IOP Conference Series: Materials Science and Engineering

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To cite this article: Beh Chong You *et al* 2020 *IOP Conf. Ser.: Mater. Sci. Eng.* **864** 012198

IOP Conf. Series: Materials Science and Engineering **864** (2020) 012198 doi:10.1088/1757-899X/864/1/012198

The Effect of the Amylose/Amylopectin Contents of Starch on Porosity and Dielectric Properties of the Porous Hydroxyapatite/Starch Composites

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Abstract. This study aims to determine the effect of the amylose/amylopectin contents of starch on the porosity and dielectric properties of porous hydroxyapatite/starch composites. The porous hydroxyapatite/starch composites were prepared by utilizing the starches (rice, corn and potato starch) via gelatinization and retrogradation process. The complex permittivity of the porous hydroxyapatite/starch composites were evaluated in the frequency range of 12.4-18.0 GHz. The porous composites were exhibited the higher average porosity by using the starch with higher amylopectin content. The highly porous hydroxyapatite/starch composites with higher amylopectin content show the significant fluctuation peaks (at 13.8 and 16.6 GHz) and the higher imaginary part of the complex permittivity (ε″) at higher frequency in the dielectric spectrum, respectively. The real (ε′) and imaginary part (ε″) of the complex permittivity of the porous composites could be enhanced by increasing the average porosity and the amylopectin contents.

1. Introduction

The material components of natural bone mainly consist of organic and inorganic components. Numerous organic and inorganic material components are discovered and developed which aims to mimic the nature of bone in order to create the appropriate organic-inorganic bone scaffold [1,2]. The designed porous composite is used to replace the bone defects which initially provide a biomimetic template to support the cell adhesion, proliferation, and differentiation during bone tissue regeneration [1,3]. Starch is one of the most likely organic materials to mimic the material component of nature bone which exhibits the significant biocompatibility, biodegradability, bioresorbability and processability [1,4]. Hydroxyapatite has been frequently used as the inorganic material component in the bone scaffold fabrication which exhibited good biocompatibility and osteoconductivity [2,3]. Starch has variety physicochemical properties due to their dissimilar amylose (linear chain structure) and amylopectin (branched chain structure under the different botanical sources [5,6]. Starch molecules are gelatinized under shearing force when heated at high temperature with the presence of water. The intermolecular bonds between amylose and amylopectin break down during gelatinization process which indicated that native starch crystals are melted in this mechanism.

Consequently, the intermolecular bonds are reformed between amylose and amylopectin molecules during the retrogradation process. A new crystalline structure of starch is formed by the rearrangement and recrystallization of the macromolecules under the decrement of the kinetic energy and Brownian motion [4–6]. The reinforced hydroxyapatite incorporates in the starch matrix through the recrystallization process of starch could complement each other in term of performance. The interconnected porous structure of the organic-inorganic composite could be obtained via bone scaffolding techniques. it is important for bone scaffold to facilitate nutrient perfusion and mass transport during the bone growth phase [1,2]. Although non-invasive sample characterization techniques in bone tissue engineering are developed rapidly, many researchers paid less attention on microwave sample characterization techniques.

Thus, development of microwave dielectric spectroscopic technique bone scaffolds characterization is required. The polarization and energy dissipation in the composite occur due to exposure of electromagnetic field. Polarization occurs as the orientation movements of dipolar molecules of the composite whereas the switch of polarization direction leads to energy [7–9]. In the Maxwell–Wagner–Sillars polarization, the interfacial phenomena of the inhomogeneous system in the porous composite obtain the interfacial polarization which contributed to the different permittivity [7,10]. The dielectric permittivity is a significant parameter to determine the microwave response. In this study, an attempt has been made to investigate the effect of the amylose/amylopectin content and the average porosity on the dielectric properties of the porous composites over Ku-band (12.4-18.0 GHz).

2. Experimental

2.1. Material

The porous composite scaffolds were manufactured using commercial rice starch (Rs), cornstarch (Cs), potato starch (Ps), hydroxyapatite nanopowder (HAp) and Sodium Chloride (NaCl) porogen particles.

2.2. Sample fabrication

The porous composites were manufactured via solvent casting/particulate leaching (SCPL) method. The starch was dissolved in distilled water to prepare a starch solution for heat-moisture treatment (temperature range of 45-65°C for around 30-60 minutes). The hydroxyapatite nanopowder proportion as listed in table 1 was mixed in the starch solution. The HAp/starch mixture was stirred and heated from 50°C to 100°C with a heating rate of 5°C/min. Then, the NaCl particles was added and stirred with the mixture. The homogeneous HAp/starch/NaCl composite was casted and cooled (2-10°C for about 1-2 hours). The composite was dehydrated (80-90°C for 20-24 hours) and further dried at 110-140°C for 2-3 hours. Lastly, the porous composite were dried at 85-95°C for 3-4 hours after particles leaching process. The porosity of porous composite is needed to be studied by sample characterizations.

