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Research Article

Performance of Biocomposite Materials Reinforced by Hydroxyapatite and Seashell Nanoparticles for Bone Replacement

Ahmed Namah Hadi[1] **and Mohammed Razzaq Mohammed**[2]

[1]*Department of Biomedical Engineering, College of Engineering, University of Babylon, Hillah, Iraq*
[2]*Department of Mechanical Engineering, College of Engineering, University of Misan, Amarah, Iraq*

Correspondence should be addressed to Mohammed Razzaq Mohammed; mohammedrazzaq14@uomisan.edu.iq

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Bone defects and disorders include trauma, osteonecrosis, osteoporosis, bone tumours, arthritis rheumatoid, osteosarcoma, and iatrogenic injury. Obtaining a composite material with characteristics that mimic what bones in the human body have is a vital target for the purpose of replacing or repairing damaged bones. The key objective of this study was to develop a composite having mechanical and biological properties that resemble to a large extent native bone features. Highly biocompatible epoxy resin was reinforced by various weight fractions of seashell nanoparticles. The morphologies of the pristine bioepoxy, seashell-bioepoxy, and hydroxyapatite-bioepoxy composites were observed by scanning electron microscopy. Moreover, the mechanical properties were examined by the means of tension and Izod impact tests. Besides, the influence of seashell and hydroxyapatite nanoparticles on the bioepoxy chemical structure and thermal properties was also evaluated using Fourier transform infrared spectroscopy and differential scanning calorimetry technique, respectively. The tensile strength, modulus of elasticity, and impact strength of the seashell nanoparticle-reinforced bioepoxy were revealed to be higher than those of the unmodified bioepoxy and were significantly depended on the filler content. When the mass fraction of the reinforcement was 7 wt%, the improvement in the tensile strength, modulus of elasticity, and impact strength was around 46.7%, 37%, and 57%, respectively, compared to that of blank bioepoxy. In addition, these properties were higher for the composites loaded with seashell nanoparticles than those filled with commercially available hydroxyapatite nanoparticles. An enhancement in glass transition temperature for the bioepoxy after modification with both of these nanofillers was also achieved. All these features make these kinds of composites a promising option that could be used in the orthopaedic field. Furthermore, the use of seashell nanoparticles may reduce the cost of the resulted composite and alleviate the negative consequences of large quantity by-product waste seashells on the environment.

1. Introduction

Regenerating or replacing damaged tissues or organs that could be caused by accidents or diseases is utterly indispensable. The most common substitutes for bone replacement are autogenous and allogeneic bone grafts [1]. The former involves transplantation of a part of an intact site into the damaged place for the same patient; therefore, this technique provides immunocompatible bone cells and reduces the probability of rejection. Nonetheless, such procedure is not only expensive but may also cause pain, severe damage to other body parts, and increase the risk of infection [2]. In the second method, the bone is transferred from another person; hence, it does not need to perform a second surgery, unlike the other approach. Moreover, this technique does not cause the loss of healthy parts of the patient's body. Nevertheless, it is clear that the use of a part taken from another individual may increase body rejection and cause transmission of diseases [3, 4].

As a consequence of the significant drawbacks of the two abovementioned strategies, there has been a growing interest at present in the use of engineering materials for replacing or repairing bone tissue [5, 6]. Epoxy is one of the most unique resins that have been broadly employed as a matrix for composites. This is because of several aspects, including its high strength and modulus, high adhesion strength,

chemical and electrical resistance, processing simplicity, and low polymerisation shrinkage [7]. Polymerised epoxy resins have a tight network resulting from the use of various agents, including amines and thiols [8]. These chemical and processing flexibilities make this resin suitable for a broad range of applications. Epoxy resins of diglycidyl ether of bisphenol-A (DGEBA) have been shown to be favour matrix to form composites for orthopaedic and dental applications [9, 10]. Even so, the use of this biocompatible epoxy in the field of biomedical applications can be thought to remain relatively limited. Garcia et al. examined mechanical, blood compatibility, and in vitro biological properties of various epoxy networks based on this resin plus several initiators including isophoronediamine (IPD). A satisfactory cytocompatibility was indicated, in which these materials have not been toxic toward Chinese hamster ovary cells [11].

For the last few years, the performance of composite materials has remarkably been enhanced by accessing novel characteristics and exceptional interaction between materials that could be promoted due to the use of nanocomposites [12, 13]. In this regard, several studies have demonstrated that high mechanical and thermal properties could be obtained for nanocomposites compared with microscale-based composites [14, 15]. In order to enhance the mechanical performance of microsized composites, a high content of fillers is typically added to the matrix, and this in turn causes a rise in the weight of the composite [16]. Conversely, lightweight composites with high mechanical properties can be easily achieved when nanocomposites with low filler content are utilised [17]. Nanomodification of polymers can improve material properties without negatively affecting other properties. For instance, it can enhance stiffness without influencing toughness [18].

