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Effect of Hydroxyapatite on Structure, Morphology and Tensile Properties of Polyethylene/Starch Blend

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A B S T R A C T

Linear low-density polyethylene (LLDPE)/starch blends filled with hydroxyapatite were synthesized by injection moulding to study the effect of hydroxyapatite (HAp) on surface modification of polyethylene/starch blend and its influence on tensile properties. Hydroxyapatite contents were varied from 1.0% to 3.0% in intervals of 0.5% by parts and the blends were characterised. Seven different samples were formed for the study and each sample was tested in five replicates for the tensile modulus, strength and elongation to failure. Two of the samples, one composed of only LLDPE and the other of 60% LLDPE, 40% starch, and 0% hydroxyapatite, were used as controls. The 2Theta peak transpositions of the XRD patterns, crystallinity and microstructure of the blends have been noticed to affect the tensile strength, modulus, and elongation to failure. The incorporation of HAp content into LLDPE/starch returned an increase in strength from 11.05±0.3 to 11.98±0.2 ($p = 0.0008$). Modulus increased up to 2.0% by parts of HAp and declined. Conversely, elongation to failure declined up to 2.0% by parts of HAp and then increased ($p = 0.0007$). HAp influence on the blend has been explained as HAp having affected the intermediate phase of the blend through hydrogen bonding. Amount of HAp introduced into the blend affects the structure, morphology and tensile properties of the blends. Further study is needed to determine the degradation characteristics of the blends.

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Introduction:

Polymer-starch blends present immense potential for applications in bone replacement implants, bone cements, drug delivery systems and tissue engineering scaffolds (Arutchelvi et al., 2008; Guo & Ait-Kadi, 2002; Marques, Reis, & Hunt, 2002). In applications such as bone fixation, bio-base biodegradable materials are more desirable than biodegradable materials since bio-base polymers have controlled degradation. Biodegradable materials from low molecular weight polymers degrade faster and pose danger to physiological systems. Attempts have been made to blend starch with high molecular weight polymers since starch is totally biodegradable and inexpensive compared to other biodegradable polymers such as polyglycolic acid (PGA), polylactic acid (PLA) and polyhydroxybutyrate (PHB) (McGlashan & Halley, 2003; Yu, Dean, & Li, 2006; Zhang & Fazeli, 2010). Starch has been adopted as a filler of polyolefin in concentrations as low as 6 – 15% (Lu, Xiao, & Xu, 2009) but such a system is partially biodegradable and not feasible for biomedical application. This is because incorporating such low amounts of starch does not promote biodegradability of the implant. Enhancing the biodegradability of polyolefin (polyethylene) has been investigated by incorporating 40% starch to a carbon-carbon backbone matrix (Alberta Araújo, Cunha, & Mota, 2004). This increases the surface area available for attack by microorganisms thus promoting

biodegradation (Arutchelvi et al., 2008; Avérous, 2004; Vroman & Tighzert, 2009).

Since starch is hydrophilic, as opposed to polyethylene that is generally hydrophobic, there are poor starch-polymer interfacial interactions with a resultant loss of mechanical strength in starch-filled polymer blends (Matzinos, Bikiaris, Kokkou, & Panayiotou, 2001; Sailaja & Chanda, 2001). This behaviour in phase separation may arise from saturated hydrocarbon polymers that interact only through dispersive, van der Waals forces (Lohse, 2005). In other words, high surface energy between the hydrophobic polymer and hydrophilic starch yields a low degree of adhesion (Fabunmi, Tabil, Chang, & Panigrahi, 2007) and results in immicibility or incompatibility. In a perfect adhesion state, loading stresses are transferred to the filler phase without any reduction in the effective surface area (Fabunmi et al., 2007). However, a stronger interaction between the starch granules and the polyethylene matrix can be achieved with gelatinized or destructive starches or in the chemically modified form (Fabunmi et al., 2007) by addition of stabilisers or compatiblisers (Grample, 1995; Guo & Ait-Kadi, 2002; Matzinos et al., 2001; Siročić, Hrnjak-Murgić, & Jelenčić, 2012; Tokiwa, Calabia, Ugwu, & Aiba, 2009). The problems with chemical stabilisers are that, they may either be toxic to organisms or slow down the rate of biodegradation of the material (Arutchelvi et al., 2008). It is therefore important to control phase separations and fabricate single phase blends for biomedical applications. Bioactive filler such as hydroxyapatite (HAp) which forms a major inorganic portion of bone can be introduced to improve tensile properties of the polymer (Bang Lee, Khang, & Ho Lee, 2000). Apatite also has biocompatibility with several cell types such as osteoblast, fibroblast and periodontal ligament cells that are found in calcified tissues. Several studies have shown the bone bonding ability of HAp and this material has been evaluated as reinforcing agent with polymers such as HDPE, PLLA, PMMA, PHB homopolymer, P (HB-HV) copolymers, starch and poly-ester-ester to form bioactive compounds (Correlo et al., 2005).

