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Original Article

Development and Characterization of PLA/Bioactive Glass Composite Filament for Biomedical Applications

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Abstract *- The use of composite materials has seen a significant improvement in the biomedical field, especially in bone regeneration. Polymer ceramic composites are ideal, as polymer provides mechanical stability while ceramic fillers enhance the bioactivity of the composite. In this work, the matrix material is PLA (polylactic acid), and the ceramic is BG45S5(bioactive glass). Bioactive glass powder is manufactured using the sol-gel technique. Ceramic filler is added in a weight proportion of 2.5%,5% and 10%, respectively, to the polymer matrix, and the resultant filament is obtained by using a desktop extruder. Filaments are extruded with a diameter of 1.75±0.02mm. The physiochemical, thermal characterization and mechanical testing of composite filaments are performed to evaluate their application for 3d printed scaffolds. The morphological study reveals the distribution of bioactive glass particles in a polymer matrix supported by XRD and FTIR results. The addition of 2.5 % bioactive glass content has led to an increase in thermal stability but has decreased with higher concentrations. The stiffness of the composite filaments has increased with the addition of bioactive glass powder, but there is a reduction in tensile strength. PLA-Bioactive glass composites have been fabricated successfully, and results indicate their potential use in 3D printed scaffolds.*

Keywords *- Bioactive glass, Polylactic acid, Biomedical applications, FTIR, Glass Composite.*

1. Introduction

There has been a rapid increase in bone defects in recent years because of accidents, surgeries and bone-related disorders [1]. The self-healing property of bone can repair bone defects less than critical bone defect size provided a suitable environment is provided for its growth [3]. Bioactive glass developed by Professor Hench has been found to be bioactive, biocompatible and promotes bone growth [2]. Silicate-bioactive glasses are found to improve connectivity with host tissue [6]. Apart from these properties, bioactive glasses have excellent anti-bacterial properties [4], but due to their brittle nature, they cannot be used alone [5]. There is increasing popularity for polymer reinforced bioactive glass composites as they possess the bioactivity of bioactive glass and strength of polymers as metallic scaffolds suffer from stress shielding [7]. Polylactic acid (PLA) is considered to be a good choice as it has good biodegradability and compressive strength comparable to natural bone [8]. Many traditional manufacturing techniques were used to manufacture polymer bioactive glass composites. However, additive manufacturing has an advantage over them due to its ability to control pore size interconnectivity according to the requirements [9]. Fused deposition modeling is an additive manufacturing process in which thermoplastic polymers are heated, and the product is manufactured by the deposition of one layer over the other [10]. The advantage of fused deposition modelling is that it does not require any solvent, and customized parts can be produced according to the needs of the patient. [11]. In this study, PLA pellets are blended with bioactive glass 45S5 prepared by a sol-gel process and extruded to get composite filaments for 3D printing. The printed parts are examined for physical and mechanical characteristics.

2. Preparation and Methods

2.1. Preparation of 45s5 Bioactive Glass using Sol-gel Method

Bioactive glass 45 S5 of the composition of 45% Silicon dioxide, 24.5% Calcium oxide, 24.5% Sodium oxide, and 6% Phosphorous pentoxide is prepared by sol-gel method. For the preparation of 20 grams of glass powder, the following reagents are mixed in order. 1M of nitric acid is prepared, and Tetraethylortho Silicate (TEOS) is added in the required proportion and stirred for 1 hour with the help of a magnetic stirrer.

Tothis mixture, the Triethyl Phosphate (TEP), grams of calcium nitrate tetrahydrate and sodium nitrate were added and stirred for 45 minutes each according to the weight ratios elaborated in Sanaz Soleymani Eil Bakhtiyari et al. [12]. Figure 1 demonstrates the preparation of bioactive glass.