Hydroxyapatite (HA) is a broadly applied ceramic filler in a wide range of biomedical applications, particularly in dental and orthopaedic replacements. This is owing to its superior biocompatibility, bioactivity, and osteointegrity characteristics. Furthermore, HA resembles the inorganic constituent of the human body [19, 20] where it has a chemical structure and a calcium-to-phosphor ratio comparable to that of native bone [21, 22]. It is reported that almost two-thirds of natural bone is composed of HA-like components [23]; therefore, HA nanoparticles can be highly favourable fillers for the remedy of bone defects [24]. Nonetheless, HA nanoparticles have insufficient mechanical properties in which they possess a brittle nature, making it necessary for these fillers to be typically incorporated within polymeric matrix to promote easy processing and overcome inadequate mechanical properties [25, 26]. Discarded by-product waste materials, particularly that are derived from natural sources, have also been applied as fillers in composites to reduce environmental pollution and improve the mechanical characteristics of the produced composites [27]. Reinforcing a polymer with natural fibres such as hemp [28, 29], eggshells [30, 31], and seashells (SS) [32–35] is an example of this growing tendency to fabricate composites. Among the numerous fillers, SS could be remarkably advantageous material as a filler in biocomposites due to its availability, low cost, thermal stability, and resistance to bacterial growth [36]. Particles of SS can be widely accessible, and they are typically composed of calcium carbonate ($CaCO_3$) with some organic compounds [37, 38]. Modification of polymers by SS can be used for a number of purposes and applications. However, the use of this natural ceramic material that has similar features to human bones and teeth is not as much as other ceramic fillers. SS-reinforced biocomposites have been shown to have higher mechanical properties than those of the particle-free resins [35, 39].

The aim of this study was to compare two nanocomposite systems that were fabricated from bioepoxy plus commercially available HA and bioepoxy with SS nanoparticles to be potentially utilised for bone replacement. The epoxy networks based on IPD were chosen, thanks to their high mechanical and biological characteristics. In order to decide which of these systems has better physical and mechanical properties, and also to make the comparison reliable, the size of the nanoparticles was the same for both fillers used at 50 nm. Some mechanical, chemical, and thermal properties of these composite systems were evaluated. The fabricated composites provided higher tensile strength, modulus of elasticity, and impact strength than that of blank bioepoxy.

2. Materials and Methods

2.1. Materials. Hydroxyapatite (HA) and SS nanoparticles were purchased from Nanjing Emperor Nano Material Co Ltd and Viet D.E.L.T.A Industrial Co Ltd, respectively. Bioepoxy resin was provided from Hangzhou Dely Technology Co Ltd.

2.2. Fabrication of Bioepoxy/HA and Bioepoxy/SS Nanocomposites. Nanocomposites of bioepoxy that contained either HA or SS nanoparticles were prepared with different concentrations of dispersed phase at 1, 3, 7, and 15 wt%. The mixture of HA or SS and bioepoxy resin was mechanically mixed for 10 minutes to allow the nanoparticles to be homogenously dispersed. After including IPD, the obtained mixture was stirred for about 5 minutes and then poured into moulds to fabricate the nanocomposites.

2.3. Transmission Electron Microscopy (TEM) and Scanning Electron Microscopy (SEM). The morphologies of the HA and SS nanoparticles were evaluated by TEM. In addition, microscopic observations of modified and unmodified bioepoxy were performed using Inspect F 50 FE-SEM. A 50 nm thick gold layer was used to coat the specimens before taking SEM images.

2.4. Mechanical Properties. Tensile tests were conducted according to ASTM D638 using Instron universal testing machine at a strain rate of 5 mm/min. Specimens of unmodified bioepoxy, bioepoxy/SS, and bioepoxy/HA were tested in order to evaluate and compare the tensile strength and modulus of elasticity of these composite systems. Impact tests were performed according to ISO-180 using XJU series pendulum Izod impact testing machine. All tested samples had a size of