As part of a broader objective to characterize biodegradation of linear low-density polyethylene (LLDPE)/starch (40%) blends filled with hydroxyapatite for bone fixation. It is important to first determine the amount of hydroxyapatite required to produce miscible blends and the effect of HAp incorporation on the blend structure, morphology and mechanical properties since biodegradation could be inferred from these parameters. The blends were synthesized using injection moulding. Injection moulding was selected over extrusion because during processing of native starches, the semicrystalline structure, as present in the starch granules is melted and destroyed (van Soest, Hulleman, De Wit, & Vliegenthart, 1996). Extrusion changes the double helical A-type, B-type, or C-type structure of starch to a single helical structure (van Soest et al., 1996) and then completely destroys the crystallinity (Sriburi, Sandra, & Fiona, 1999), hence negatively affecting the mechanical properties (Matzinos et al., 2001).

Materials and Methods:

Materials:

Linear low-density polyethylene, melt flow index of 2.16 g/10 min at 190 °C, provided by SEEKTEC Honam Petrochemical Corp (Seoul, Korea) was used. Cassava starch (*Manihot esculenta crantz*) of 17% amylose content was purchased from the Ghanaian local market. Hydroxyapatite was extracted from cortical bovine bone.

Blend Preparation:

The bovine bone was cleaned, soaked in 10% sodium hypochlorite for 24 h, rinsed in water and boiled in 5% sodium hydroxide for 3 h. It was then incubated in 5% sodium hypochlorite for 6 h, washed and soaked in 10% hydrogen peroxide for 24 h. The material was subsequently sintered at $1100\,℃$ and pulverised and then sieved to particle size $\leq 60\ \mu m$ (Rodrigues et al., 2003). DPE/starch/hydroxyapatite blends were obtained by measuring different quantities of 60% LLDPE, 40% starch and 1.0%, 1.5%, 2.0%, 2.5%, 3.0% by parts of hydroxyapatite in a volumetric flask. The measured powders were blended in a Kenwood blender for 4 min. The powders were then transferred into the hopper of a plastic injection moulding machine (designed and manufactured by JB Engineering (Chippenham) Ltd). The experimental moulding temperature was 170 °C and the setting time was 4 min. LLDPE alone and LLDPE (60%) / starch blends were used as controls.

Characterization:

X-ray diffraction and scanning electron microscopy (SEM) were used to characterize samples. Specimens were cut at the middle cross-section and the (new) surfaces were placed on a stub. The magnification was X920 in all cases and specimens were observed with a ZEISS EVO-500 SEM. The phases of the specimens were studied using a PANalytical Empyrean X-ray diffractometer, equipped with a Cu K_α X-ray radiation. The diffraction patterns were recorded over 2θ angles ranging from $5°$ to $90°$ and crystallinity calculated using HighScore (Plus) 4.0. The average crystallite size of the hydroxyapatite was calculated from the diffraction patterns using the Scherrer's equation (Ravi Krishna, Gerraar Eddy, & Derek, 2013).

$$t_{(hkl)} = \frac{0.9\lambda}{B cos\theta_{(hkl)}} \qquad (1)$$

where λ is the wavelength of the x-ray radiation, B is full width at half maximum (FWHM) of the peak at maximum intensity, $\theta_{(hkl)}$ is the peak diffraction angle

that satisfies the Bragg law for the (h k l) plane and $t_{(hkl)}$ is the average crystallite size.