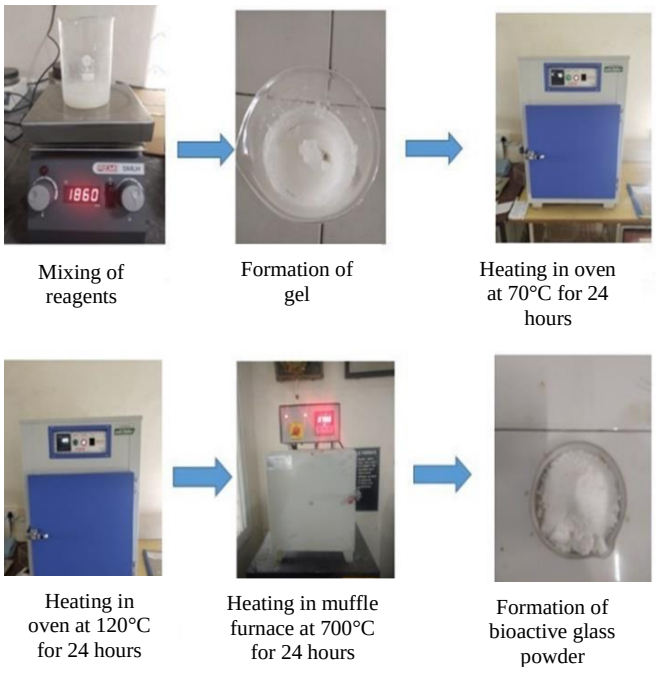

Fig. 1 Preparation of 45s5 bioactive glass powder using sol-gel method

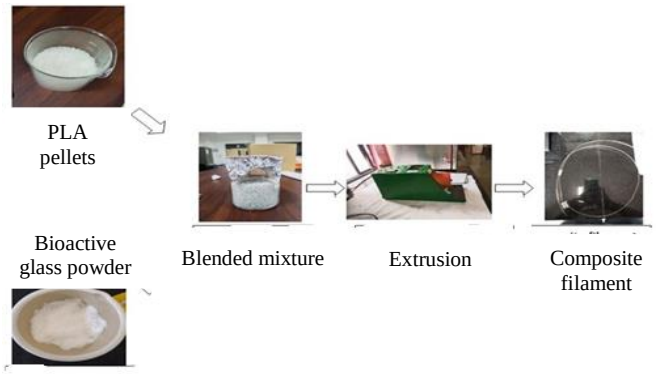

Fig. 2 Extrusion of composite filament

Fig. 3 Tensile testing of composite filament

2.2. Extrusion of PLA/BG Composite Filament

The composite filament is prepared by mixing polymer pellets and bioactive glass powder with a blender, and the resultant mixture is fed into a Filabot desktop filament extruder. Filaments with a uniform diameter of 1.75 mm are extruded at an extrusion speed of 6 rpm and extrusion temperature of 170◦C. Figure 2 shows the composite filament-making process.

2.3. Characterization of Bioactive Glass

2.3.1. FTIR of Bioactive Glass Powder

In order to determine the functional groups, present in the prepared sample, spectroscopy is performed using Jasco J-1500 spectrophotometer.

2.3.2. XRD Analysis of 45s5 Bioactive Glass Powder

X-ray diffraction analysis of the Sol-gel synthesized powder was done to analyze the peak pattern using Rigaku-Ultima IV under operating conditions of 40kV,30mA with K-beta filter and scanning speed of 2 deg/min.

2.3.3. FE-SEM of Bioactive Glass Powder

To study the microstructure, particle size, particle distribution, and composition of the samples, Field emission scanned electron microscopy is done with resolution 127eV and gold sputtering is done using Mn-kα Leica Microtome EM UC7.

2.4. Characterization of PLA-Bio Active Glass Composites

The physical characterization like FTIR, XRD, FE-SEM, and EDX is carried out similarly to the characterization of bioactive glass powder and thermal characterization like Differential Scanning Calorimetry is done by Shimadzu (DSC-60) subjected to nitrogen atmosphere with an increment of 10˚C/min from 30˚C to 450˚C with aluminum pan material, Thermal Gravity Analysis is done by Shimadzu (DTG-60) similarly with an increment of 10˚C/min with platinum pan material under nitrogen atmosphere.

2.5. Tensile Testing of Composite Filament

Tensile testing of composite filaments is done using ASTM D638 standard by BISS nano servo hydraulic universal testing machine. The gauge length of the filament taken is 100 mm, and the cross-head speed is 100mm/min. Figure 3 shows the tensile testing of the filament.

3. Results and Discussion

3.1. FTIR of Bioactive Glass Powder

Figure 4 shows the FTIR spectrum of the Bioactive glass. Si-o-Si stretching is observed at absorption band peaks at 922 cm^{-1} and bending vibration at 1035$cm^{-1,}$ respectively, which can be correlated with the literature [13]. The peak at 620 cm^{-1} indicates a P-O bond [14].

