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Mechanical properties improvement of epoxy composites by natural hydroxyapatite from fish scales as a fillers

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ABSTRACT

This study was carried out to prepare epoxy/ natural hydroxyapatite composite for potential biomedical application. Natural hydroxyapatite (nHAp) powder was extracted from Tilapia fish scales via the thermal method. The natural hydroxyapatite was milled for 48 hours and dried by spray method. The nHAp particle size was determined using mastersizer 2000 particle size analyser and the chemical structure was confirmed using (XRD) and FTIR analysis. The particle size of nHAp was identified to be between 1 and 10 microns. Mechanical properties of epoxy/ natural hydroxyapatite were investigated by using impact and flexural test. The highest flexural strength of epoxy/nHAp composite was recorded when the nHAp filler was 10 wt% which is 77 % increment as compared to epoxy alone. The impact strength was increased up to two-fold as compared to neat epoxy. The scanning electron micrograph (SEM) and EDX analysis showed uniform dispersion of nHAp particles within the epoxy matrix for the composites with 10 wt% filler loading.

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INTRODUCTION

Epoxy material, which is one of the most crucial thermosetting materials, are commonly being used for adhesives, coatings, electrical laminates, and structural components due to their mechanical properties of low cure shrinkage, good solvent and chemical resistance, versatility, excellent adhesion (V. S. Mathew, *et al.,* 2014; J. R. Kim and J. J. Kim, 2017; P. V. P, D. Puglia, *et al.,* 2017). Epoxy is also widely used in medical products such as medical-grade disposable and reusable devices like catheters and surgical instruments (L. C. Kontaxis, *et al.,* 2018). The application of epoxy materials is often limited by their intrinsic brittleness due to cross-linking 3D network (S. Chuayjuljit, *et al.,* 2006). Many researchers investigations had been focusing on toughening the epoxy materials (M. H. Kothmann, *et al.,* 2014; K. P. Aswathi, *et al.,* 2017). and it was claimed that it could be achieved by adding the organic or inorganic fillers, such as reactive liquid rubbers (V. S. Mathew, *et al.,* 2010), high-performance engineering thermoplastic and inorganic particles (W. Sonoyama *et al.,* 2002). Since 1970, the application of composite materials has widely increased due to development of new fillers such as carbon fibre, boron, aramid, quartz, ceramic and glass fibre. Attempt to use epoxy in the medical field was reported by Filiberto *et al.,* (2008). Since epoxy is biocompatible one of the requirements for fillers is also must be biocompatible and not toxic during degradation. The application of hydroxyapatite as a filler in epoxy was reported by Oladele *et*

al., (2018). Hydroxyapatite (HA) is one of the common inorganic fillers used in polymer composites due to their improvement in mechanical properties as well as biocompatibility of the composites. This is because HA has excellent biocompatibility properties (L. Chen, *et al.,* 2011). Many studies reported the advantages of HA, especially in stimulating bone healing, and it was claimed that it had been used in orthopaedic as bone void fillers, dental surgery, orthopaedic and dental implant coating, traumatology, spine, maxillofacial (H. Im and J. Kim, 2012; I. O. Oladele, 2018). HA is not only bioactive, but it also is known to be non-toxic, non-immunogenic, osteoconductive, and its crystallographic structure is almost similar to the bone mineral (M. E. Leyva, *et al.,* 2008). Both the physical and mechanical properties of the corresponding epoxy matrix can be improved due to the inherent properties of the hydroxyapatite.

Hydroxyapatite was synthesised via chemicals reaction such as chemical precipitation technique (D. N. Ungureanu, *et al.,* 2011) but high manufacturing cost associated with chemicals used in the synthesis process. Therefore, in this study natural hydroxyapatite was extracted from fish scale which is lower the manufacturing cost, biologically safe for human, suitable for potential medical device applications and halal sources for Muslims around the world.

The effect nHAp extracted from Tilapia fish scales in modified epoxy composites have not yet been reported. Thus, in this study epoxy resin was mixed with natural hydroxyapatite (nHAp) powder extracted from Tilapia fish scales to improve mechanical properties as well as biocompatibility of the composites.