Determination of Tensile Properties:

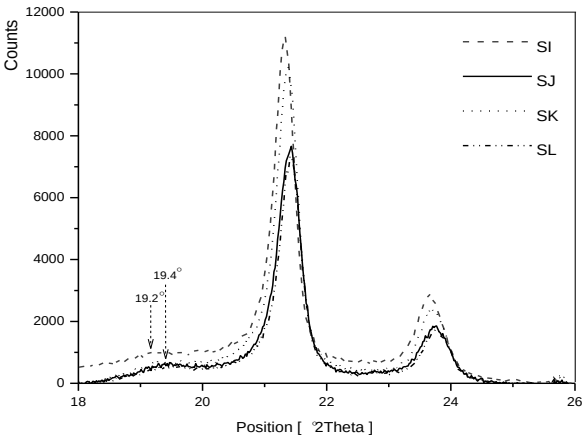
Tensile modulus in dry state was measured using ISO 527 -1B (X Head) cylinder measurement at 23 ± 2 ℃, grip distance of 40 mm long, diameter of 5 mm and pretension load of 1.00 N. The cross head speed was 5 mm / min. Five measurements were conducted for each sample, and the results were averaged to obtain a mean value.

Results:

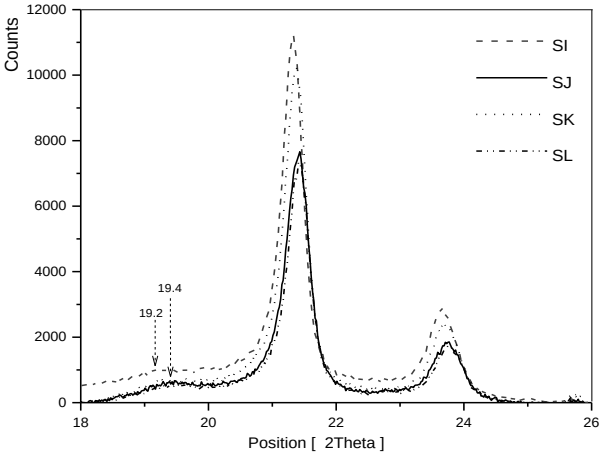
X-ray Diffraction:

XRD patterns of the samples are shown in Figure 1. Unmoulded LLDPE has two major peaks at 2Theta = 21.5° and 23.8° which reflect the orthorhombic unit cell but when processed the moulded LLDPE major peaks appeared at 2Theta = 21.4° and 23.7° with a minor peak at 2Theta = 19.5° (SP in Figure 1. (a)) which shows presence of monoclinic phase.

Cassava starch exhibits a semi-crystalline structure, the crystalline region is assigned to the well-ordered structure of amylopectin molecules inside the granule with typical crystallinity peaks of A- type, C-type or a mixture pattern with three major peaks at 2Theta = 15.1°, 17.1° and 23.6°. Incorporation of cassava starch into LLDPE shifted the 2Theta position from 19.9° to 19.5° (SS in Figure 1 (a)). Introduction of 1.0% by parts hydroxyapatite of crystallite size of 38.4 nm into the blend further shifted the 2Theta peak position of 19.5° to 19.1° (see SH in Figure 1 (a)). Addition of 1.5% and 2.0% by parts of hydroxyapatite into the blend shifted the 19.1° 2Theta peak position to the right; 19.2° and 19.4°, respectively (Figure 1 (b)). Addition of 2.5% and 3.0% of hydroxyapatite shifted the peak back to lower angles. The peak positions with their corresponding crystal structures and percentage crystallinity of the diffraction patterns of Figure 1. are shown in Table 1**.** The peak intensities of all the blends were lower than that for pure LLDPE.



(a)



(b)

Figure: 1. XRD patterns of (a) SP: moulded LLDPE, SS: LLDPE/starch (60/40 w/v) blend and SH: SS filled with 1.0 % by part of hydroxyapatite (b) XRD patterns of LLDPE/starch blend filled with w/v % by parts of hydroxyapatite particles, SI: 1.5, SJ: 2.0, SK: 2.5, SL: 3.0

Table: 1. Diffraction data (peak positions for identified crystal structures) for LLDPE and LLDPE/starch hydroxyapatite blend samples