Table 1. Proportion of the porous HAp/Starch composites

Designation	Proportion	
	Starch (wt%)	HAp nanopowder (wt%)
Hap/Rs	50	50
Hap/Cs	50	50
Hap/Ps	50	50

2.3. Sample characterization

The porosity of the samples was determined by using the Archimedes liquid displacement technique. The porosity of the porous composite was determined via the following equation (1):

$$\text{Porosity} = \frac{\left(\dfrac{W_{Wet} - W_{Dry}}{p_{ethanol}}\right)}{\left(\dfrac{W_{Wet} - W_{Immersed}}{p_{ethanol}}\right)} \times 100\% \tag{1}$$

where W_{wet} is the sample saturated weight in ethanol; W_{Dry} is the dry sample weight; $W_{Immersed}$ is the weight of the sample submerged in ethanol; and $P_{ethanol}$ is the ethanol density (0.798 g/mL). The dielectric parameters of the porous composites were measured by using a E8362B PNA microwave network analyser. The real part (ε') and imaginary part (ε'') of the complex permittivity in Ku-band (12.4 GHz to 18.0 GHz) was determined. The samples were prepared in the dimension of 8mm x 16mm x 12mm. It is dimension of WR62 waveguide adapter which compatible with Ku Band dielectric measurement.

3. Results and Discussions

The average porosity and the macromolecules (amylose and amylopectin) content of the starch used in the fabricated porous hydroxyapatite/starch composites are listed in table 2. The amylopectin content of the rice starch-based porous composite (65.0%) is lowest compare with the potato-based porous composite with the highest amylopectin content of 82.2%, resulting in the lowest average porosity of HAp/Rs (54.2%). The amylopectin content increases with the porosity of the porous hydroxyapatite/starch composites. This might due to the branched-chain structure of the amylopectin that contribute to the stiffness of the recrystallized composite in order to enhance the formation of porous structure. ε' and ε'' were measured for dielectric properties of the porous composites. ε' and ε'' for the porous hydroxyapatite/starch composites are shown in figure 1 and figure 2, respectively. The ε' and ε'' of the porous composites for the selected frequencies were listed in table 3.

Table 2. Average porosity and starch contents of the porous HAp/Starch composites

		Starch contents [4]	
Sample	**Average porosity (%)**	**Amylose (%)**	**Amylopectin (%)**
HAp/Rs	54.2	35.0	65.0
HAp/Cs	58.9	28.0	72.0
HAp/Ps	62.6	17.8	82.2

In figure 1, ε' of the porous HAp/Starch composites exhibited three fluctuations at about 13.8, 15.2 and 16.6 GHz. The interfacial polarization and relaxation polarization contribute prominently in gigahertz frequency range for the ε' of the porous composites [8]. Thus, the peaks of permittivity spectrum are caused by various polarization mechanisms. The peak at about 13.8 GHz shifts to the higher frequency and the peak at around 16.6 GHz increase (as shown in table 3) as the amylopectin content and the average porosity of the porous composites increase (table 2). It might due to the highly porous structure of the composite and the rearranged branched amylopectin molecules have abundant current density that enhance the polarization relaxation mechanisms. However, the peak at 15.2 GHz shows that the HAp/Cs shift to higher frequency and higher ε′ (table 3) can be noticed when compare with the HAp/Rs and HAp/Ps in figure 1. This might be due to its different morphological feature variations that cause the other polarisation of the porous composites.

