2020). The formation of an apatitic layer on an implant creates an osteocompatible surface (Wypych, 2018), which prevents the fixation’s instability over a long period (Kokubo et al., 2016). Although a study argues that AFA of a material may not be a predictor of bioactivity (Pan, Zhao, Darvell, & Lu, 2010), the formation of apatite has been established as a part of the implant-bone bonding process (Kazek-Kesik et al., 2020; Kokubo et al., 2016).

One of the most prominent biopolymers on the list of biodegradable polymers as fixations is the Polylactide (PLA). PLA is a biodegradable thermoplastic that has been copiously processed for biodegradable applications (Akpan et al., 2019; Aworinde, Adeosun, & Oyawale, 2020a; Aworinde, Adeosun, Oywale, Akinlabi, & Akinlabi, 2019; Aworinde, Kehinde, Emagbetere, Adeosun, & Akinlabi, 2021; Gbenebor et al., 2018a; 2018b; Wang, Wang, Ito, Zhang, & Chen, 2016). Its biodegradation products (CO₂ and H₂O) are entirely non-toxic, and its biore sorbability neither overburdens the body absorptive capacity nor creates foreign material in the body. However, its biodegradation profile is quite slow as a...
result of its degree of hydrophobicity (Aworinde, Adeosun, Oyawale, Akinlabi, & Akinlabi, 2020b; Salazar-Sánchez, Campo-Erazo, Samuel Villada-Castillo, & Fernando Solanilla-Duque, 2019). Attempts have been made to improve the hydrophobicity of PLA by ion implantation (Kurzina et al., 2020), melt blending (Aworinde et al., 2020b), gamma irradiation (Qi et al., 2019), copolymerisation (Hendrick & Frey, 2014) and so on.

The biodegradation of PLA is expected to be controlled whenever it is used as an implant for bone fracture healing. Biodegradation is neither supposed to be excessively accelerated nor unduly slow. Fractured bone, especially with operative management, typically requires patients to be non-weight bearing while healing is in progress (Jones & Waterson, 2020). The minimal weight that should be borne by bone during fracture healing is usually transferred to the implants. The load is gradually transferred back to the bone as healing begins to take place so as to avoid stress shielding or off-loading. The dynamics of load transfer imply that the implant is expected to lose its mechanical strength after a period of time. For this to happen, the implant loses mass (i.e., after it has swollen as a result of fluid intake) and then degrade. Biodegradation commences at the exterior of the bio-implant and progresses to its interior (Azevedo & Reis, 2004). These processes were studied in this work by immersing three melt-blended composites of PLA in phosphate buffer solution (PBS). Two composites had organic fillers, namely chitin and chitosan, while the third had an inorganic (titanium) powder additive. The effects of these fillers on the hydrophobicity of PLA had been reported in our previous work (Aworinde et al., 2020b), the biodegradation profiles of the composites developed using these fillers were compared in this study.

2. Materials and methods

2.1. Materials

PLA with a monomeric molecular weight of 144 g/mol, having an overall lactide purity of $\geq 99.5\%$ was used in this study as the matrix. Chitin (Ct) and chitosan (Ch) served as organic fillers and were separately used to reinforce PLA, while titanium (Ti) powder (Ti-6Al-2Sn-2Mo-2Cr-0.25Si) was the inorganic additive. The effects of these fillers on the hydrophobicity of PLA had been reported in our previous work (Aworinde et al., 2020b), the biodegradation profiles of the composites developed using these fillers were compared in this study.

2.2. Methods

2.2.1. Composites development

The matrix was melt-blended with each of the fillers at the weight percentages reported in our previous work (Aworinde et al., 2020c). Each of the molten composites was mould-pressed at the pouring temperature of $290^\circ C$ to form solid cylinders with 12.5 mm diameter and 7.0 mm length. The cylinders were weighed, and their masses recorded, as shown in Table 1.

2.2.2. Morphological examinations

A Tescan Vega 3LMH scanning electron microscope was used for the surface morphological examinations of the reinforcements and the developed composites. An accelerating voltage of 20 kV was applied to all the samples. However, the beam intensity of 12 W/m$^2$ was applied to titanium powder, while 17 W/m$^2$ beam intensity was applied to the rest of the samples. Apart from the titanium powder, all other samples were first carbon coated on copper grids with Agar Turbo Carbon Coater to enhance the quality of the images generated.