MATERIALS AND METHODS

The materials used to prepare the composites were epoxy resin, Dow 331 (Dow Chemical Company, USA) and curing agent, JointMine 905-3S (Epochemie International Pte Ltd, Singapore). The Tilapia fish scales were collected, washed and dried in an oven before thermal degraded at 1000 °C in a furnace to produce fish scales ash. The fish scales ash was ball milled to produce natural hydroxyapatite (nHAp) powder. The particle size of nHAp was estimated using mastersizer 2000 particle size analyser. Meanwhile, the most common method to dry the hydroxyapatite slurry is a thermal dying technique in which the slurry was heated in the oven for 1 day at 80°C to remove water after the ball milling process. However, drying in the oven was caused the hydroxyapatite fish scales particles to clump to each other and difficult to separate them to be used as some fillers in polymer composites. Thus, this study evaluated properties of hydroxyapatite fish scales particles prepared by spray method in which hydroxyapatite fish scales slurry was not oven dried after the ball milling process.

The epoxy/nHAp composite was prepared by mechanical mixing technique followed by mixing using sonicator Q700. Meanwhile, the natural hydroxyapatite filler loading was used from 5 to 25 wt % summarized in Table 1. The fillers mixed with epoxy resin using mechanical mixing for 30 min followed by 30 min mixing using sonicator Q700 until it becomes homogenous at room temperature. The mixture was poured into molds made of galvanized steel with a dimension of (20 *20*5) cm. The surface of the mold was applied with high-temperature honey wax for easy removal of the epoxy composite sheet. The samples were then procuring at temperature 80°C for 1 hour and post cure for 2 hours at 110°C according to manufacturer procedures.

Table 1: Designation of Composites

Sample	Epoxy (%)	nHAp (%)	Mixer milling time (min)
1	100	0	30
2	100	5	60
3	100	10	60
4	100	15	60
5	100	20	60
6	100	25	60

Some characteristics of morphology and mechanical properties were investigated. A Hitachi SU 8020 UHR field emission scanning electron microscope (FESEM) and EDX were used to confirm the surface morphology of the epoxy /nHAp composites and the mastersizer 2000 was used to determine the particle size of nHAp. A Fourier transform infrared (FTIR), Model Nexus was applied to identify the functional groups of the nHAp and composite. The FTIR analysis was performed in the wavenumber ranged from 4000 to 400 cm^{-1}. Phase identification and crystallinity of nHAp samples were analyzed using X-ray diffraction (XRD) model D8 Advance, Bruker AXS model, Germany.

Three points flexural testing was conducted to determine flexural strength according to ISO 178 using Universal Testing Machine (Instron, Model 3365). A Charpy impact test was conducted according to ASTM A370.

RESULTS AND DISCUSSION

The functional groups of natural hydroxyapatite were determined by FTIR spectra, as shown in Figure 1(a). Based on the FTIR spectra result, the hydroxyl group OH appeared sharp peak around 3569 cm^{-1}. Peaks in the region of 472 cm^{-1}, 569 cm,

