EPOXY/FISH SCALES HYDROXYAPATITE (FsHAp) COMPOSITES TOUGHENED BY LIQUID NATURAL RUBBER FOR BIOMEDICAL APPLICATIONS

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ABSTRACT

The aims of this study were to improve the mechanical properties, thermal stability and biocompatibility of epoxy/fish scales hydroxyapatite (FsHAP) composite toughened with liquid natural rubber. The FsHAp was extracted from *Tilapia* fish scales using thermal method while liquid natural rubber was produced from poly(methyl methacrylate) grated natural rubber (MG30) via oxidative and photo degradation methods label as LMG30A and LMG30B, respectively. The analysis of liquid natural rubber was carried out using Fourier transform infrared spectroscopy (FTIR), nuclear magnetic resonance spectroscopy (NMR) and gel permeation chromatography (GPC) have shown that no significant chemical structure change between both LMG30 (A and B) and MG30. GPC analysis exhibited that the average molecular weight of LMG30A (29,307Da) was lower than LMG30B (97,693Da). The fracture toughness of the epoxy was increased up to 23 fold (15.2 MPa.m$^{1/2}$) when epoxy loading with 10 wt% FsHAp and toughened with 6 phr LMG30A, whereas impact strength and flexural test increased up to twice as compared to neat epoxy. The morphology was characterized using field emission scanning electron microscope (FESEM) showed uniform dispersion of rubber particles within the epoxy matrix with average diameter between 0.7 and 1.2 μm. Differential scanning calorimetry (DSC) and thermo gravimetric analysis (TGA) curves have showed the thermal stability of the epoxy/FsHAp/LMG30A composite higher as compared to neat epoxy. The epoxy/FsHAp/LMG30A composite was proven to be biocompatible through cytotoxicity test. In conclusion, the epoxy/FsHAp/LMG30A composite shown higher mechanical properties, thermal stability and biocompatibility as compared to neat epoxy. As an implication, the developed epoxy/FsHAp/LMG30A composite is potential to be used as medical device applications.

KOMPOSIT EPOKSI/HIDROKSIAPATIT SISIK IKAN (FsHAp) YANG DITEGUHKAN DENGAN CECAIR GETAH ASLI UNTUK APLIKASI BIOPERUBATAN

ABSTRAK

Kajian ini bertujuan untuk meningkatkan sifat mekanik, kestabilan terma dan bioserasi komposit epoksi/hidroksiapatit sisik ikan (FsHAp) diteguhkan dengan cecair getah asli. FsHAp diekstrak daripada sisik ikan *Tilapia* menggunakan kaedah terma manakala cecair getah asli dihasilkan daripada getah asli tercangkuk poli(metil metakrilat) (MG30) melalui kaedah degradasi oksidatif dan foto di label masing-masing sebagai LMG30A and LMG30B. Analisis cecair getah asli dijalankan menggunakan spektroskopi Fourier transformasi inframerah (FTIR), spektoskopi resonans magnetik nuklear (NMR) dan kromatografi penyerapan gel (GPC) menunjukkan tiada perubahan struktur kimia yang nyata antara LMG30 (A dan B) dan MG30. Analisis GPC mendapati purata berat molekul LMG30A (29,307Da) lebih rendah daripada LMG30B (97,693Da). Kekuatan teguhan epoksi meningkat sehingga 23 kali ganda (15.2 MPa.m$^{1/2}$) apabila ditambah dengan 10 wt% FsHAp dan dikuatkan dengan 6 phr LMG30A, manakala kekuatan hentaman dan lenturan meningkat sehingga dua kali berbanding dengan epoksi tulin. Morfologi dicirikan menggunakan mikroskop pengimbas pancaran medan elektron (FESEM) menunjukkan penyebaran seragam partikel getah dalam matriks epoksi dengan purata diameter antara 0.7 dan 1.2 µm. Kalorimetri pengimbasan pembezaan (DSC) dan analisis gravimetri terma (TGA) menunjukkan kestabilan terma bahan epoksi/FSHAp/LMG30A yang lebih tinggi berbanding epoksi tulin. Komposit epoksi/FsHAp/LMG30A terbukti bersifat bioserasi melalui ujian sitotoksisiti. Kesimpulannya, komposit epoksi/FsHAp/LMG30A menunjukkan sifat mekanik yang lebih tinggi, kestabilan haba dan bioserasi berbanding dengan epoksi tulin. Implikasinya, komposit epoksi/FsHAp/LMG30A yang dibangunkan berpotensi digunakan sebagai peranti perubatan.