2.2.3. Fourier Transform Infrared Spectroscopy (FTIR) test on the solid composites

The solid composite samples were crushed to get powder-like samples suitable for the FTIR test. Each sample in its powder form was placed in the FTIR spectrometer and scanned. Acetone and tissue paper were used to clean the probe of the machine at the end of each test sample to avoid contamination. Spectra were recorded at 32 scans with a resolution of 2 cm$^{-1}$. The transmittance measurements were carried out in the range of 400 cm$^{-1}$ to 4000 cm$^{-1}$. MATLAB R2019a (9.6) was used to further analyse the spectra.

2.2.4. X-Ray diffraction test

XRD was carried out to determine the crystalline nature of the composites and measure the percentage crystallinity using Equation (1) (Tufekci, Brantley, Mitchell, Foreman, & Georgette, 1999). The XRD analysis of the composites was carried out using Rigaku Miniflex 600 powder diffractometer equipped with Cu K$\alpha$ radiation source generated at 18 kW and

| Filler (wt. %) | Initial mass (g) |
|---------------|-----------------|
|               | PLA/Ch | PLA/Ct | PLA/Ti |
| 0.00          | 1.2473 | 1.2473 | 1.2473 |
| 1.04          | 1.2094 | 1.3011 | 1.1973 |
| 2.08          | 1.0173 | 1.3290 | 1.1813 |
| 4.17          | 1.1857 | 1.1184 | 1.2092 |
| 8.33          | 1.3278 | 1.3618 | 1.1859 |
| 16.67         | 1.2272 | 1.4951 | 1.3791 |

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The XRD spectra were obtained at room temperature. High angle measurement was performed at a range of $2\theta = 10 - 90^\circ$ at a step rate of 0.40/min. The spectra obtained were processed using OriginLab 2019b (9.75).

\[
\%\text{Crystallinity} = \frac{A_c}{A_T} \times 100 \tag{1}
\]

$A_c$ is the area of crystalline peaks, while $A_T$ is the area of all peaks (that is, the area of crystalline peaks and amorphous peaks).

### 2.2.5. Biodegradation test

In a beaker (1 L), phosphate buffer solution (PBS) was prepared by mixing sodium phosphate dibasic heptahydrate (20.209 g) and sodium phosphate monobasic monohydrate (3.394 g) in distilled water (800 mL). Each of the solutes was allowed to dissolve before adding the other. A few drops of sodium hydroxide (NaOH) were added to adjust the final pH to 7.4 (that is, the pH of human blood). Distilled water was thereafter added until the volume was 1 L. Test tubes were each filled with 20 mL of PBS.

The test tubes containing PBS were put in the racks and kept in an oven with a preset temperature of 36.5°C. The test tubes were left in the oven for about 30 minutes to ensure the conditioning of the PBS to 36.5°C (Kokubo & Takadama, 2006). The weighed samples were then immersed in 20 mL of PBS. The test tubes were returned to the oven, and the temperature maintained at 36.5°C.

The biodegradation test was left on for ten (10) weeks. Changes in mass, which is considered as the progress of biodegradation (Azevedo et al., 2004), were measured after the first four (4) weeks and at the end of the tenth week. The percentage change in mass after weeks of immersion, $M_{\Delta}$, was calculated for every sample using Equation (1).

\[
M_{\Delta} = \frac{M_f - M_i}{M_i} \times 100\% \tag{2}
\]

where $M_{\Delta}$ = percentage change in mass, $M_i$ = initial mass before immersion, and $M_f$ = final mass after immersion

### 3. Results and discussion

#### 3.1. Micrographs of fillers from scanning electron microscopy

Figure 1 shows the micrographs of the fillers obtained from the scanning electron microscope test. Visual inspection reveals the flaky structure of Ch (Figure 1a), the sheet-like property of Ct (Figure 1b) and the hard sphere of Ti (Figure 1c). The micrographs of Ch and Ct are different from those obtained in some studies because morphological structures of crustacean shells-based derivations differ with species (Gbenebor, Adeosun, Lawal, & Jun, 2016) and type of chemical treatment (Gbenebor, Philips Akpan, & Adeosun, 2017). The flaky structure of Ch presents an increased surface area for reaction. The morphology of Ch is very close to the sheet-like structure of Ct. The structure of Ct also contributes to an increased rate of reaction, although not as much as it would be obtained in Ch. However, the spherical structure of Ti presents a reduced surface area leading to a much lower rate of reaction than the flaky Ch and the sheety Ct (Ollila, 1997). The difference in the fillers’ shapes is possibly one of the
reasons for the varying degree of the biodegradation of their respective composites.