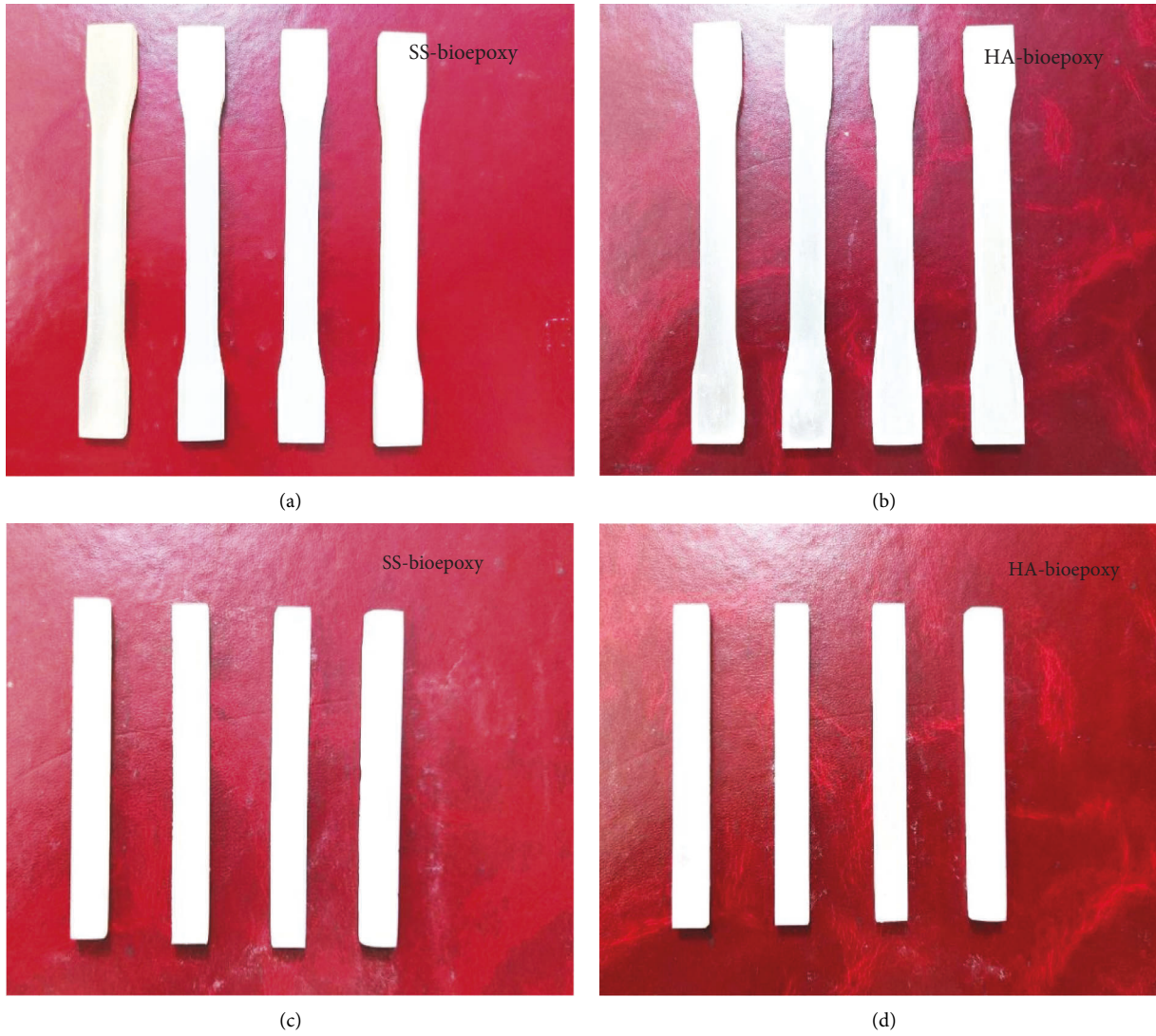


Figure 1: Specimens of SS- and HA-bioepoxy nanocomposites prepared for (a) and (b) tensile test (c) and (d) impact test.

$80 \times 10 \times 4$ mm. Specimens of tension and impact tests are presented in Figure 1.

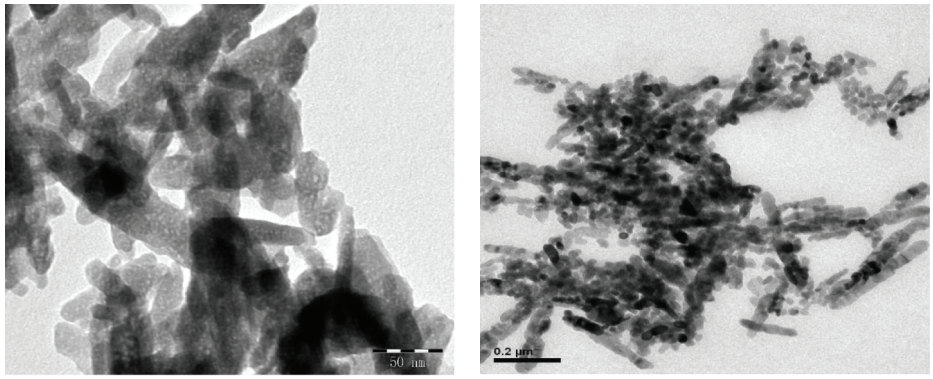
2.5. Fourier Transform Infrared (FTIR) Spectroscopy. FTIR analysis was conducted to examine the impact of the incorporation of each of HA and SS on the chemical composition of bioepoxy-based composites. The FTIR test was performed according to ASTM E1252 using the TENSOR-27 Bruker Optics device. After the specimen was placed inside the device, infrared spectrums were obtained in absorption form.