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ATBN	Amine-terminated butadiene acrylonitrile
CTBN	Carboxyl terminated butadiene acrylonitrile
DSC	Differential Scanning Calorimetry
XRD	X-ray diffractometers analysis
Dn	Number average domain diameter in µm
Da	Area average domain diameter in µm
Dw	Weight average domain diameter in µm
Dv	Volume average domain diameter in µm
ENR	Epoxidized natural rubber
ETPB	Epoxy terminated polybutadiene
FTIR	Fourier transform infrared spectroscopy
FsHAp	Hydroxyapatite from Tilapia Fish Scales
GPC	Gel permeation chromatography
HTLNR	Hydroxyl terminated liquid natural rubber
HA	Hydroxyapatite
^{1}H-NMR	Proton Nuclear Magnetic Resonance spectroscopy
HTPB	Hydroxyl-terminated polybutadiene
LNR	Liquid natural rubber
LENR	Liquid epoxidized natural rubber
LMG30	Liquid poly (methyl methacrylate) grafted natural

	rubber
MG30	Poly (methyl methacrylate) grafted natural rubber
M_W	Weight average molecular weight
NR	Natural rubber
PDI	Polydispersity indices
phr	Parts per Hundred
SEM	Scanning electron microscopy
Si	silica
TGA	Thermo gravimetric analysis
T_g	Glass transition temperature

CHAPTER 1

INTRODUCTION

1.1 Research Background

Epoxies are important thermosetting materials commonly used in adhesives, coatings, electrical laminates and structural components because of their excellent mechanical properties, cure shrinkage, good solvent and chemical resistance, versatility and excellent adhesion (Gazi, 2019; Kim & Kim, 2017; Mathew, George, Parameswaranpillai, & Thomas, 2014).

Epoxies are also widely used in medical products, such as medical-grade disposable and reusable devices including catheters and surgical instruments (Ahmadi, 2019; Bobby & Samad, 2019; Kontaxis, Pavlou, Portan, & Papanicolaou, 2018; Madhav, Singh, & Jaiswar, 2019). Moreover, they can be found in orthopaedic devices and in diagnostic equipment, such as MRI machines and ultrasound devices. Part of the reason is that the materials can be specially formulated to resist chemicals (Oladele, Akinola, Agbabiaka, & Omotoyinbo, 2018). Epoxies also adhere well to metals, plastics, glass and other substrates used in medical devices. Figure 1.1 shows some of the applications of epoxy/carbon fibre composites in orthopaedic prosthetics (Scholz, Blanchfield, Bloom, Coburn, Elkington, Fuller, & Trevarthen 2011).

Figure 1.1. Epoxy/Carbon Fiber Composites Are Ideal Materials For Orthopedic Prosthetics.

However, the applications of epoxy materials are limited by their intrinsic brittleness due to high 3D crosslink network (Chuayjuljit, Soatthiyanon, & Potiyaraj, 2006). Many studies focused on toughening epoxy materials (Jansen, Tamminga, Meijer, & Lemstra, 1999; Kumar & Kothandaraman, 2008; Ratna, Banthia, & Deb, 2005; Tan, Ahmad, Chia, Mamun, & Heim, 2013) by adding organic or inorganic fillers, such as reactive liquid rubbers, high-performance engineering thermoplastic (Sonoyama, Kuboki, Okamoto, Suzuki, Arakawa, Kanyama, & Yamashita 2002), inorganic particles (Jin & Park, 2012) and hyper branched polymers (HBPs) (Jin, Huang, Zhu, Zhou, & Yan, 2012).

Since the 1970s, the application of composite materials has widely increased with the development of new fillers, such as carbon fibre, boron, aramid, quartz, ceramic and glass fibre (Im & Kim, 2012; Feng, Lauke, & Mai, 2008). Considering that epoxy is biocompatible in fillers for biomaterials applications, Leyva et.al., (2008) attempted to use this material in the medical field and assumed that it is also biocompatible and non-toxic during degradation in the human body (Leyva, Antonio, & Queiroz, 2008).