3.2. Micrographs from scanning electron microscopy test of PLA and its composites
In Figure 2, the surface morphologies of PLA and its composites are presented. Similar surface morphology of PLA composites have been reported (Murariu et al., 2010). Since biodegradation usually starts from the external surface of the bio-implant and proceeds to its inner part (Azevedo & Reis, 2004), the cracks on the surfaces of unreinforced PLA (Figure 2(a)), PLA/Ch (Figure 2(b)) and PLA/Ct (Figure 2(c)) seemed to be a catalyst to biodegradation. These cracks were not conspicuous on the surface of PLA/Ti. These surface cracks made these composites more percolative, hence the possible gradual filtering of PBS through the surface cracks. Additionally, the rough surfaces of PLA, PLA/Ch and PLA/Ct have the potentials to support cell adhesion and possibly cell proliferation more than PLA/Ti.

3.3. FTIR spectra of PLA and its composites
Figure 3 shows the spectra of PLA and the three developed composites. As discussed in our previous work, apart from the peaks at 1450 and 1360 cm\(^{-1}\) other peaks were indicative of hydrophilic contents (Aworinde et al., 2020b). We had shown that PLA/Ch was the most hydrophilic sample. The study also showed that the unreinforced PLA was the least hydrophilic sample. The effect of hydrophilicity was pronounced in the AFA of the samples, hydrophilicity being one of the crucial factors for AFA (Liu et al., 2018). The least hydrophilic unreinforced PLA had the least ability to form apatite (Figure 6(a)).

3.4. Percentage crystallinity from XRD
The percentages of crystallinity of the developed composites were calculated from the XRD data analysed using OriginLab 2019b by Equation (1) and graphically presented in Figure 4 using MATLAB R2019a (9.6). The percentages of crystallinity of unreinforced PLA, PLA/Ch, PLA/Ch and PLA/Ti (Table 2) were 13.36%, 0%, 11.03% and 41.23%, respectively. The percentage of crystallinity of PLA obtained here must have been due to the application of heat (Vadas, Nagy, Csontos, Marosi, & Bocz, 2020) via the fabrication method employed in the development of the composite, considering the fact that no peaks were seen when the solvent volatilising method was used (Chu, Zhao, Li, Fan, & Qin, 2017). The addition of chitosan gave an approximately 100% amorphous composite, while chitin loading resulted in \(\approx 11.03\%\) crystalline composite (Figure 4 and Table 2). A trend similar to this was reported when PLA was loaded with 5% chitin (Nasrin et al., 2017). Besides, the reduction in crystallinity of PLA appears to be the norm whenever it is reinforced with biomaterials (Nizamuddin et al., 2019). However, reinforcing PLA with titanium gave the PLA composite with the highest percentage crystallinity (Table 2). The increase in the percentage of crystallinity seems to be the characteristic behaviour of PLA whenever it is loaded with inorganic filler (Chu et al., 2017).

The implication of the amorphous nature of the developed composites is the fast degradation profile since the denser structure of a crystalline material
could make it, to some extent, impervious to fluid attack (Pantani & Sorrentino, 2013; Tokiwa & Calabia, 2006). Hence, the most amorphous sample satisfactorily responded to fluid imbibition within the weeks of immersion. PLA/Ti, the most crystalline sample, presented a somewhat erratic swelling index.

3.5. Fluid imbibition properties of the composites

Table 3 shows the masses of the samples after 4 and 10 weeks of immersion of PLA and its composites in PBS due to fluid uptake. Figure 1 displays the percentage change in mass after 4 and 10 weeks of immersion in PBS. It details information on the fluid intake properties of the solids.

The biodegradation (in vitro) results of the immersion of all the composites produced in the phosphate buffer solution for ten (10) weeks are shown in Table 3. Figure 5 illustrates the quantitative measure of the mass gained as a result of fluid absorption (especially during the first four weeks) or lost in mass as seen after ten weeks of immersion. At the end of the first four (4) weeks, it was observed that all the composites responded to fluid uptake by a noticeable change in mass. They all absorb the fluid into which they were immersed, causing them to increase in mass. The organic reinforced composites were on the lead. This fluid absorption property (or hydrophilicity) is an essential initial stage in the biodegradation of any biopolymer and biopolymer composites (Adeosun, Aworinde, Diwe, & Olaleye, 2016; Azevedo et al., 2004; Huang, Xiong, Liu, Zhu, & Wang, 2013). Generally, fluid absorption is important where the application requires the material to be in contact with a fluid, such as in tissue engineering and drug delivery systems (Adeosun et al., 2016; Azevedo et al., 2004). The fluid absorption property,
as displayed by these composites, is an indication of the possibility of biodegradation of the composites.

In Figure 1, the percentage change in mass during biodegradation, using Equation 1, is presented. As noted earlier, both the unreinforced PLA and all reinforced PLA absorbed the PBS in which they were immersed. This fluid uptake is a sign of degradation (Azevedo et al., 2004).