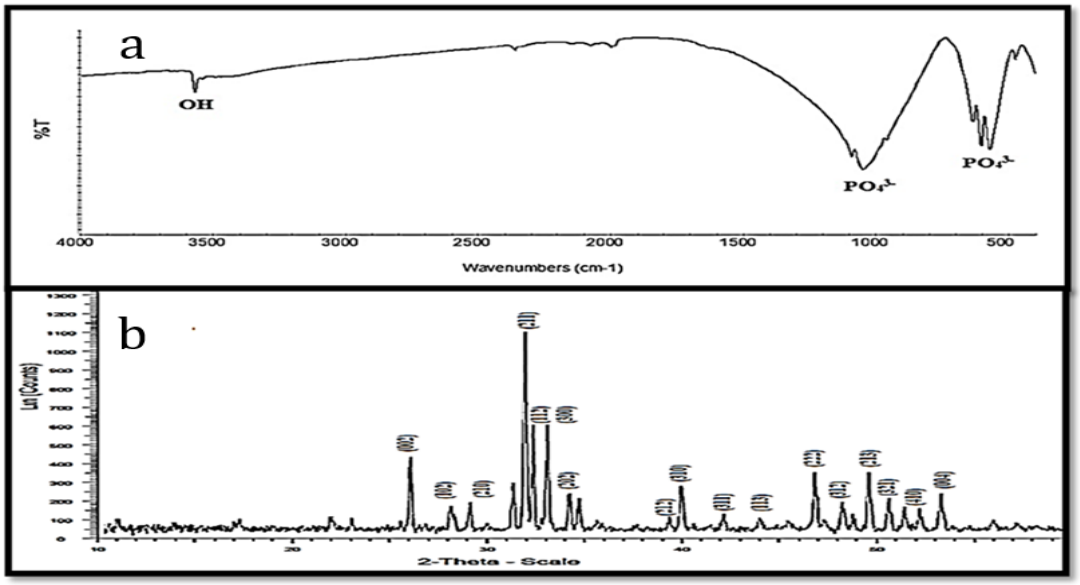

Figure 1: (a) FTIR spectrum and (b) XRD pattern of natural hydroxyapatite from fish scales

601 cm^{-1}, 1046 cm^{-1} and 1091 cm^{-1} were correspond to phosphate group (M. S. M. Arsad, *et al.,* 2011). The FTIR results showed a typical FTIR spectrum for highly crystalline hydroxyapatite as reported by several types of research (I. Zainon, *et al.,* 2012).

In the further structural investigation, the XRD spectroscopy was employed to confirm the existence and crystallinity of natural hydroxyapatite sample. Based on the XRD pattern given in Figure 1(b). The results indicated the prominent peaks corresponded to the high crystalline standard hydroxyapatite materials as reported elsewhere (D. Zhang *et al.,* 2012). The spectrum has also resembled to the standard XRD pattern of hydroxyapatite-based on library collection (ICDD 9–432) (S. Shahabi *et al.,* 2014). This result has proved the high crystalline nHAp was produced from the fish scales.

From mastersizer 2000 particle size analyzer, the particle size of nHAp is between 1 to 10 micron as shown in Figure 2.

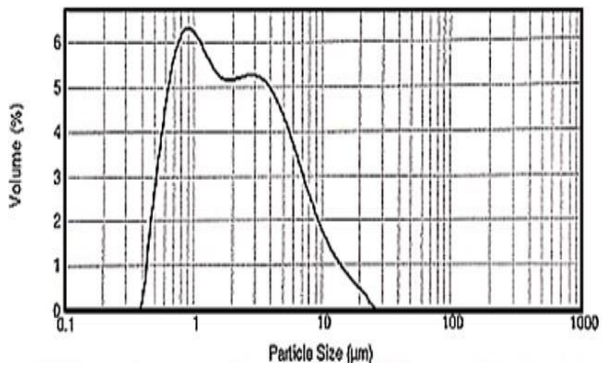

Figure 2: Particle size distribution of nHAp

The morphology structure analysis of natural hydroxyapatite powder is presented in Figure 3(a). The results show the particulate form of nHAp after the milling process. Meanwhile, the Ca/P ratio obtained products via thermal degraded at 1000 °C process of fish scales were further investigated via the EDX technique, EDX image is presented in Figure 3(b). According to the chemical formula of the standard hydroxyapatite, the calcium to phosphorous molar ratio is approximately 1.67. The calculated Ca/P ratio for the hydroxyapatite powder is 1.67. This results further confirm that the white powder extraction from tilapia fish scales via thermal degraded is natural hydroxyapatite.

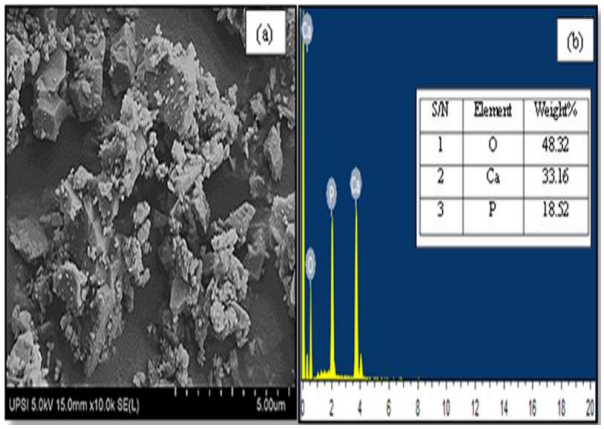

Figure 3: (a) FESEM Images, and (b) EDX analysis of natural hydroxyapatite.