3.2. XRD of Bioactive Glass Powder

X-ray diffraction pattern reveals crystalline phases and

peaks corresponding to 24.55˚,27.58˚, 34.41˚,34.89˚,49.38˚ indicating major crystalline phase combetite ($Na_2Ca_2Si_3O_9$) (PDF #22.1455) [15]. Figure 5 shows the XRD pattern of Bioactive glass powder.

3.3. Morphology of 45s5 Bioactive Glass Powder

SEM and Edx images of bioactive glass powder are shown in Figure 6. SEM analysis shows uniform distribution and particle size ranging from 4.9 μm to 31 μm. Edx analysis shows the presence of all elements of Silicon, Oxygen, Calcium, Sodium and phosphorus in 45S5 bioactive glass composition.

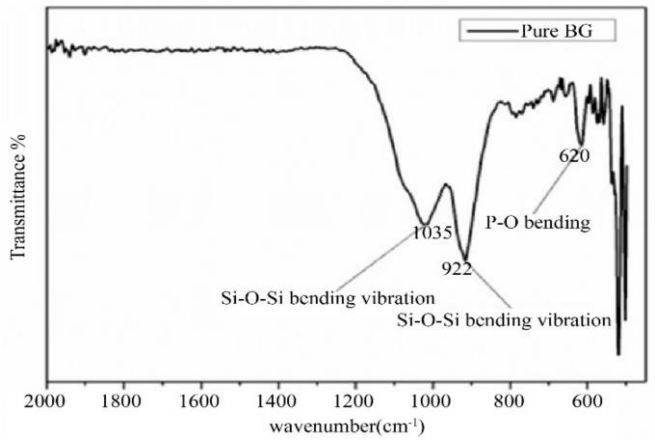

Fig. 4 FTIR spectra of bioactive glass

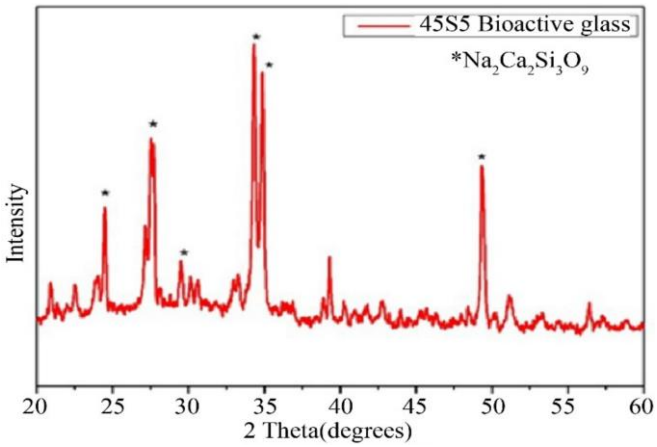

Fig. 5 XRD pattern of 45S5 bioactive glass

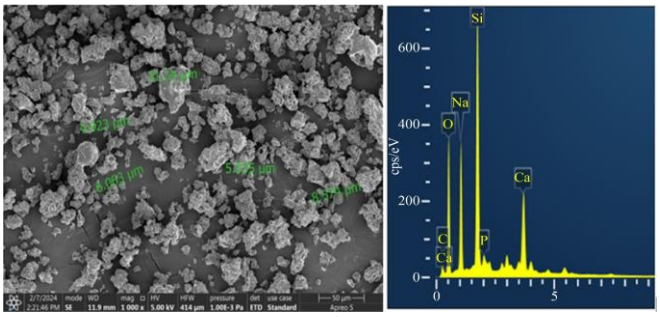

Fig. 6 SEM and Edx images of 45S5 bioactive glass powder

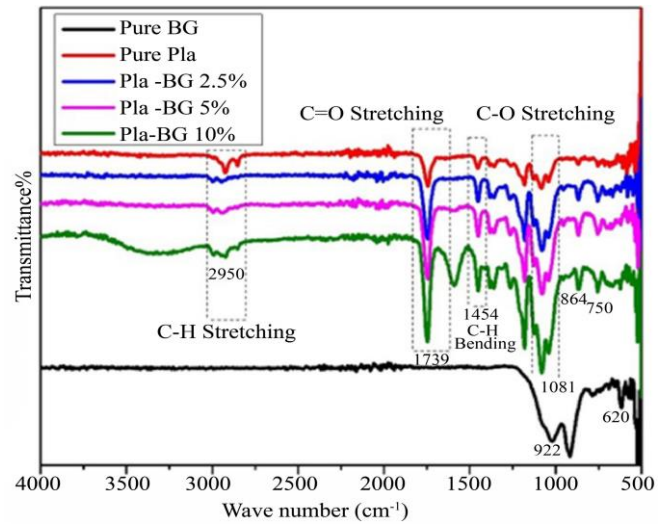

Fig. 7 FTIR analysis of PLA-bioactive glass composites

3.4. FTIR Analysis of PLA-Bioactive Glass Composites

Figure 7 shows FTIR spectra of PLA-BG composites with varying bioactive glass content of 2.5%,5% and 10%, respectively. The frequencies at 2950cm^{-1} indicate C-H stretching, 1739 cm^{-1} indicate C=O