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Dynamic mechanical properties of hydroxyapatite-ethylene vinyl acetate copolymer composites

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Abstract

Dynamic mechanical thermal analysis (DMTA) was carried out to explore the dependence of temperature on the viscoelasticity of composites consisting of synthetic hydroxyapatite (HAP) particulate filled ethylene vinyl acetate copolymer (EVA). Two forms of HAP, differing in their surface characteristics and particle size, were used for the study. The freeze-dried HAP (FDHAP) had a mean particle size of 49.18 μm and an irregular surface morphology. In the contrary the spray dried form of HAP (SDHAP) had a mean particle size of 5.84 (m and a spherical morphology. The dynamic mechanical analysis of the composites showed that both, particle size and morphology, had a significant effect on viscoelastic properties. A tremendous increase of the storage modulus was noted with the addition of HAP. Above the T_g of the polymer matrix, the values were marginally higher for the composites containing FDHAP than for those with SDHAP. The damping (tan δ) was found to decrease with the inclusion of HAP. A marginal upper shift in the value of the glass transition temperature (T_g) was observed for the composites fabricated from SDHAP indicating a slightly strong interaction between this HAP and the EVA matrix.

Keywords: Composite materials; Cranioplasty; Dynamic mechanical analysis

1. Introduction

Bone is a natural composite material consisting mainly of a mineral phase, hydroxyapatite (HAP) and a protein phase, collagen [1]. This makes the bone viscoelastic within the range of physiological loading, providing an important energy dissipating mechanism during deformation. Studies have shown that viscoelastic properties of bone can play a significant role in high impact type fractures [2,3]. Furthermore, considering that the majority of head injuries occurs under dynamic conditions, such as accidents or sporting activities for the young and falls for the elderly [2,4], it is important to understand the dynamic mechanical behaviour of the cranioplastic analogue. It is hence rightly hypothesized that the existence of viscoelasticity should be recognized as an essential feature of an optimized prosthetic material for bone [5].

Over the past decade there has been a fabulous growth in the development of HAP–polymer composites for hard tissue augmentation. The key interest in these materials grew because composites for specific applications could be easily tailored by appropriately varying the polymer matrix as well as the reinforcing material [6–8]. Hydroxyapatite filled ethylene vinyl acetate copolymer (EVA) composite is a novel material that has been designed for cranioplastic applications [9]. The unique combination of bioactive ceramic HAP and thermoplastic elastomer EVA imparts the composite two distinctive advantages: (1) the presence of HAP improves the mechanical properties of the composite and also makes the composite bioactive, (2) the presence of EVA would render the composite malleable and facilitate precise sculpting of the composite according to the defect formed/created in the skull. This makes the composite an attractive material as a cranioplastic analogue. However, composites based on

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thermoplastic polymers are viscoelastic and the mechanical properties are temperature and strain rate dependent. Furthermore, the response of the material under dynamic conditions cannot be predicted by quasi-static tests alone. The study of response of the material under dynamic loading thus becomes essential for the overall mechanical characterization.

In this study, a dynamic mechanical thermal analyzer (DMTA) has been used as a tool for investigating the viscoelastic properties of HAP–EVA composites. DMTA measures the response of a material to sinusoidal stress over a range of temperature and frequencies, and it is sensitive to chemical and physical structures of polymers and their composites [10]. The main variables obtained from DMTA are the storage modulus (E'), which represents the elastic component, the loss modulus (E'') representing the viscous component, and tan δ (the damping factor), given as the ratio of E''/E' [11]. The study presented here investigates the effect of HAP particle size on the viscoelastic properties of EVA matrix. Two grades of HAP particles, which differed with respect to both size and morphology, were utilized for the study. Scanning electron microscopy was also employed to gain an insight into the nature of interaction between the polymer matrix and HAP.

2. Experimental

2.1. Materials

Cryogenically ground EVA powder with particle size less than 300 μm and a vinyl acetate content 28 wt.% was procured from Shriswasan Chemical (M) Pvt. Ltd., Mumbai, India (Table 1).

Hydroxyapatite was synthesized by the precipitation reaction between ammoniated calcium nitrate and dihydrogen ammonium phosphate according to the established procedure [12]. The precipitated HAP was washed to remove soluble by products and converted into powder form. Two techniques of powder preparation were adopted: (1) freezing and drying technique and (2) spray drying technique. In the freezing and drying technique, the precipitated HAP was froze in a laboratory model freeze drier and dried in air oven at 100 °C for 24 h. The oven-dried HAP was ground to 125 μm or less in radius of secondary particles. The HAP prepared by this technique is designated as FDHAP. In the spray drying technique, the precipitated HAP was converted into slurry and spray dried in a laboratory size spray drier (Buchi Mini Spray Drier, B-181, Switzerland), with a maximum through put of dry air 35 m^3/h and at a chamber temperature 90–92 °C. The HAP prepared by this technique is designated as SDHAP.

2.1.1. Characterization of hydroxyapatite

The HAP powder was characterized for the particle size using a Malvern Mastersizer 2000 particle size analyzer (Malvern Instrument, UK). The morphology of HAP powder was observed using a scanning electron microscope (JOEL JSM-5400). Chemical analysis of the as prepared FDHAP and SDHAP was performed to confirm the molar Ca/P ratio. The calcium content was estimated by substitution titration method using 1,2-diaminoethanetetra-acetic acid (EDTA) solution. Phosphovanadomolybdate method was used to determine the phosphorous content. The bright yellow phosphovandatemolybdate complex formed between the phosphate, ammonium vanadate and ammonium molybdate was estimated spectrophotometrically in the absorbance range 460–480 nm [13]. The infra-red data of FDHAP and SDHAP, calcined at 300 °C for 3 h in a muffle furnace, were collected using a Nicolet Inc. (Madison, USA) model Impact 410 FTIR spectrophotometer. The phase consistency and crystallinity of the HAP powder was analyzed by X-ray diffraction technique. The measurement was performed on Siemens D5005 X-ray powder diffractometer, with computer data acquisition facility and the diffraction data was compared with Joint Committee for Powder Diffraction Standards (JCPDS) Data Sheet for HAP (9–432).

2.2. Preparation of composites

Composites with 40 vol.% of HAP were prepared for this study. Prior to preparation of the composites, both forms of HAP was dried in an air oven at 100 °C for 2 h and stored in desiccators. Measured quantities of the polymer and hydroxyapatite were dry blended in a domestic mixer. This blend was then melt-mixed in a Polylab Haake torque rheometer (Thermohaake, Germany) attached with a 120 cm^3 mixing chamber. The mixing chamber was provided with counter-rotating cam rotors. The temperature of mixing was 120 °C, and the rotor speed employed was 40 rpm. The composite chunks obtained at the end of mixing were sheeted out by passing through a laboratory model two-roll mill. It was then compression moulded into sheets of 2 mm thickness. The composite fabricated from FDHAP is designated as c-FDHAP, and that from SDHAP is given as c-SDHAP.

2.3. Dynamic mechanical thermal analysis

Dynamic mechanical thermal analysis was carried out using a DMTA instrument (Eplexor 150N Gabo Qualimeter, Ahlden, Germany) under oscillating tensile loading. Rectangular bars of the dimensions 10 mm × 6 mm

Table 1
Properties of EVA (Shriswasan Chemical (M) Pvt. Ltd., Mumbai, India)

Density (mg m^{-3})	Vinyl acetate (wt.%)	Melt flow rate (g/10 min)	Tensile modulus (MPa)	Yield strength (MPa)	Elongation to fracture (%)
0.95	28	25	12	9	1800