Many studies reported the advantages of hydroxyapatite (HA), especially in stimulating bone healing, and claimed that it has been used in orthopaedics as bone void fillers, dental surgery, orthopaedic and dental implant coating, traumatology, spine and maxillofacial (Nandi, Kundu, Mukherjee, Mahato, Datta, & Balla 2015; Swetha, Sahithi, Moorthi, Srinivasan, , Ramasamy & Selvamurugan 2010; Inoue, K., Ohgushi, Yoshikawa, Okumura, Sempuku, Tamai & Dohi 1997; Moore, Chapman, & Manske, 1987). HA is bioactive, non-toxic, non-immunogenic and osteoconductive with a crystallographic structure almost similar to that of the bone mineral (Hongjian Zhou & Lee, 2011). Figure 1.2 displays biomedical applications of HA.

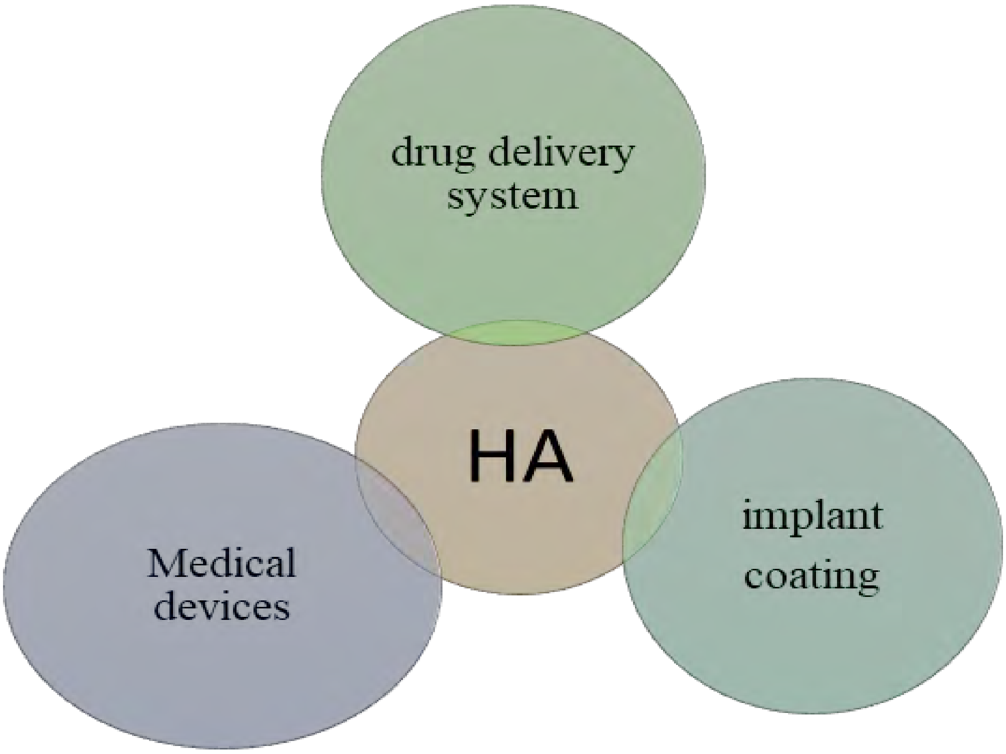

Figure 1.2. Schematic Illustration of Biomedical Applications of Hydroxyapatite.

HA with a molecular formula of $Ca_{10}(PO_4)_6(OH)_2$ is a common inorganic filler used to improve the mechanical properties and biocompatibility of polymer composites (Monmaturapoj, Srion, Chalermkarnon, Buchatip, Petchsuk, Noppakunmongkolchai & Mai-Ngam 2017; Scalera, Esposito Corcione, Montagna, Sannino, & Maffezzoli, 2014), because of its excellent biocompatibility properties (Chen, Liang, Mccrate, Lee, & Li, 2011). The chemical structure of HA is shown in Figure 1.3 (Ramli, Adnan, Bakar, & Masudi, 2011).

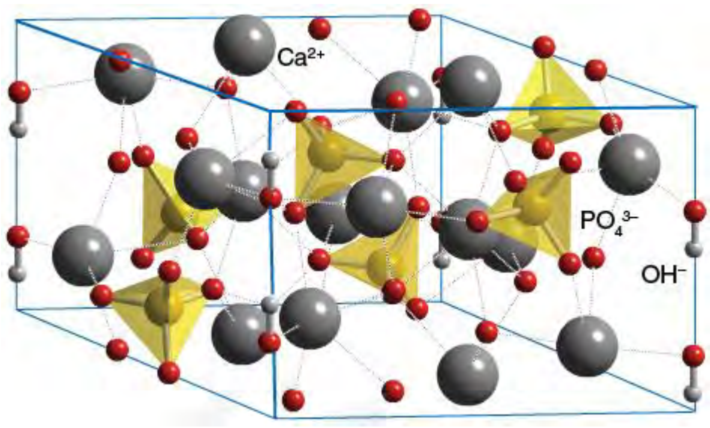

Figure 1.3. The Crystal Structures of Hydroxyapatite (Fihri, Len, Varma, & Solhy, 2017).