stretching, and 1081 cm^{-1} indicate C-O stretching, respectively, whereas the frequency at 1454 cm^{-1} indicates C-H bending of PLA [16]. The intensity of peaks corresponding to 922 cm^{-1} and 620 cm^{-1} has increased as the concentration of the bioactive glass increases, indicating the presence of bioactive glass powder in the polymer. Moreover, the increase in intensity at 1739 cm^{-1},1454 cm^{-1},1081 cm^{-1},864 cm^{-1},750 cm^{-1} with an increase in bioactive glass content indicates an increase in crystallinity of polymer and its interaction due to addition of bioactive glass.

3.5. XRD of PLA-Bioactive Glass Composites

Figure 8 shows the XRD of PLA and its composites. The X-ray diffraction pattern of extruded pure PLA indicates its semicrystalline nature.

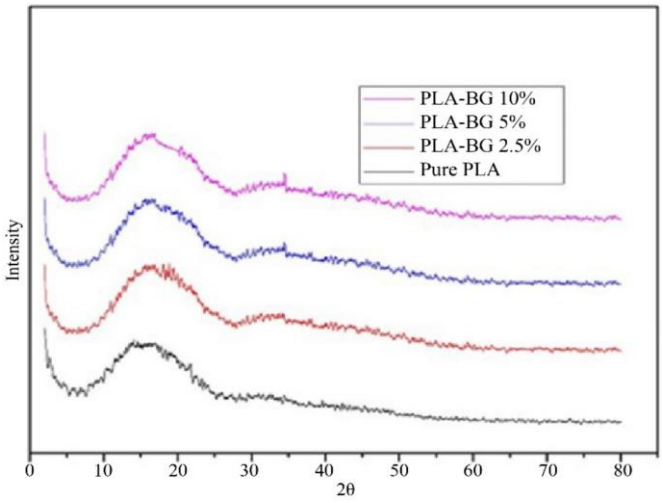

Fig. 8 XRD of PLA and its composites

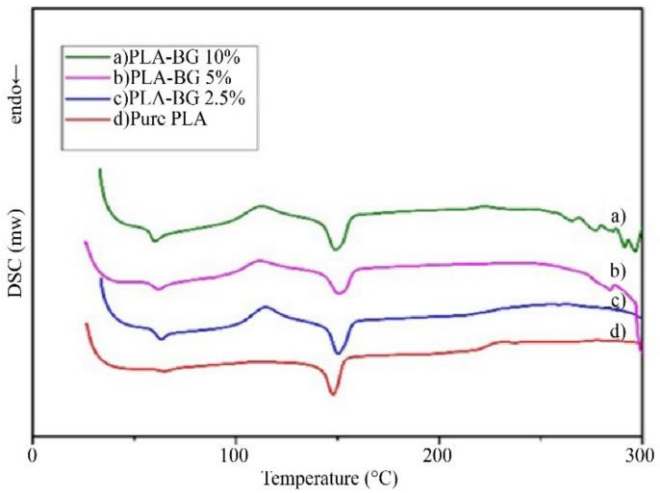

Fig. 9 DSC of PLA-BG composites

With the addition of bioactive glass content, the height of the significant peak has increased, indicating an increase in crystallinity and also a peak at 34.41˚ with an increase in intensity is seen with an increase in bioactive glass content, indicating the presence of bioactive glass particles which is in line with SEM results.