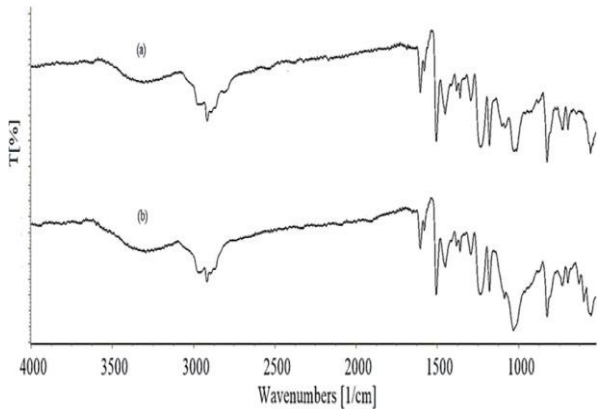

Figure 4:FTIR spectra of (a) neat epoxy and (b) epoxy/10 wt% nHAp composites

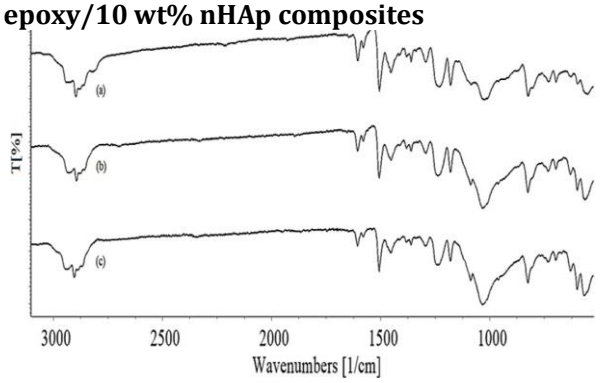

Figure 5: FTIR spectra of (a) epoxy/ 5% of nHAp composite, (b) epoxy/ 15% of nHAp composite and (c) epoxy/ 25% of nHAp

The interfacial interaction between the pure epoxy and epoxy/nHAp composite were further investigated through the FT-IR spectra, as shown in Figure 4. Before the addition of natural hydroxyapatite in the epoxy resin, the FT-IR spectrum of pure epoxy showed several characteristics. The typical peak for a functional group of neat epoxy was appeared at between 2922 cm^{-1} and 2896 cm^{-1} as a result of stretching CH_2 groups whereas the peak at 2772 cm^{-1} was as a result to the aliphatic carbon chains symmetric. The peak observed at around 1507 cm^{-1} due to 1,4 disubstituted benzene ring C=C bond of epoxy resin. The C=O peak was situated at around 1176 cm^{-1}. The peak at 3304 cm^{-1} is indicated as OH functional groups. There have no significant changes between the FTIR spectrum of epoxy composites and FTIR spectrum of epoxy filled 10 wt % nHAp. Similar results were also reported by another researcher (K. Kanimozhi, *et al.,* 2014). However, there are new peaks recorded at 602 cm-1, 314 cm-1 and 1039 cm^{-1} which correspond to phosphate group from nHAp. The hydroxyl group of nHAp was not observed as it was overlapped with OH absorption band from epoxy resin at 3305 cm^{-1} regions (M. S. M. Arsad, *et al.,* 2011) (Figure 4b). The FTIR analysis recorded that there was no interaction between nHAp and the epoxy resin since there was no treatment on the surface of nHAp particles. The interaction between nHAp and epoxy resin was only weak surface interaction.

Figure 5. show the changes recorded at 603 cm^{-1}, 631 cm^{-1} and 1035 cm^{-1} which correspond to phosphate group with different loading of natural hydroxylapatite powder 5wt% nHAp, 15wt % nHAp and 25 wt % nHAp. Moreover, as observed added excess amount of natural hydroxylapatite powder to epoxy composite has exhibited the intensity of the increase of phosphate group at 603 cm^{-1}, 631cm^{-1} and 1035 cm^{-1}.