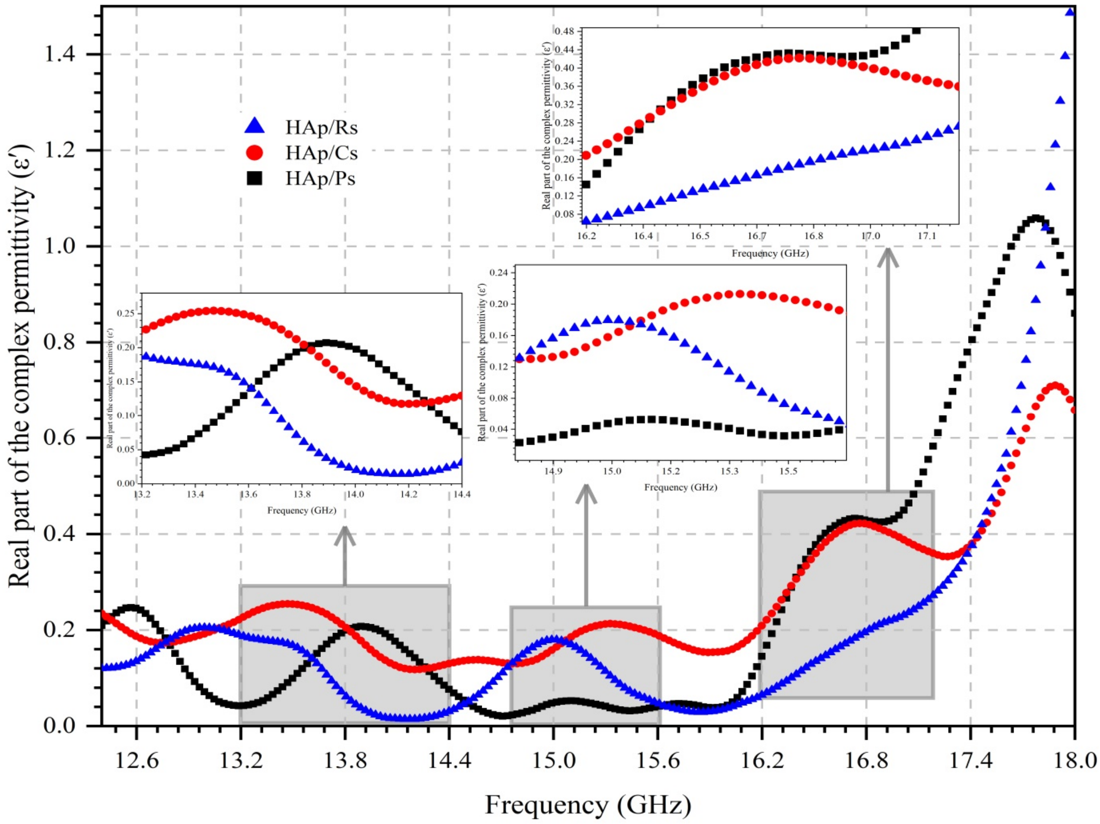

Figure 1. Permittivity spectrum for the porous HAp/Starch composites (Real part)

In figure 2 and table 3, ε″ of HAp/Rs and HAp/Cs decrease from -1.34 to -1.45 for frequency range from 13.8 to 15.2 GHz and then increase from -1.25 to -1.38 for frequency range from 15.2 to 16.6 GHz. The ε″ of the HAp/Ps increase from 13.8 to 16.6 GHz. The trend of the ε″ for the porous hydroxyapatite/starch composites increase with the frequency when the average porosity and the amylopectin content increase. Meanwhile, the HAp/Rs and HAp/Cs in figure 2 exhibit significant fluctuation peaks compare with the HAp/Ps in the ε″ spectrum at lower frequencies of Ku band. The higher ε″ lead to higher electromagnetic radiation dissipation for the corresponding polarisation mechanisms in the porous composites [7,10]. On the contrary, the HAp/Ps show higher ε″ in the range of higher frequencies in Ku band. It might due to higher branched-chain structure of amylopectin content in the HAp/Ps has performed the energy dissipation more effectively from the alternating current electrical field in higher frequency.