Sample codes	Monoc	Ortho	Mono	Ortho	Crystallinity (%)
SP	19.9	21.3	-	23.6	56.98
SS	19.5	21.4	23.5	23.8	42.88
SH	19.2	21.5	23.7	23.8	38.96
SI	19.2	21.3	-	23.6	44.02
SJ	19.4	21.4	-	23.7	52.13
SK	19.2	21.4	-	23.7	52.29
SL	19.3	21.4	23.8	23.9	52.29

Scanning Electron Microscopy (SEM):

The morphology of the composites under scanning electron microscopy was studied in order to determine the surface texture aggregation reinforcing phase. Figure 2 compares the surface topology of the moulded LLDPE and that of the LLDPE/starch blend. Figure 2 (a) shows the surface of the moulded pure LLDPE. It can be seen in Figure 2.0 (b) that addition of 40% hydrophilic starch into LLDPE produced a differential swelling of the surface. Addition of 1.0% by parts of hydroxyapatite to the blend reduces the surface swelling (Figure 2 (c)).

Increasing the mineral content from 1.0% to 1.5% and to 2.0% by parts caused depressions on the surface which resulted in a spongy topology (Figure 2 (d) and (e)). Further increase of minearal content from 2.0% to 2.5% showed wider depressions in the surface and this resulted in creating dents with perforations and microcracks at the surface (figure 2 (f)). Finally increase in hydroxyapatite content from 2.5% to 3.0%

resulted in a multiphase structure which is an indication of immiscibility (see Figure 2 (g)).

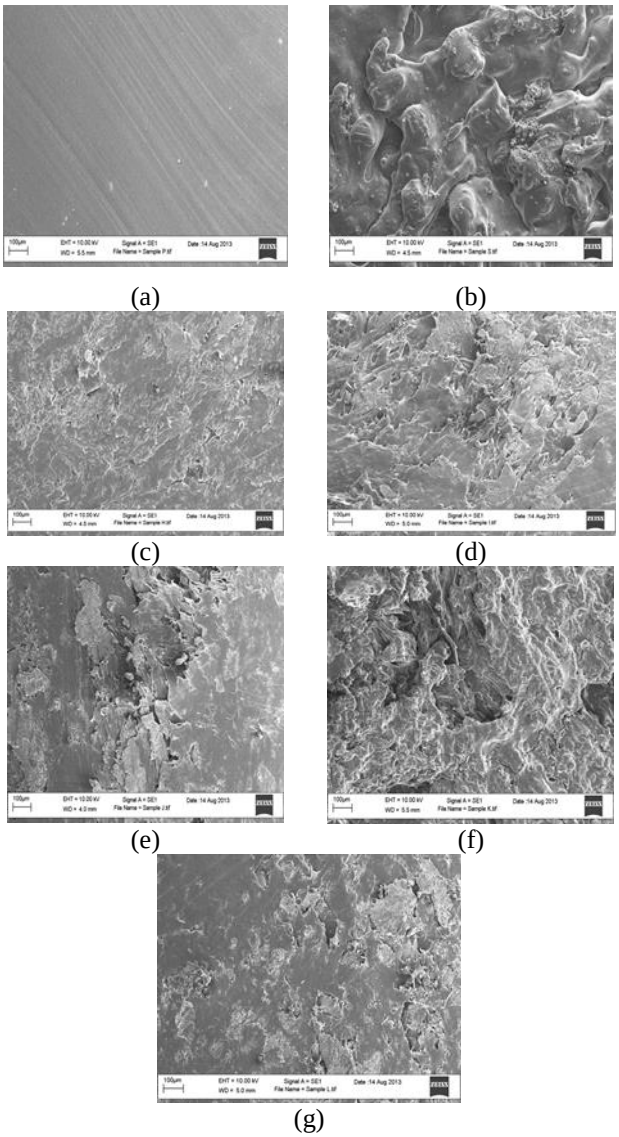


Figure: 2. SEM micrographs of (a) pure LLDPE (b) LLDPE/starch blend containing (60%) LLDPE and (40%) starch (c) – (g) LLDPE/starch blend filled with 1.0%, 1.5%, 2.0%, 2.5%, and 3.0% by parts hydroxyapatite, respectively.

Tensile Properties:

The tensile strength, tensile modulus and the elongation at break of the LLDPE, LLDPE/starch blend and blends filled with hydroxyapatite are shown in Figure 3 and Figure 4. The tensile modulus of the LLDPE/starch blend is highest and almost twice the modulus of LLDPE alone.