Figure 6 (a) and (b) shows the flexural strength and flexural modulus of post-cured epoxy /nHAp composites at different nHAp loading. From the results, as the hydroxyapatite loading increase, the flexural strength and modulus increased. Addition of 5 wt% of nHAp to the epoxy resin has improved the flexural strength and modulus by 30 MPa and 2000 MPa. The optimum flexural strength was achieved when the nHAp filler loading was 10 wt% with flexural strength and modulus have increased up to 77 % as compared to epoxy alone. The increase in flexural strength of the composites is well known when incorporating any mineral filler into it (T. P. Selvin, *et al.,* 2004). Flexural strength and modulus start to reduce as the nHAp filler loading above 10 wt% as shown in Figure 4 and 5. However, after 10 wt% of nHAp was added to the epoxy resin, the flexural strength and modulus start to reduce. This probably because at high filler loading the nHAp particle gets agglomerated during processing the sample. Therefore, the dispersion becomes poor and the modulus decreases.

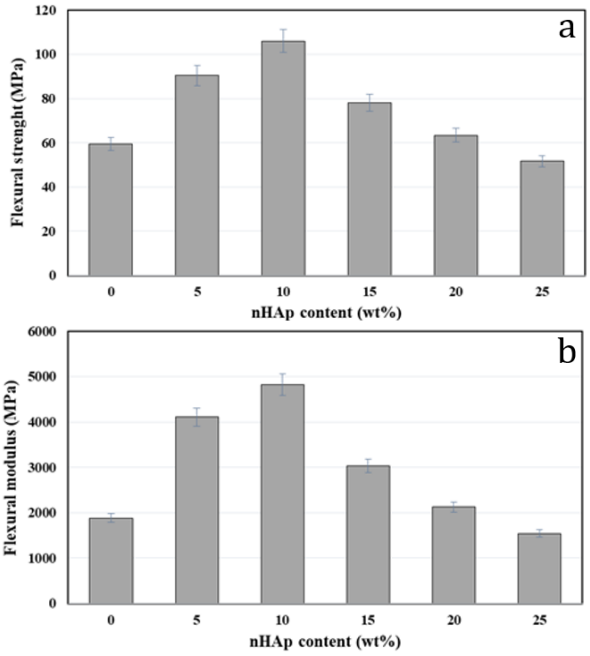

Figure 6: Effect of filler content on (a)flexural strength and (b) flexural modulus of epoxy /nHAp composite

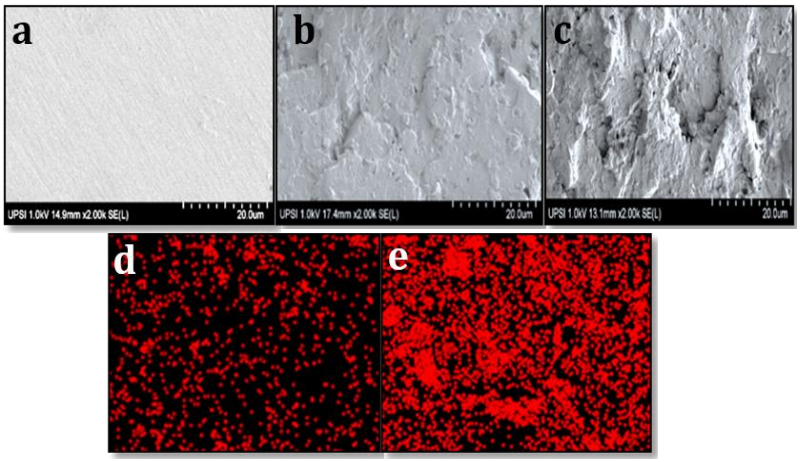

Figure 8: Scanning electron micrograph for (a) neat epoxy, (b) epoxy/ 10 wt % of nHAp composites , (c) epoxy/25 wt % of nHAp composite , EDX mapping of (d) epoxy/ 10 wt % of nHAp composites and (e) epoxy/25 wt % of nHAp composite

