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Comparative effects of organic and inorganic bio-fillers on the hydrophobicity of polylactic acid

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ABSTRACT

The use of Polylactic acid (PLA) has been limited in the biomedical field because of its slow degradation profile which is traceable to its degree of hydrophobicity. In this work, 16.67 wt. % of chitosan (Ch), chitin (Ct) and titanium (Ti-6Al-2Sn-2Mo-2Cr-0.25Si) (Ti) powders weremelt blended with PLA and the resulting composites examined using Fourier Transform Infrared Spectroscopy (FTIR). Chitosan was found to reduce the hydrophobic peak due to $\delta_s(CH_3)$ in PLA by 13.92%, chitin by 10.65% and titanium by 8.04%. Summarily, the organic bio-fillers produced more hydrophilic PLA composites than the inorganic filler. The percentage reduction in hydrophobicity renders the developed composites more suitable for orthopaedic applications.

1. Introduction

Polylactic acid (PLA) is a thermoplastic polymer belonging to the α-hydroxy acid family [1–3]. It has become a choice material due to its amazing characteristics. However, its high level of hydrophobicity has rendered it clinically unsuitable for use in the biomedical field [4] because of the difficulty in the formation of apatite (a bone-bonding material) [5] and slow degradation profile [14]. The degree of hydrophobicity found in PLA has been traced to the presence of large methyl groups, CH_3, which are non-polar, covalent groups [2,6]. Attempts have been made by researchers to develop a more biodegradable PLA composites [7–10] but none has stated in a quantitative term the percentage reduction in its hydrophobic contents. To successfully influence the behavioural characteristics of a hydrophobic polymer via composite production with a hydrophilic filler, critical factors such as volume fraction, filler pre-treatment, compositing method, etc. are remarkable [11]. This work studied and stated quantitatively the effect of organic fillers (chitosan and chitin) and inorganic additive (titanium powders) on the reduction rate of CH_3, the essential radical that is responsible for hydrophobicity in PLA.

2. Materials and method

Polylactic acid (PLA) pellets with a molecular weight of 144 g/mol were purchased from Natureworks, China. 16.67 wt. % of chitosan, chitin and titanium (Ti-6Al-2Sn-2Mo-2Cr-0.25Si) powders were each melt-blended, in turn, with PLA at 290 °C and mould-pressed to form solid cylinders (Ø = 12.5 mm, l = 7 mm). The solids were crushed into powder-like and subjected to Fourier Transform Infrared Spectroscopy examinations. Spectra were recorded at 32 scans with a resolution of 2 cm^{-1}. The transmittance measurements were carried out in the range 400–4000 cm^{-1}. MATLAB R2019a was used to filter the noisy regions and superimpose the spectra for comparison.

3. Results and discussion

Fig. 1 shows the Fourier Transform Infrared Spectroscopy (FTIR) results while Table 1 lists the characteristic infrared bands found in PLA and its composites. The examinations of the peaks showed that there were neither removal of peaks nor formation of new peaks. This is similar to the observations of other researchers [12,13]. This implies that the compositing method employed achieved more of a physical mixture process between the matrix and the fillers used than a chemical reaction. It also shows that the three bio-fillers did not significantly affect the molecular structure of PLA. The sharp peaks at 1748 and 1183 cm^{-1} are indicative of the carbonyl group. A carbonyl group is essentially a functional group composed of a carbon atom double-bonded to an oxygen atom. It is a group with strong electron-withdrawing tendency with

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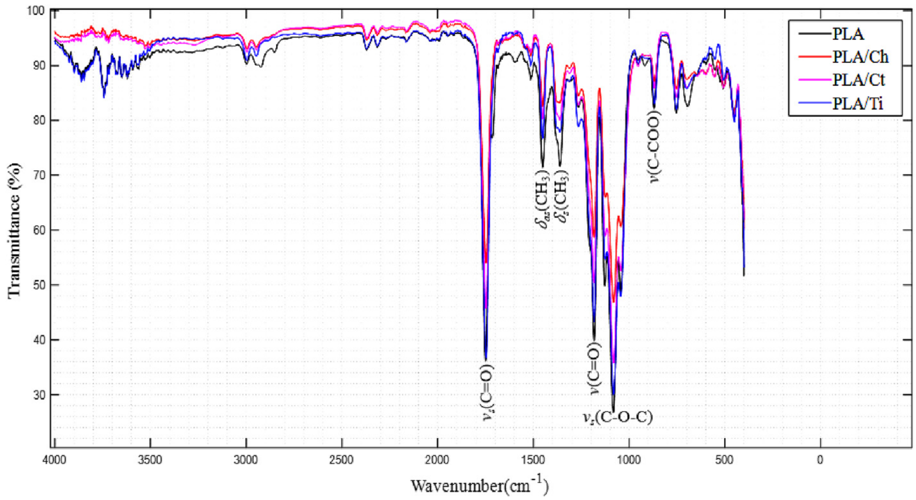

Fig. 1. FTIR of PLA and its Composites.

Table 1
Characteristic infrared bands of polylactic acid.