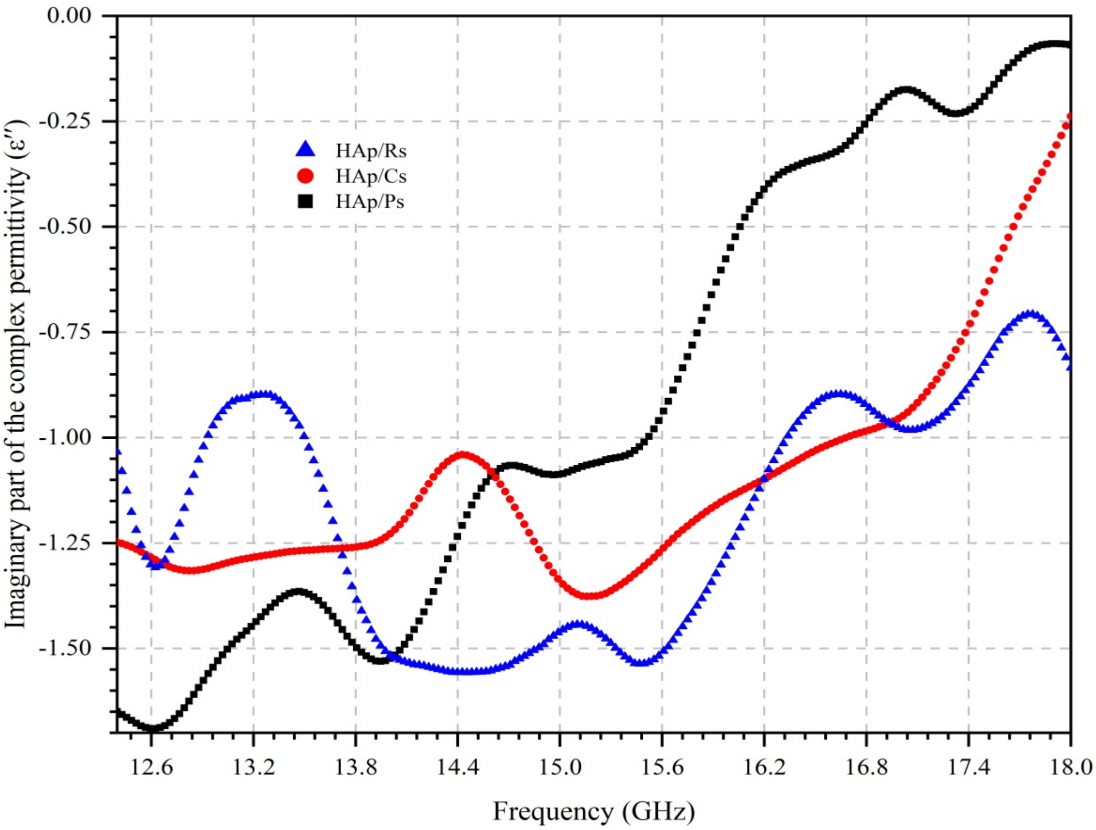

Figure 2. Permittivity spectrum for the porous HAp/Starch composites (Imaginary part)

Table 3. Real (ε′) and imaginary (ε″) parts of the complex permittivity for the porous HAp/Starch composites

	ε′			ε″		
Sample	**13.8GHz**	**15.2GHz**	**16.6GHz**	**13.8GHz**	**15.2GHz**	**16.6GHz**
HAp/Rs	0.07	0.15	0.16	-1.35	-1.45	-0.90
HAp/Cs	0.21	0.20	0.40	-1.26	-1.38	-1.01
HAp/Ps	0.19	0.05	0.42	-1.49	-1.06	-0.32

4. Conclusions

In this study, the porous HAp/starch composites were fabricated by using several types of starch with different amylose and amylopectin contents. The different amylose/amylopectin contents of the starch lead to the variation of the average porosity of the porous composites. As the amylopectin contents increase, the average porosity of the porous hydroxyapatite/starch composite increased. It can be concluded that the increment of the amylopectin might strengthen the porous structure of the porous composites. Subsequently, it enhances the dielectric properties of the porous composites. The more significant dielectric responses in the complex permittivity spectrum can be observed as the average porosity and the amylopectin content increase. This result shows that the microwave technique is convincing as a non-invasive sample characterization in bone tissue.

Acknowledgement
The author would like to acknowledge the support from the Fundamental Research Grant Scheme (FRGS) under a grant number of RACER/1/2019/STG07/UNIMAP/2 from the Ministry of Education Malaysia.

References

[1] Mirab F, Eslamian M and Bagheri R 2018 *Biomed. Phys. Eng. Express.* **4** 055021
[2] Ragunathan S, Govindasamy G, Raghul D R, Karuppaswamy M and VijayachandraTogo R K 2020 *Mater. Today Proc.* **23** 111–118
[3] Koski C, Onuike B, Bandyopadhyay A and Bose S 2018 *Addit. Manuf.* **24** 47–59
[4] Marichelvam M K, Jawaid M, Asim M 2019 *Fibers* **7** 1–14
[5] Tako M, Tamaki Y, Teruya T, Takeda Y 2014 *Food Nutr. Sci.* **05** 280–291
[6] Zakaria N H, Muhammad N and Abdullah M M A B 2017 *IOP Conf. Ser. Mater. Sci. Eng.* 209
[7] Bera R, Das A K, Maitra A, Paria S, Karan S K and Khatua B B 2017 *Compos. Part B Eng.* 129 210–220
[8] Ding D, Li Z, Xiao G, Yang S 2018 *Mater. Res. Express.* **5** 025039
[9] Zhang Z, Zhao H, Gu W, Yang L and Zhang B 2019 *Sci. Rep.* **9** 1–10
[10] Wang F, Sun Y, Li D, Zhong B, Wu Z, Zuo S, Yan D, Zhuo R, Feng J and Yan P 2018 *Carbon N. Y.* **134** 264–273