3.6. DSC of PLA-Bioactive Glass Composites

Figure 9 shows the differential scanning calorimetry of PLA-BG composites. It is observed that the glass transition temperature of the polymer is reduced as the Bioactive glass content is increased, which is beneficial in 3d printing, such as lower processing temperature, reduction in warping and distortion, improved printability, better adhesion and broader compatibility.

With the incorporation of bioactive glass, cold crystallization is evident at a temperature of around 112˚C, indicating an increase in the crystallinity of the PLA polymer. The change in the melting point of the polymer is insignificant.

3.7. TGA of PLA-Bioactive Glass Composites

Figure 10 shows a thermogravimetric analysis of PLA-BG composites. It is observed that the onset temperature of PLA with 2.5% bioactive glass compared to pure PLA has increased, improving the thermal stability of the polymer. Meanwhile, with higher concentrations of bioactive glass, such as 5% and 10%, the onset temperature has decreased, resulting in a decrease in the thermal stability of the polymer. The residue left closely matches the filler content added.

3.8. Morphology of PLA-Bioactive Glass

Figure 11 shows the FESEM and EDX analysis of the composites. SEM images show that there is a uniform distribution of bioactive glass in the PLA matrix, and with an increase in filler concentration, the particle distribution has increased. The EDX analysis shows the constituents of PLA and bioactive glass.