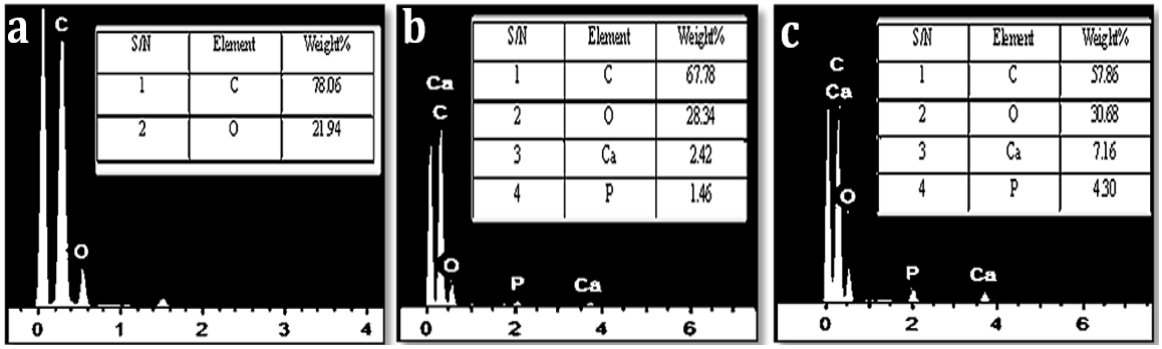

Figure 9: EDX spectra of (a) Neat epoxy, (b) epoxy/10 wt% of nHAp composites and (c) epoxy/25 wt% of nHAp composite

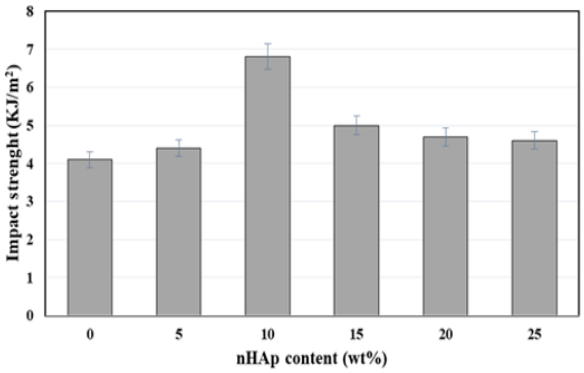

Figure 7: Effect of filler content on the Impact strength of epoxy /nHAp composite

Impact Charpy test was used to determine the impact strength of epoxy/nHAp composite as presented in Figure 7. It can be seen that the impact strength increased with different nHAp content. The increase in impact strength is an indication of improved toughness as the incorporation of nHAp fillers. Meanwhile, a similar observation was seen for flexural strength where 10 wt% nHAp loading give the highest impact strength of around 6.6 kJ/m^2.

The surface morphologies analysis of the neat epoxy resin was observed through FESEM as shown in Figure 8. It is clearly to observe that the clean surface of the neat fractured epoxy was indicated brittle of the resin. Figure 8 (b) shows the SEM micrograph of 10 wt% nHAp filled epoxy composite. The dispersion of nHAp was good with small porosity observed. The dispersion of nHAp particles however poor at filler loading of 25 wt%. The dispersion of filler in the matrix plays a vital role in the composite mechanical properties. The distribution of calcium in surface composite was determined by EDX mapping analysis, and the results are presented in Figure 8 (d) and (e). Based on the results from SEM micrograph and EDX analyses, homogeneity between the composite and the increasing loading of natural hydroxyapatite in composite due to the highest atomic percentage of calcium on the surface composite which leads to increasing agglomeration as well as start to reduce the surface matrix interaction, these will result in poor mechanical properties. Epoxy composite with 10 wt % nHAp shows the highest impact strength.

These results were supported by EDX analyses in Figure 9 (a)-(c). The epoxy resin has a carbon and oxygen contents of 78.06 and 21.94 %, respectively. Meanwhile, the epoxy/natural hydroxyapatite shows the increasing content of natural hydroxyapatite in the composite lead to the highest

atomic percentage of oxygen as well as the atomic percentage of carbon decreased indicating the successful intercalation and tightly bond between the natural hydroxyapatite and epoxy resin.

CONCLUSION

High crystalline nHAp from fish scales was prepared with particle size between 1 and 10 microns. FTIR results revealed that no chemical interaction between natural hydroxyapatite and epoxy resin. The effect of natural nHAp filler loading on mechanical properties of epoxy composites was investigated. The results show incorporation of nHAp fillers in epoxy resin does affect the mechanical properties of epoxy composites. With the optimum nHAp filler loading for highest flexural and impact strength of epoxy composites was 10 wt%.

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