2.6. Differential Scanning Calorimetry (DSC). The DSC test was performed based on ASTM D3418 using a Shimadzu-DSC-60 PerkinElmer apparatus to observe cure reactions and determine the glass transition temperature (Tg) of the blank bioepoxy and bioepoxy-based nanocomposites. All measurements were carried out on samples of 10 mg placed inside a closed aluminium crucible in the temperature range between 20 and 250°C with rate of heating at 10°C/min.

3. Results and Discussion

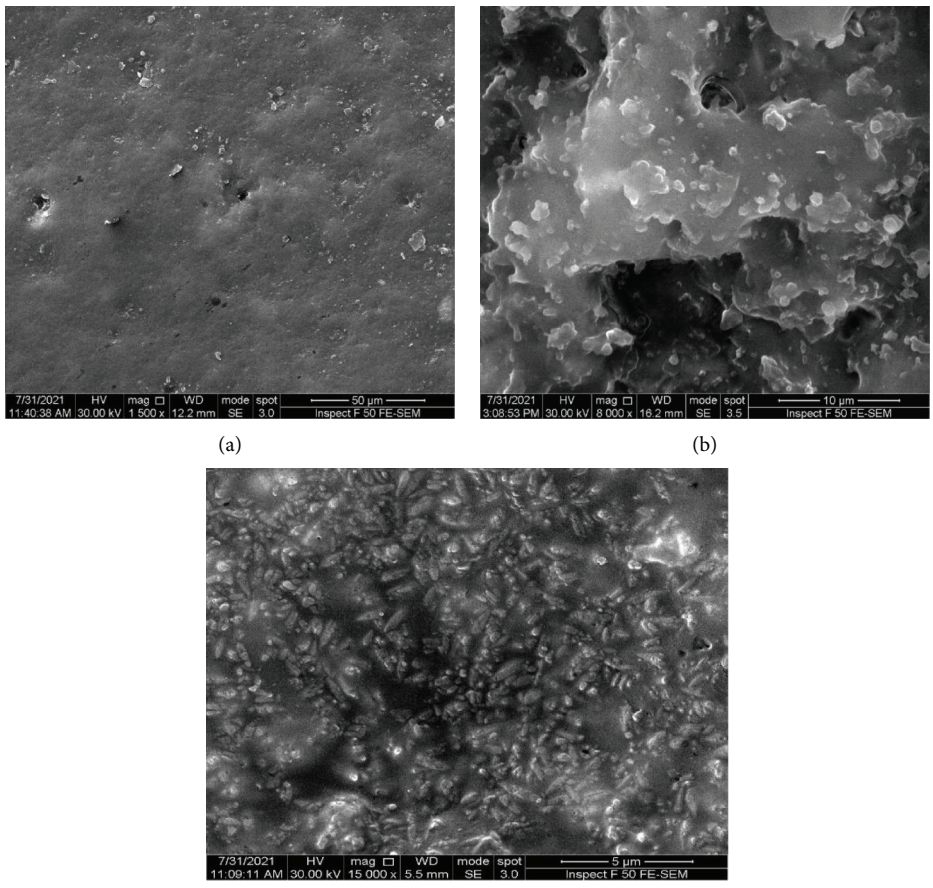
3.1. Nanoparticle and Nanocomposite Morphologies. Figure 2 illustrates the TEM images of the HA and SS nanoparticles. The miniature size of nanoparticles results in the possession of these particles high surface area and energy, leading to the creation of agglomerations and clusters. The agglomeration of the nanoparticles is because of the adhesion of the particles to each other by weak forces [40]. Both HA and SS were revealed to have rod-like shapes.

It can be seen from Figure 3 that there was a significant change in the morphology of the specimens before and after modification with HA or SS nanoparticles. Figure 3(a) shows the pristine bioepoxy morphology, where it had an even surface; however, the presence of the nanoparticles can be



(a) (b)

Figure 2: TEM images of (a) HA nanoparticles and (b) SS nanoparticles.