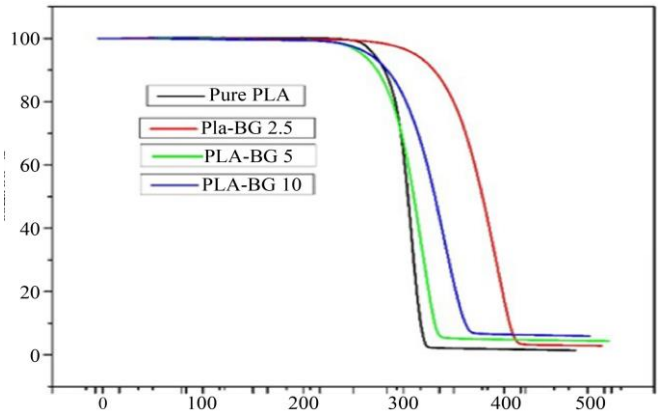

Fig. 10 TGA of PLA-BG composites

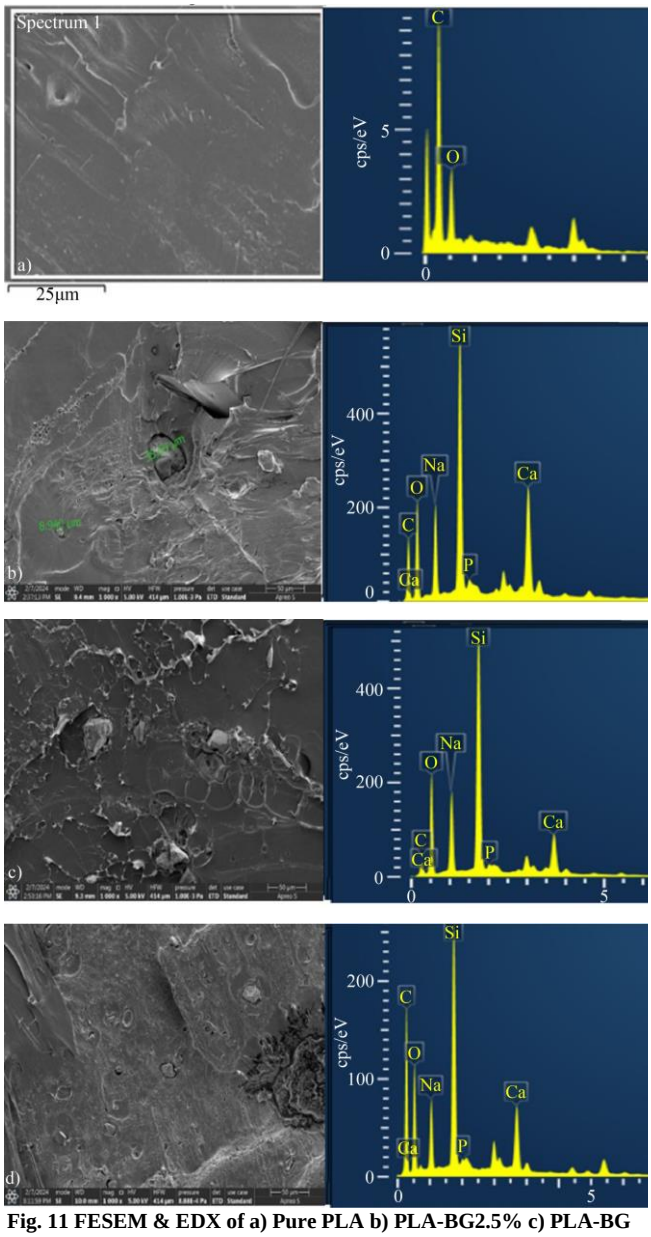

Fig. 11 FESEM & EDX of a) Pure PLA b) PLA-BG2.5% c) PLA-BG 5% d) PLA-BG 10 %

Fig. 12 a) Filament failure under tensile loading

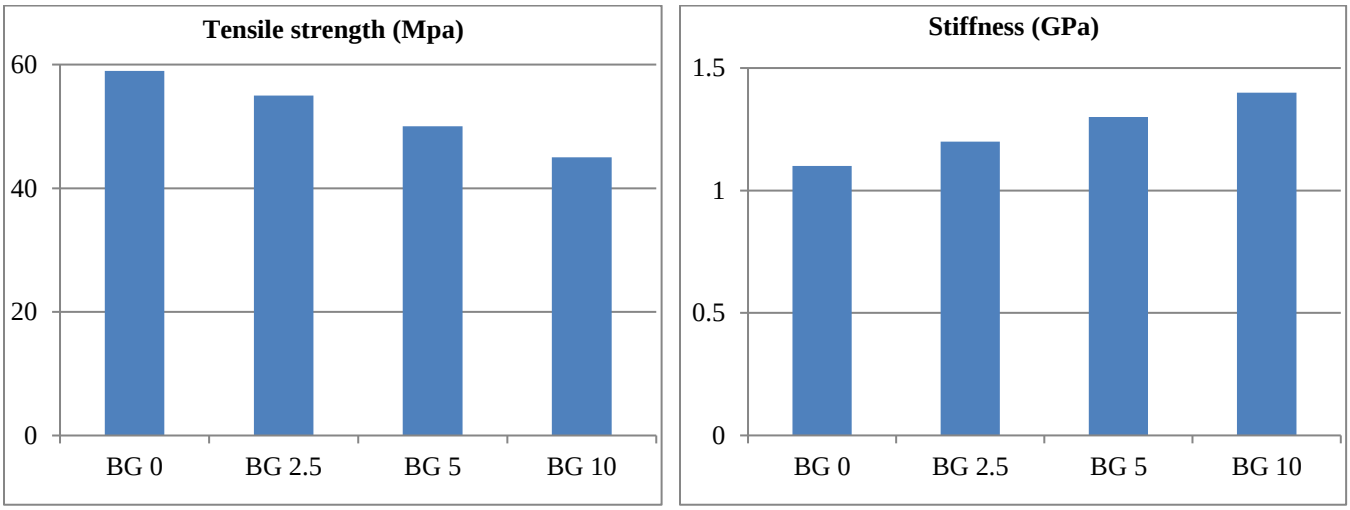

Fig. 12 b) Tensile strength and stiffness of the composites

3.9. Tensile Strength of Composite Filaments

Figure 12 a) shows the filament failure under tensile loading. 5 samples of testing have been done for each case, and the average value has been taken. Figure 12b) shows the effect of bioactive glass content on tensile strength and modulus. It is observed that the tensile strength has decreased, but the stiffness has increased with an increase in bioactive glass content.

4. Conclusion

By using the Sol-gel method, 45S5 bioactive glass was prepared, and the composite filaments with uniform diameters of 1.75 mm were extruded. The influence of the addition of bioactive glass content on the physiochemical, thermal and mechanical behavior of the composites is evaluated. It is observed that bioactive glass powder is uniformly distributed in the polymer matrix as seen in FESEM results and can be correlated with XRD and FTIR results, and thermal tests indicate with increase in bioactive glass content, thermal stability has reduced, and tensile tests indicate a reduction in tensile strength and enhancement in modulus with an increase in bioactive glass content. The resultant composite filaments can be 3d printed to make customized scaffolds for bone regeneration.

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