Introduction of the hydroxyapatite into the blend improves tensile strength and modulus indicating significant change in the means of the tensile strength and modulus ($p<0.05$). The percentage elongation has an inverse relation with the tensile modulus. Increasing modulus decreases elongation.

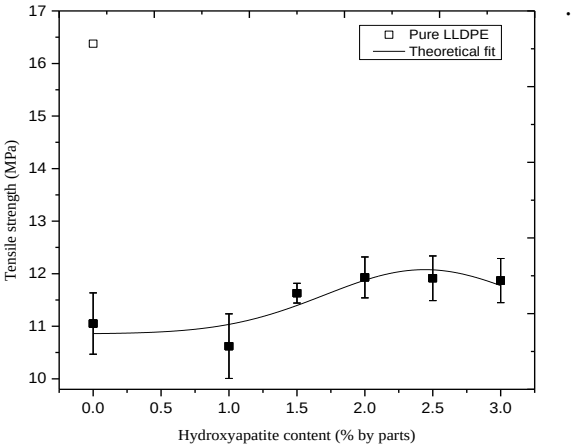


Figure: 3. Variation of tensile strength with hydroxyapatite content. Adj. r square value: 0.49234.

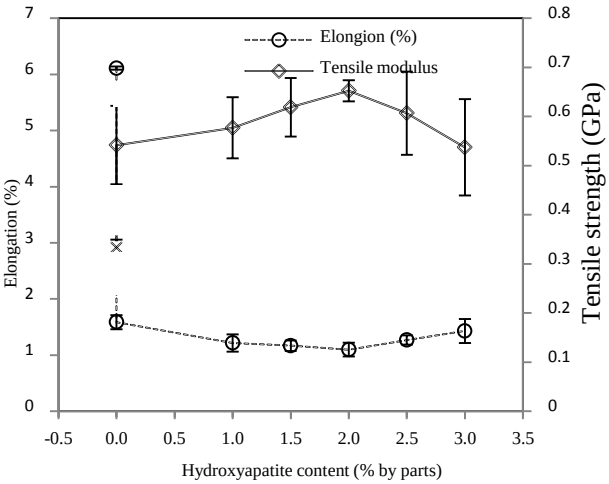


Figure: 4. Tensile modulus and elongation at break versus hydroxyapatite content. × and ● mark the tensile modulus and elongation at break of pure LLPDE, respectively. Adj. r square value for modulus: 0.89316 and for elongation: 0.94667.

Discussion:

The tensile strength, tensile modulus and elongation at break of the moulded LLDPE, LLDPE/starch blend and LLDPE/starch blend filled with hydroxyapatite shown in Figure 3 and Figure 4 depended on percentage crystallinity, 2Theta peak transposition and morphology. The tensile strength of the moulded LLDPE is high, compared to the blended samples. Tensile strength of a material is greatly affected when a material undergoes small or large scale plastic deformation. The crystallinity and lattice planes of the material are altered, thus returning high tensile strength values. The blending of starch and LLDPE reduced crystallinity and introduced more amorphous phases into the LLDPE (see crystallinity (%) in Table 1). This occurred because starch has a semi-crystalline structure with high amorphous phase content; due to the presence of amylose (van Soest et al., 1996). The

reduction of percentage crystallinity resulted in the reduction of tensile strength of LLDPE. Introduction of hydroxyapatite into the LLDPE/starch blend showed increase in crytallinity (Table 1) and improved tensile strength (Figure 3). Varying HAp content in the blend increased the tensile strength to 2.0% by parts after which the strength stabilized. Incorporation of Hap did not give strength values comparable to that of LLDPE probably due to the fact that inclusion could not cause large enough lattice deformation. Inter lamellar slip/rotation was evidently not achieved. Russel (Russell, Hunter, & Heyding, 1997) reported that large strain deformation leading to high tensile strength could be achieved by applying excessive trauma (tension or compressive) to PE.