(a) (b)

(c)

Figure 3: SEM images of (a) pristine bioepoxy, (b) bioepoxy/7 wt% HA composite, and (c) bioepoxy/7 wt% SS composite.

easily observed after modification (Figures 3(b) and 3(c)). The nanoparticles of both fillers appeared to be well distributed within the nanocomposites, indicating the rod shape of the nanoparticles, particularly for the composite reinforced by 7 wt% SS (Figure 3(c)). It is also observed that some of these nanoparticles tend to aggregate with each other within the composites.

3.2. Mechanical Properties

3.2.1. Tensile Strength and Modulus of Elasticity. Tensile tests were carried out on pristine bioepoxy and particulate-based bioepoxy composites. As it can be noticed from Figures 4 and 5, the tensile strength and modulus of elasticity were enhanced after adding 1 wt% of SS nanoparticles. Increasing the content of SS up to 7 wt% further enhanced the tensile strength and modulus; when the percentage of the

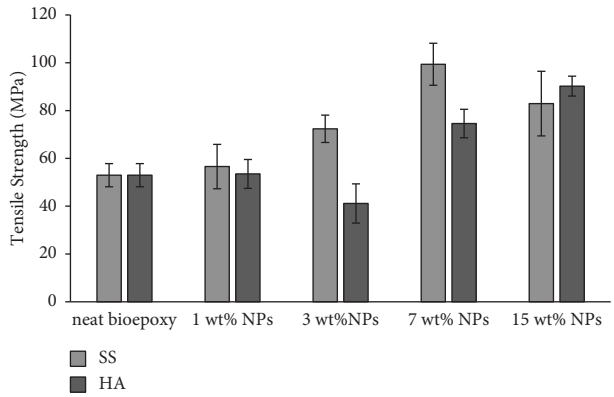


Figure 4: Impact of the incorporation of different mass fractions of HA or SS nanoparticles on the tensile strength of bioepoxy.

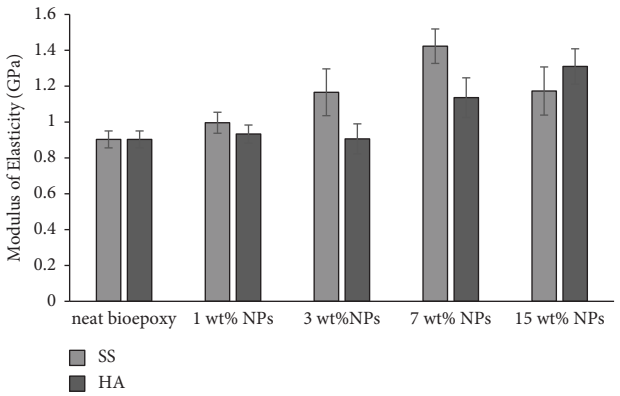


Figure 5: Impact of the incorporation of different mass fractions of HA or SS nanoparticles on the modulus of elasticity of bioepoxy.

reinforcement material was 7 wt%, the improvement in the tensile strength was even better than that for the composites containing 1 wt% and 3 wt%. Such improvement was approximately 46.7% in the tensile strength and 37% in the elastic modulus compared with those of blank bioepoxy. Nonetheless, increasing the nanoparticle content up to 15 wt % caused a decrease in both tensile strength and modulus. Despite this reduction in the tensile strength and modulus, these properties remained higher than the values reported for the nanoparticle-free bioepoxy by about 36.12% and 23%, respectively. The improvement in tensile modulus at low mass fraction of filler at 1, 3, and 7 wt% was because of the chain mobility restriction. As a result of their tiny size, nanoparticles provide a larger surface area, and high interaction and sound bonding between reinforcement and resin, which in turn can transfer the load, and provide a high tensile strength. In contrast, the fabricated composites consisting of 15 wt% fillers had relatively lower tensile strength and modulus, since they had insufficient nanoparticle dispersion within the matrix. There is a direct relationship between Van der Waal forces occurring between the nanoparticles and the increase in the percentage of these fillers within the composite, and this may lead to less dispersion of these particles. For that reason, the interaction between the matrix and nanoparticles decreases, causing an

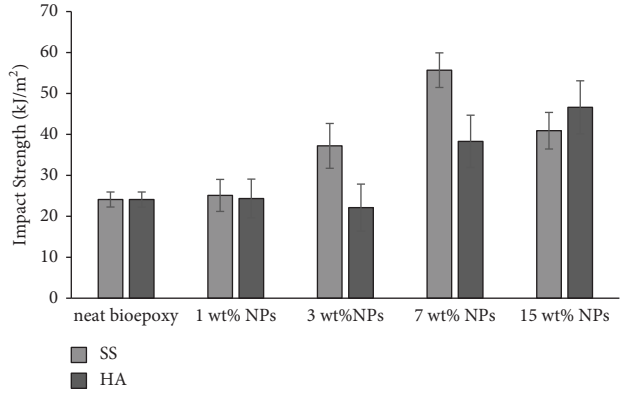


Figure 6: Influence of the incorporation of different mass fractions of HA or SS nanoparticles on the impact strength of bioepoxy.

inefficient load transferring system inside the composites and dropped mechanical properties.