Functional Group	Wavenumber (cm^{-1})	Vibrational Mode	Abbreviation	Remarks
Carbonyl	1748	Symmetrical Stretching	ν_s(C=O)	Hydrophilic
Methyl	1452	Asymmetrical Scissoring	$\delta_{as}(CH_3)$	Hydrophobic
Methyl	1360	Scissoring	$\delta_s(CH_3)$	Hydrophobic
Carbonyl	1183	Stretching	ν(C=O)	Hydrophilic
Ether	1083	Symmetrical Stretching	ν_s(C-O-C)	Hydrophilic
Carboxyl	869	Stretching	ν(C-COO)	Hydrophilic

oxygen having a greater electronegativity (strong affinity for electron) than carbon. This makes it mix with water by bonding with the partially positive hydrogen. Succinctly, the peaks at 1748 and 1183 cm^{-1} indicate hydrophilic groups. Other peaks are similar in their hydrophilic properties (as shown in Table 1) except the peaks at 1452 cm^{-1} and 1360 cm^{-1}, which are largely hydrophobic because of their non-polar nature. These peaks were also identified in the work of other researchers [6].

Fig. 2 expands on the two hydrophobic peaks. It was discovered that PLA and its composites transmitted infrared rays at varying degrees at these two peaks as observed by other researchers [12]. The unreinforced PLA transmitted 71.40% and 71.46% at 1452 cm^{-1} and 1360 cm^{-1} respectively (Table 2). The transmittance value of the neat PLA at 1452 cm^{-1} compared to the developed composites implies 6.88, 11.04 and 13.54% reduction in $\delta_{as}(CH_3)$ due to the addition of Ti, Ct and Ch respectively. From Table 2, it is also deducible that $\delta_s(CH_3)$ reduced by 8.04, 10.65 and 13.92%. These findings are at variance with what was discovered when PLA was composited with sisal [12] possibly because the fibre was not pre-treated [11], which further corroborates the fact that the fillers used in this work have hydrophilic contents. The organic fillers (Ch and Ct) produced greater reductions in the methyl group in PLA than inorganic filler (Ti). This is due to the hydrophilic nature of chitosan and chitin. Chitosan reduced the hydrophobicity of PLA more than chitin because of the varying degrees of acetyl group present in

Table 2
Percent transmittance and indexed values of methyl group reduction.

Sample	Transmittance (%)		Indexed Value (%)			
	At 1452	At 1360	Hydrophobicity		Reduction in Hydrophobicity	
			At 1452	At 1360	At 1452	At 1360
PLA	71.40	71.63	100	100	–	–
PLA/Ti	76.67	77.89	93.12	91.96	6.88	8.04
PLA/Ct	80.26	80.17	88.96	89.35	11.04	10.65
PLA/Ch	82.58	83.21	86.46	86.08	13.54	13.92

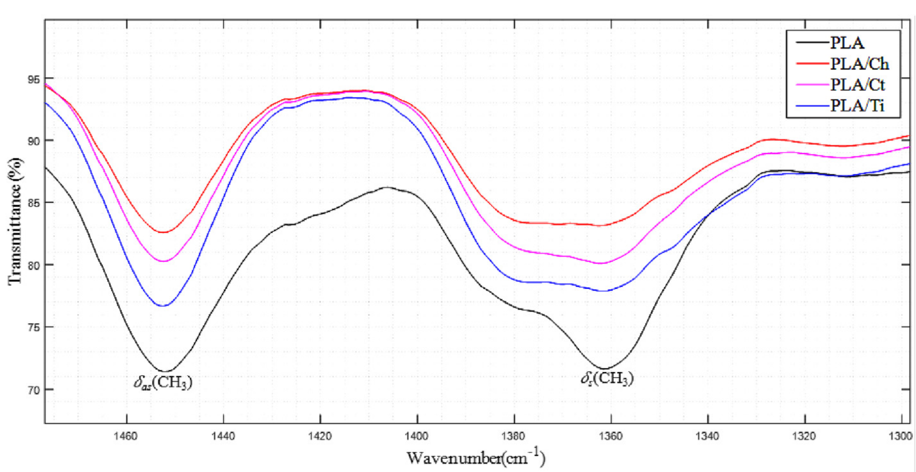

Fig. 2. Reduction in hydrophobic content of PLA.

them. Acetyl is lower in chitosan than in chitin. The reductions in CH_3 noticed as a result of loading PLA with Ti powder could be because of the oxygen gained as a result of its exposure during compositing.

4. Conclusion

This study addressed the issue of slow biodegradation in polylactic acid by loading it with three biocompatible fillers. The fillers used have track records in the biomedical fields. PLA composites were produced using the melt-blending technique with the fillers volume fraction of 16.67%. The results obtained showed that the addition of the fillers successfully reduced the hydrophobicity of PLA without any interfacial interaction or significant alteration in the molecular structure. Chitosan, because of its high hydrophilic content, resulted in the highest percentage of hydrophobic reduction. Chitin, being a natural organic filler, also reduced the hydrophobic peaks than titanium powder.

The organically reinforced PLA will have application in the orthopaedics, where revision surgery necessary for the removal of metallic bone implants have always been with extreme difficulty and high cost. The composites will also find application in areas where accelerated biodegradability is on demand.

Authors contributions

Abraham K. Aworinde: Conceptualization, Methodology, Investigation, Writing - Original Draft, Writing - Review & Editing, Visualization. Samson O. Adeosun: Conceptualization, Writing - Review & Editing, Supervision, Project administration. Festus A. Oyawale: Writing - Review & Editing, Supervision, Project administration. Esther T. Akinlabi: Conceptualization, Investigation, Resources, Supervision. Stephen A. Akinlabi: Resources, Investigation, Supervision.

Declaration of competing interest

None.

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