The 2Theta peak transposition of the XRD patterns has been noticed to affect the tensile modulus of the blends. Introduction of starch into LLDPE stretched the LLDPE lattice and the 2Theta peak positions were translocated. This result might be due to starch flowing through the amorphous phase of LLDPE resulting in interlamellar separation (Nikolov & Issam, 2000). The interlamellar separation caused the peak transpositions and resulted in evolvement of the second monoclinic phase of LLDPE (Table 1). The evolvement could be likely responsible for the higher modulus of LLDPE/starch blend. The interlamellar separation of the amorphous tie chains in blends could also be explained using the SEM micrograph in (Figure 2 (b)). The swelling shown in the micrograph results from high surface tension existing between the intermediate phase of LLDPE/starch blend and was due to non-covalent bonding between the starch molecules and attributed to the presence of the hydroxyl group of starch (Hoque, Ye, Yong, & Mohd Dahlan, 2013). Amylose has inherently absorbed water molecules which are liberated under high temperature and pressure and this was observed during processing.

Even though the introduction of small amounts of hydroxyapatite in the blend did not produce large lattice deformation, its role might be to improve the intermediate phase of the blend through hydrogen bonding and this might affect the rate of degradation of the blends. Addition of 1.0% by parts of hydroxyapatite reduces surface tension. Percentage crystallinity declined and tensile strength decreased. This retrogression is suspected to be due to hydroxyapatite elongating amorphous tie chains of the blend (Figure 1 (a) for pattern stretching), in effect enhancing tensile modulus. The SEM micrograph in Figure 2 (c) shows the disappearance of the surface swelling and that confirms a reduction of the surface tension of the blend.

Reduction of interfacial surface tension is characteristic of a compatiblizer. The surface tension depended on layer thickness by Alamo. et al , 1994. Addition of 1.5% and 2.0% by parts content of hydroxyapatite showed improved interactions at the blend surface. The spongy morphology in (Figure 2 (d) and (e)), respectively is believed to be a result of interactions between the hydroxyl groups of hydroxyapatite and the hydroxyl groups of LLDPE/starch. The blends were miscible and gave relatively high tensile strength and tensile modulus. The blends containing 2.5% and 3.0% by parts hydroxyapatite did not show much improvement in tensile strength. Rather, there was a decline in modulus for samples with 2.0% by parts hydroxyapatite. The XRD results in (Table 1) show that as hydroxyapatite content increased, crystallinity of the blend also increased. The high crystallinity is suspected to have decreased the intermediate phase volume fraction and thus increased the surface tension. This reason is in line with the explanation from Alamo. et al for polyethylene (Alamo, Londono, Mandelkern, Stehling, & Wignall, 1994) **.** The high surface tension resulted in wider depressions in the surface thus creating dents with perforations and microcracks at the surface (SEM micrograph in (Figure 2 (f)). The SEM micrographs of the blend showed immiscibility.

Percentage elongation at break of moulded LLDPE is highest. Incorporation of starch into LLDPE reduced the elongation at break. Elongation is highly sensitive to the interface state of the blends. The elongation at break which decreased with the starch content could be attributed to the phenomenon that the starch containing hydroxyl groups on its surface is highly hydrophilic, whereas LLDPE is nonpolar. This reason is similar to the explanation for the behaviour of sago starch mixed-LDPE (Hoque et al., 2013) at higher starch contents, filler-filler interaction becomes more pronounced than filler-matrix interaction which reduces the effective cross-sectional area of the polymer sample caused by the presence of starch and hence the effective stress experienced by the matrix is essentially higher in LLDPE.

Conclusion:

LLDPE/starch blends have been synthesised by injection moulding. The blends showed higher tensile modulus than the moulded LLDPE alone but compromise in tensile strength. The high modulus was attributed to the structure evolvement of the monoclinic phase of LLDPE due to starch flow in the amorphous phase of LLDPE. In order to improve the tensile properties of the blend for bone fixation application, hydroxyapatite was introduced as a compatiblizer to enhance the intermediate phase through hydroxyl group interactions. The results obtained show that the structure, morphology and tensile properties of the blends are dependent on the amount of hydroxyapatite introduced into the blends.

Introduction of 1.0% by parts of hydroxyapatite does not affect the cystallinity but is rather suspected to elongate amorphous tie chain of the LLDPE and then enhance the tensile modulus. Further increase of hydroxyapatite to 1.5% and 2.0% by parts increases the crystallinity, and results in improvement in the tensile

properties. The introduction of 1.5% by parts of hydroxyapatite into the blend provided the required intermediate thickness to mediate the blend thereby improving tensile properties.

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