During the first four weeks of immersion, the composites with organic fillers demonstrated a higher rate of fluid absorption than the titanium-reinforced PLA. This may be due to the nature of the fillers (Figure 1(a) and (b)) and the surface cracks (Figure 2(a)–(c)) on the organic reinforced samples. PLA/Ch showed a higher rate of fluid absorption than PLA/Ct. This can be attributed to the flakier structure of chitosan (Figure 1(a)) than chitin structure (Figure 1b). PLA/Ti also absorbed fluid to a reasonable extent. Its fluid absorption property must have been due to the onset of hydrolytic degradation (Azevedo et al., 2004).

The mass changes observed after ten (10) weeks of immersion showed that some of the composites exhibit excessive swelling propensity. Their masses after the tenth week of immersion exceeded their masses after the fourth week of immersion. PLA/Ct (16.67 wt. %), for instance, may not be proper as an implant because of the excessive increase in mass. Disproportionate change in mass can lead to bulkiness, thereby causing postoperative palpability (Leonhardt et al., 2008) and create an absorption capacity problem for the patient.

Similarly, all the PLA/Ti composites continued to increase in mass after four weeks. They all show the tendency to create the same problem that was observed in PLA/Ct at 16.67 wt. % of the filler, namely: bulkiness and postoperative palpability. Another problem envisaged with PLA/Ti is the possible health issue that can be raised by particulate titanium either close to the implant site or in some organs away from the implants (Frisken, Dandie, Lugowski,
& Jordan, 2002) as the composites degrade. Titanium particles are not expected to biodegrade; these particles will eventually accumulate in the body and possibly affect the body organs.

All PLA/Ch composites and all PLA/Ct composites except PLA/Ct at 16.67 wt% appear to give satisfactory results in terms of biodegradation. Variation in mass has been a valid sign of biodegradation (Rudnik, 2013). The mass variation pattern of all PLA/Ti and PLA/Ct at 16.67 wt%, however, is worrisome. There was a proportionate change in the percentage in mass of other composites, especially after the first four weeks, which was not the case with all PLA/Ti and PLA/Ct at 16.67 wt %.

### 3.6. Formation of apatitic layer on the surface of the composites

Figure 2 presents the physical changes observed when the solids were immersed in PBS. It was observed that at the end of the fourth week, a thin film of white deposits confirming the formation of apatite (Jose & Alagar, 2015; Ramadas, El Mabrouk, & Ballamurugan, 2020; Swe, Shariff, Noor, Ishikawa, & Mohamad, 2019) was seen. These white deposits continued to grow until it completely covered the entire surfaces of the reinforced composites (Figure 2b). The neat PLA did not show much of apatite formation as recorded in reinforced PLA. The white deposits could be scarcely seen on the unreinforced PLA, as seen in Figure 2a. Studies have established that a material that forms apatite on its surface has the tendency to bond to living bone through the layer of the apatite formed on its surface in the living body (Kokubo et al., 2006). This implies that the fillers used in this work aided the formation of an apatic layer on the composites. By inference, the reinforced composites possessed AFA needed to facilitate the bonding of an implant with the living bone.

### 4. Conclusion

This study focused on the two critical factors that dictate the quality of an ideal scaffold. These factors (i.e., biodegradability and apatite formation) have been identified as strong indications of a good implant. Findings from this study showed that unreinforced PLA does not combine these two important factors. Although the biodegradation of PLA was not outrageous, the formation of apatitic layer on its surface was unduly scanty. The fillers used influenced biodegradation and apatite formation in varying degrees. Organic reinforced PLA samples (i.e., PLA/Ch and PLA/Ct), for instance, increased the rate of biodegradation and apatite formation while the inorganic reinforced PLA samples (i.e., PLA/Ti) enhanced apatite formation but put biodegradation at risk as a result of their erratic hydrolytic behaviours.

This study equally identified hydrophilicity as an essential factor in the formation of apatitic layer on the surface of a scaffold. Therefore, the reinforced PLA that showed reduction in hydrophobicity also showed the formation of apatite more than the unreinforced PLA. In the same vein, biodegradation was linked to the degree of crystallinity of an implant. Hence, the more amorphous samples showed a more promising biodegradation profile. Findings showed that organic reinforced PLA would make better scaffolds in term of biodegradability than the PLA composites produced using inorganic filler. Besides biodegradation, postoperative palpability seemed inevitable with the use of PLA/Ti composites due to their pattern of swelling within the duration of in vitro study. AFA of a material is, therefore, not sufficient to qualify a biodegradable polymer as an ideal scaffold.

### Disclosure statement

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