Regarding the influence of adding HA to the bioepoxy resin, it had somewhat similar trends in terms of tensile strength and modulus of elasticity behaviours for SS-bioepoxy composites (Figures 4 and 5). Interestingly, the tensile strength and elastic modulus of the bioepoxy-based nanocomposite formed by the addition of 7 wt% of SS were greater than those strengthened using the same weight fraction of HA. These results may display a great benefit of the use of the large available quantities of SS, since these materials could promote preserving the environment as well as providing a low-cost alternative reinforcement compared to the commercially available HA.

3.2.2. Impact Strength. Izod impact tests were carried out to measure the impact strength of pristine bioepoxy and bioepoxy-based composites. Unnotched specimens were used in which the impact energy required to fracture the samples in this case can be much higher than that for notched specimens. Herein, the resulting impact strength is influenced by the energy required for crack initiation and propagation; conversely, the measured impact strength of the specimens with notches is typically affected by only crack propagation. Figure 6 shows the impact strength of bioepoxy-based nanocomposites based on HA or SS contents. In general, the composite materials reinforced by SS had better impact strength than those reinforced by HA at the same percentages of reinforcements, except for the composite filled with 15 wt% of HA, which had a higher impact strength than its counterpart that was reinforced by 15 wt% of SS.

An enhancement in the impact behaviour of the nanocomposites was revealed after adding 1 wt%, 3 wt%, and 7 wt% of SS and HA nanoparticles. Including a reinforcement at 1 wt%, 3 wt%, and 7 wt% of SS led to an increase in the impact strength by around 4%, 35%, and 57%, respectively, compared with that of the bare bioepoxy. The small size, the high surface area, and relatively low concentration may have allowed for a good distribution of these fillers and generate an appropriate bonding between the nanofillers and