HA in the form of particles with particle size < 10 microns is classified as particulate fillers. It is similar to the silica powder used in epoxy composites (Brusentseva, Filippov, Fomin, Smirnov, & Veretennikova, 2015). The application of HA as a filler in epoxy was reported by Oladele et al., (2018). Meanwhile, Scalera et al., (2014) prepared epoxy/HA suspensions for stereo lithography in bone tissue engineering and found that the prepared epoxy/HA exhibits good mechanical properties (Scalera et al., 2014).

Fracture toughness is the property of resisting fracture by absorbing and dissipating energy during deformation prior to ultimate fracture. Toughness is a highly important property in applications where the material repeatedly encounters mechanical shock and vibration. Meanwhile, a small amount of a miscible liquid rubber is incorporated into the matrix of the curing agent-incorporated epoxy resin, and then the whole mass is subjected to curing. Phase separation is affected by the formulation, processing and curing conditions. Fracture toughness improves through the dissipation of mechanical energy by cavitation of the rubber particles, followed by shear yielding of the matrix. Improvement of fracture toughness is influenced by different factors, such as rubber particle size, curing agent and cross-linking density (Kargarzadeh, Ahmad, & Abdullah, 2017).

The fracture toughness of epoxy can be improved by adding impact modifiers (Seng et al., 2011), such as liquid rubber. Epoxidised carbonyl-terminated butadiene acrylonitrile copolymer liquid rubber (CTBN) is a commercial liquid rubber used as a toughening agent (Kargarzadeh, Sheltami, Ahmad, Abdullah, & Dufresne, 2015; Ben Saleh, Mohd Ishak, Hashim, & Kamil, 2009) . Zainol et al., (2006) first reported the potential of liquid natural rubber (LNR) as an impact modifier for epoxy resin. They proved that the impact properties of epoxy resin improve by 22-fold after adding 5 phr liquid poly(methyl methacrylate) grafted natural rubber (LMG30). The rubber used in their study was poly(methyl methacrylate) grafted natural rubber (MG30) (Zainol, Ahmad, Zakaria, Ramli, HaslanFadli, & Abdul Aziz 2006). Other researchers were reported the modification of thermoset resin with other types of LNR (Hisham, Ahmad, Daik, & Ramli, 2011; Mathew et al., 2014; Saleh, Ishak, Hashim, Kamil, & Ishiaku, 2014).

NR can be modified into LNR with a similar microstructure but shorter polymeric chain. LNR has a molecular weight (M_w) less than 50,000 Dalton (Sivaraman et al., 2017; Ibrahim & Board, 2016). Previous studies prepared LNR via different methods, such as photochemical oxidation, redox reaction, photodegradation and oxidation (Ibrahim, Othman, Nor, & Ismail, 2017; Giang, Thao, Huong, & Thu

Hiep, 2016; Abdullah, 1994). Preparation of LNR has been an interesting subject for decades because of its application as a strong adhesive, reactive plastic, coating and LNR which can be easily modified chemically given its low molecular weight (Rooshenass, Yahya, R., & Gan, 2018).

1.2 Problem Statement

Epoxy resins are highly cross-linked polymers used in material adhesives, aerospace, coatings and electrical and medical devices because of their high strength and stiffness and good solvent resistance (Abdul, Yop, Jin, & Hui, 2013). However, epoxy resins have limited applications in medical devices because of the brittle properties of epoxy after crosslinking. Hence, considerable efforts have been devoted to improving the toughness of epoxy resins (Unnikrishnan & Thachil, 2012). Numerous methods, such as adding rubber particulate, inorganic fillers and other engineering polymers, have been proposed to enhance the impact properties of epoxy. One successful method is the addition of synthetic liquid rubber (e.g. CTBN) and LNR (e.g. LENR).

Most studies on epoxy toughening modified epoxy with LNR (Tan et al., 2013). However, the addition of rubber usually decreases other properties (mainly the modulus and the thermal properties). A new approach for improving the thermal stability, toughness and modulus of thermoplastic and thermoset systems has recently emerged through the formation of a nanophase structure in the polymer matrix; the nanophase consists of small, rigid particles, whiskers or tubes (e.g. layered silicates, silica particles or carbon nanotubes) (Maghsoudian, Salimi, & Mirzataheri, 2019; Mentlík, 2018). In this study was added natural hydroxyapatite (FsHAp) powder was extracted from Tilapia fish scales via thermal method as a filler to improve modulus properties, thermal stability and the biocompatibility of the composites.