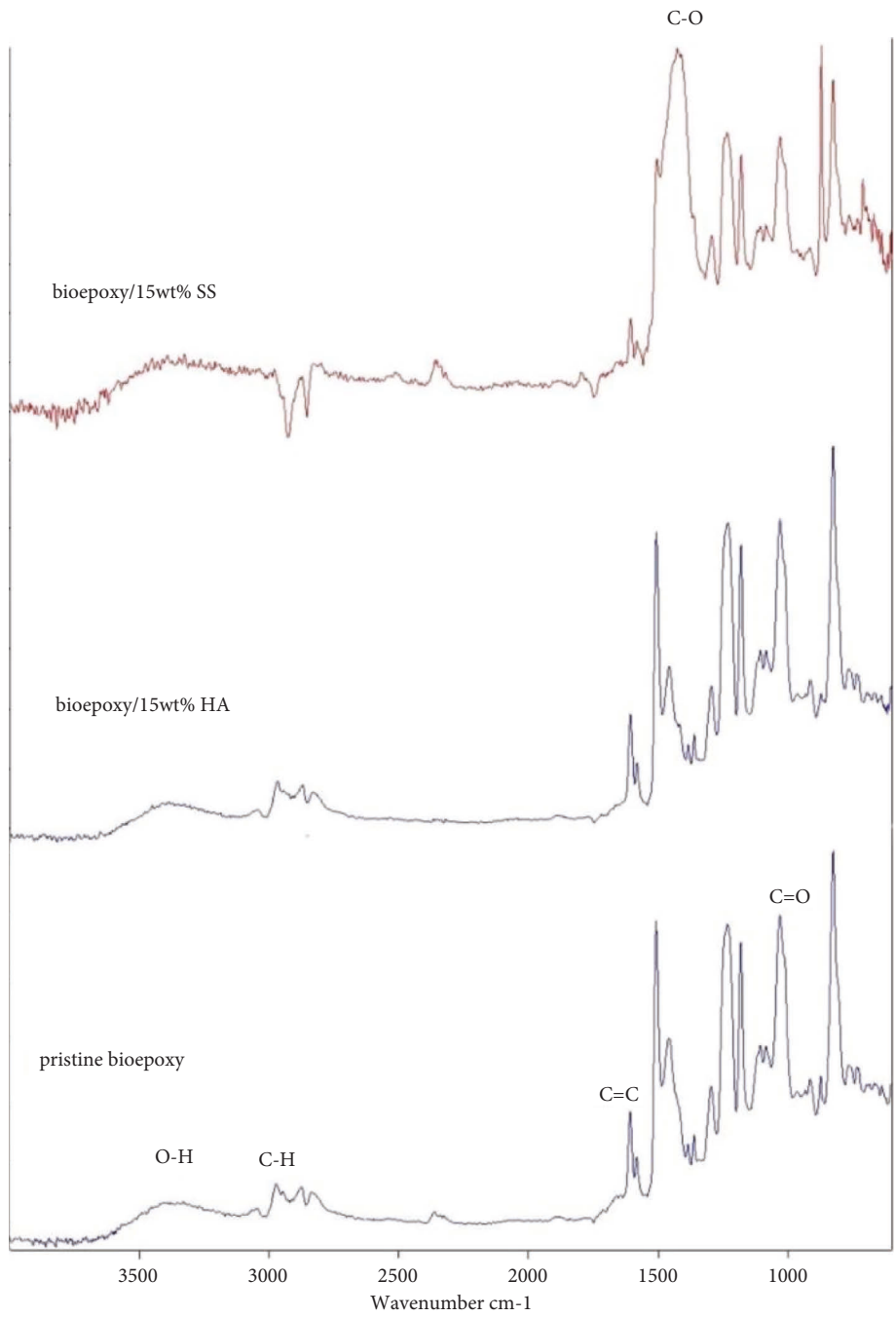


Figure 7: FTIR spectra of pristine bioepoxy, bioepoxy/15 wt% HA nanocomposite, and bioepoxy/15 wt% SS nanocomposite.

the matrix. This may not only cause a restricted motion of macromolecule chains but may also lead to reducing the crack propagation and enhancing mechanical properties. Such an increment in impact strength was not detected with the rise in these nanoparticle mass fractions. The incorporation of 15 wt% of SS into bioepoxy resulted in a reduction in the strength by about 27%, compared to that of the composite fabricated from 7 wt% of SS nanoparticles. The reason for such a notable decline in the impact energy may be due to the presence of the brittle-nature inorganic fillers. The composites reinforced with high levels of these fillers cannot withstand and disperse sudden forces and stresses; thus, a defect or crack will form and expand rapidly, and eventually the brittle fracture will occur. Besides, the lack of distribution of the nanoparticles, particularly at high weight fractions, makes the interaction between the resin and the nanoparticles insufficient and hinders the distribution of loads homogeneously. The remedy of this phenomenon could be by using coupling agents to increase the interface interaction between composite components; furthermore, the use of high-load-resilience absorption materials can improve this property.

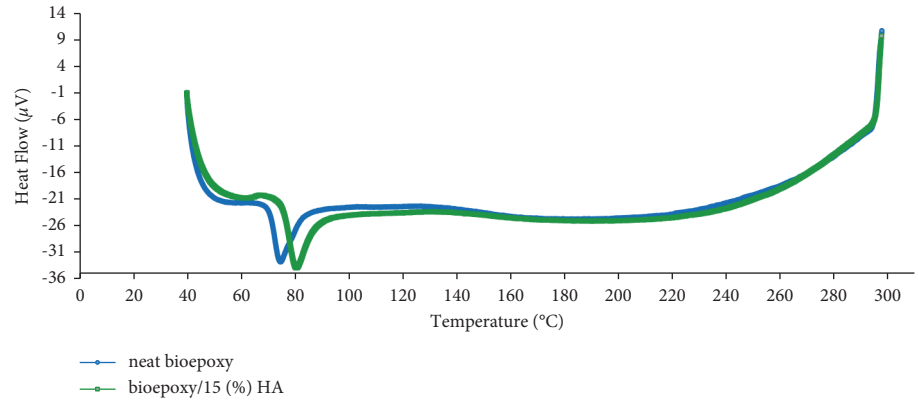


Figure 8: DSC curves for pristine bioepoxy and bioepoxy/15 wt% HA nanocomposite.

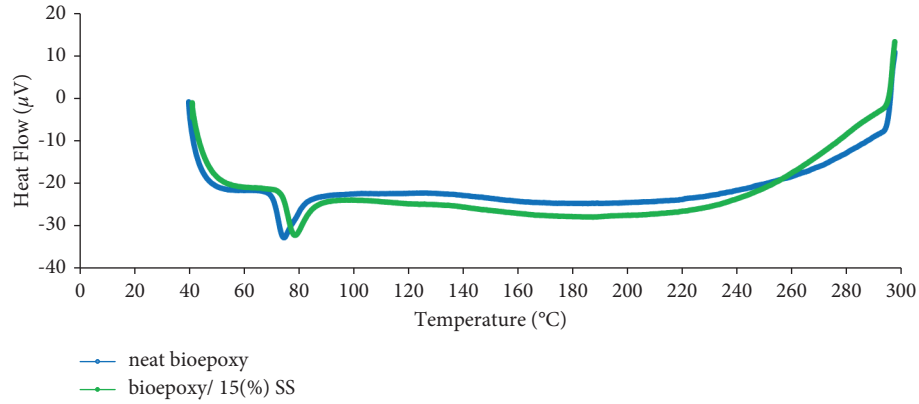


Figure 9: DSC curves for pristine bioepoxy and bioepoxy/15 wt% SS nanocomposite.

3.3. Structural Properties. FTIR was conducted to figure out the effect of incorporating each of HA and SS on the chemical composition of bioepoxy-based composites. The interaction between pristine bioepoxy and HA- and SS-loaded epoxy was investigated through the FTIR spectra. As can be indicated from Figure 7 that prior to the addition of HA into the bioepoxy resin, the FTIR spectrum of epoxy displayed various characteristics. The typical peaks for functional groups of pristine epoxy were appeared between 2964 cm^{-1} and 2889 cm^{-1} that corresponded to stretching CH_2 groups, whereas the peak at 2829 cm^{-1} was attributed to the aliphatic carbon chain symmetric. The peak was detected at about 1507 cm^{-1} because of the presence of 1,4 disubstituted benzene ring C=C bond, whereas the C=O peak was situated at approximately 1182 cm^{-1}. The peak at 3357 cm^{-1} is related to OH functional groups [41]. The incorporation of HA and SS did not cause a noteworthy change in the chemical structure and the FTIR spectrum that was obtained for bioepoxy, apart from some of functional groups that indicate the presence of these fillers within the reinforced composites. The FTIR spectrum of bioepoxy filled with 15 wt % of HA or SS nanoparticles revealed some new peaks that represent the phosphate group and the C–O bond vibration of $CaCO_3$ at around 1084 cm^{-1} and 1459 cm^{-1}, respectively. On the base of these findings, it can be assumed that there was no evident interface interaction between the nanoparticles and the matrix, where this interaction between HA and the resin was only a weak surface interaction. The reason may be due to the absence of a bonding agent that could increase the interfacial interaction between the reinforcement phase and the matrix material. Therefore, this point will be taken into consideration in future work to improve the mechanical and chemical properties even more of these composite systems.

3.4. Thermal Properties. DSC test was conducted to examine the thermal characteristics and to determine Tg of neat bioepoxy, bioepoxy/HA, and bioepoxy/SS nanocomposites. Figure 8 illustrates the DSC curves for pristine bioepoxy and bioepoxy/15 wt% HA composite while the effect of including 15 wt% of SS on the DSC behaviour of bioepoxy can be seen from Figure 9. The incorporation of HA and SS into epoxy led to a slight rise in the Tg due to the creation of an interphase between these nanofillers and the bioepoxy matrix that restricted polymer mobility. Even though the increase in the nanoparticles could improve the Tg for the obtained nanocomposites, it was observed that the Tg for these composites that contained high nanoparticle weight fractions (15 wt%) did not differ remarkably to that of low-loaded composites and nanoparticle-free bioepoxy. The good dispersion of HA or SS within the nanocomposites at

low nanoparticle loading could generate more interphase volume between fillers and the resin, whereas the possible particle agglomeration at high concentrations did not significantly improve the values of Tg for the obtained composites. It can be concluded from these results that the addition of HA and SS could result in confining the polymer chain molecular movement due to the interaction between the nanoparticles and the matrix, causing higher thermal stability for such composite systems.

4. Conclusions

The present study compared two nanocomposite systems that were fabricated from bioepoxy plus commercially available HA and bioepoxy with SS nanoparticles in order to be potentially used for bone replacement. The size of the nanoparticles was the same for both fillers at 50 nm, while the mass fractions of the reinforcement phase were 1, 3, 7, and 15 wt%. The morphologies of pristine bioepoxy, HA-bioepoxy, and SS-bioepoxy composites were observed using SEM, where rod-shaped nanoparticles, particularly for SS, were clearly detected within the matrix after the addition of the fillers. On the basis of the FTIR spectra findings, no major alteration in the chemical structure of the used resin was noticed after reinforcing by both of the nanoparticles. Regarding the thermal properties, DSC exhibited occurring slight increases in the Tg values for bioepoxy following the modifications by HA and SS nanoparticles. Moreover, the tensile strength, elastic modulus, and impact strength of SS-modified bioepoxy composites were higher than those of the filler-free bioepoxy and the HA-loaded bioepoxy, particularly at 7 wt% of SS. Generally, the incorporation of SS nanoparticles into epoxy networks based on IPD hardener, which has been confirmed to be highly biocompatible, can create a biocomposite that not only has an appropriate mechanical performance but can also be available in a reasonable price compared to other particulate composites.

Data Availability

The research data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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