A commonly used HA for fillers in the polymer matrix composite is synthetic HA produced from the chemical reaction between ammonium phosphate [$(NH_4)_2HPO_4$] and calcium hydroxide [$Ca(OH)_2$]. It is widely used as a filler in thermoplastic materials, such as high-density polyethylene (HDPE) (Parra, Gonzalez, & Albano, 2009). However, synthetic HA is expensive to produce, and its quality is difficult to control. Biological sources of HA, such as fish scales, fish bones, bovine bones, teeth and bones of pig, are alternatives to synthetic HA (Mondal, Bardhan, Mondal, Dey, Mukhopadhyay, Roy & Roy, 2012). Fish waste, especially fish scales, is a good source of natural HA because it contains 50% by weight of scale. Fish scales are also abundant in valuable organic components, such as collagen (Sankar et al., 2008). The preparation of HA from fish scales is biologically safe, economical and biocompatible (Zainon et al., 2012). Jaafar et al., (2017) reported the use of natural HA powder (HAp) from fish scales as a filler in HDPE (Aiza, Jaafar, Zainol, & Mohd Amin 2017).

Several reports focused on the application of LNR on modified epoxy but none on modified epoxy/FsHA composites. Meanwhile, reports on the application of natural HAp from fish scales as a filler to enhance the mechanical and biological properties of epoxy resin are also lacking. Furthermore, LMG30 has yet to be prepared using oxidative degradation. In the present study, LMG30 was prepared using two methods, namely, photodegradation and modified oxidative degradation. Thus, this study aims to produce an epoxy/FsHAp composite modified with liquid rubber (LMG30) to improve the mechanical and biological properties of epoxy/FsHAp composites. Toughened epoxy/FsHAp composites have potential biomedical applications, such as in artificial limbs.

1.3 Research Objectives

The objectives of this study are as follows:

1. To prepare liquid poly (methyl methacrylate) grafted rubber (LMG30) via modified oxidative degradation and photodegradation.

2. To optimise natural hydroxyapatite (FsHAp) filler loading and LMG30 as toughness agents in the production of epoxy composites.

3. To characterise the physicochemical and mechanical properties of epoxy/FsHAp/LMG30 composites.

4. To examine the surface morphology of fractured epoxy/FsHA/LMG30 composites.

5. To investigate the cytotoxicity of epoxy/FsHAp/LMG30 composites.

1.4 Significant of the Study

HA has been used as a biomaterial because of its excellent biocompatibility properties (Pramanik, Mishra, Banerjee, Maiti, Bhargava, & Pramanik, 2009). HA is also a bioactive substance which forms a strong chemical bond with the host bone tissue; hence, it is a good bone graft material. HA bioceramics have several applications, such as in bone tissue engineering, bone void fillers for orthopaedic, traumatology, spine, and maxillofacial, dental surgery, orthopaedic and dental implant coating and desensitising agent in post teeth bleaching (Fouad, Elleithy, & Alothman, 2013).

HA is usually synthesised via chemical reactions, such as chemical precipitation (Ungureanu, Angelescu, Ion Stoian, & Rizescu, 2011). However, the high manufacturing cost associated with the chemicals used in the synthetic process has led to a new production approach. In this study, FsHAp was extracted from fish scales to reduce the production cost. Moreover, high-molecular-weight poly (methyl methacrylate) grafted NR (MG30) was depolymerised into low-molecular-weight MG30 (LMG30) as a potential toughening agent for polymeric materials. In this study, LMG30 was prepared via two methods, photodegradation and modified oxidative degradation.

The natural materials FsHAp and LMG30 are low cost and biologically safe for human body; thus, they are suitable for medical device applications and halal sources for Muslims around the world.

This study is significant to the research development that expands the information and application of epoxy in biomedical applications by toughening the matrix by adding liquid rubber to enhance the impact properties of epoxy/FsHAp composites. The new epoxy/FsHAp/LMG30 composites with good mechanical and biocompatibility properties are suitable for medical devices.

This study will open the pathway for many future studies in biomedical applications, considering that reports about the use of LMG30 to enhance the toughened properties of epoxy/FsHAp composites are lacking.