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Strength improvement of critical-sized three dimensional printing parts by infiltration of solvent-free visible light-cured resin

J. Suwanprateeb

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Abstract The use of light-cured acrylate resin as an infiltrant can enhance flexural modulus and flexural strength of natural polymers based three dimensional printing (3DP) parts to be closed to general use of polymethyl methacrylate resin. It was observed that flexural properties of infiltrated specimens were influenced by infiltration conditions. Curing by normal halogen light bulb was more practical for critical-sized 3DP parts than curing by typically small probe of dental visible light curing unit (VLC). Similar levels of flexural properties were obtained from these two methods. Post-heated treatment after curing was also observed to further increase the flexural modulus and strength of infiltrated samples. However, flexural strain at break was not affected by different curing conditions. Preliminary *In Vitro* toxicity test of infiltrated 3DP parts showed that the cells which were in contact with samples were healthy. No inhibition zone was observed.

1 Introduction

Rapid prototyping (RP) is a relatively new technology that additively builds three dimensional part layer by layer in contrast to traditionally subtractive process. This approach allows the complex physical structures to be fabricated rapidly and accurately using graphical data in computer. These benefits place RP technology in use by many industries ranging from concept modeling, fit & function trials and even small-scale manufacturing. Numerous RP systems are available in market including Stereolithography (SLA), Selective Laser Sintering (SLS), Fused Deposition Modeling (FDM), Laminated Object Manufacturing (LOM) and Three Dimensional Printing (3DP). Apart from industrial applications, RP has also been utilized in medical applications as visualization and modeling tools to aid with pre- or per-operative planning and production of patient medical models or customized implants [1–3]. Starting from the digital data of patient's organs acquired from medical imaging system such as CT or MRI, the medical models can be fabricated easily and accurately in short times by RP technology.

In the case of implant fabrication, implants can be designed digitally to fit the host site and aesthetically correct for individual patient prior to the surgery. RP is then normally employed to build positive components having the shape and size of the desired implants. These positive components are then used to create silicone or plaster moulds for further casting by biomedical materials such as bone cement or dental acrylic [4]. Alternatively, negative moulds with the internal structure similar to the size and shape of the implants can also be made, but less frequent than the previous method. These indirect processes are multi-step and prone to add error in dimension to the implant models unless carefully planned. This is due to the fact that RP techniques require the use of specific raw materials for working and these materials are usually not designed for biomedical applications. The lack of biomaterials that can be used with RP systems limits the direct fabrication of implants. Therefore, a number of biomaterial systems that have properties and characteristics appropriate for processing by some RP technologies have been studied recently to overcome the limitation [5–8].

Three dimensional printing (3DP) is a fast and low cost system that does not need support structure to build a model. The technique involves the spreading of a thin layer of a powdered material, followed by selective joining of powder through printing of a binder material. Subsequently,

J. Suwanprateeb
National Metal and Materials Technology Center, National Science and Technology Development Agency, Ministry of Science and Technology, 114 Paholyothin Road, Klong 1, Klongluang, Pathumthani 12120, Thailand

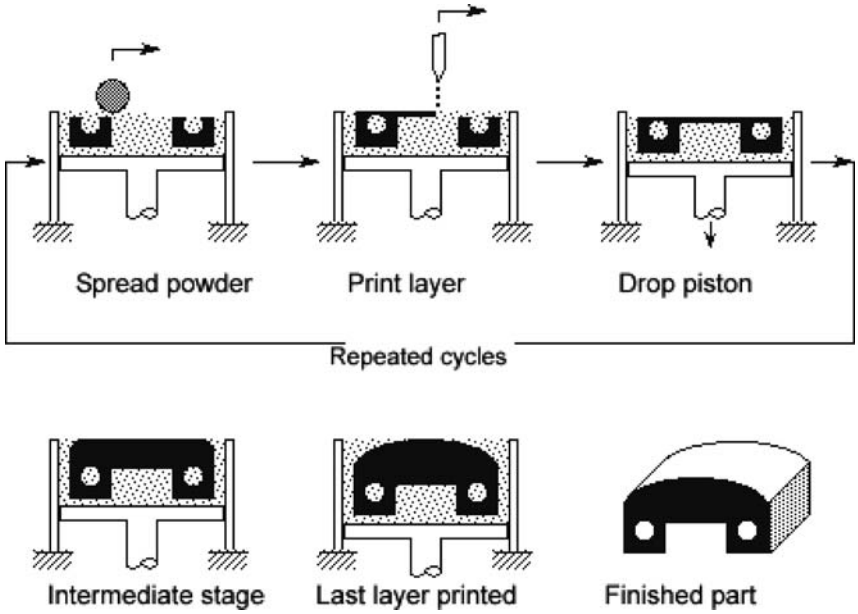

Fig. 1 Three dimensional printing process

a cylinder containing the powder bed is lowered, allowing for the spread of the next powder layer. Unbound powder temporarily supports unconnected portions of the component, allowing overhang, undercut and internal volumes to be formed. The unbound powder is removed upon process completion, leaving the finished green part,Fig. 1. Until now, 3DP has been studied to directly fabricate drug delivery devices and scaffold successfully [9–15]. However, these 3DP parts either used solvent as a binder or a polymer solution to infiltrate the parts. In the case of using organic solvents as the binder, it was found that there still remained 0.5 %wt. (5000 ppm) chloroform in samples made by 3DP after 1 week drying [13]. Recently, residual chloroform extraction using liquid carbon dioxide has been investigated [14]. This technique could reduce the level of chloroform to below 50 ppm. Alternatively, Lam *et al*. used water as a binder for 3DP to produce starch-based polymer scaffolds to avoid the use of solvent binder. However, infiltration of the porous scaffolds with solutions of poly(L-lactide) or polycaprolactone in methylene chloride was required to increase the mechanical strength [15]. In either ways, the residual solvent within the parts could be a possible source of toxicity. This study, thus, reports possibility of using light-cured dental sealant as an alternative infiltrant without using a solvent to increase the structural integrity of 3DP parts.

2 Materials and methods

2.1 Materials

Materials employed in this study were natural polymers including cassava starch (Thai Wah Co., Ltd), maltodextrin (Shandong Duqing Inc.), cellulose fiber (Opta Food Ingredients, Inc.) and gelatin (Geltech Co., Ltd). These materials were supplied in the form of powders with particle size ranging 20–200 micron. All the materials used as a component in the materials mixture system were selected based on their potentially biocompatible nature and wetting property by water. Starch and gelatin were recently studied by many researchers as biomaterials whereas maltodextrin and cellulose are found in many pharmaceutical products [16–22]. Hence, a combination of these materials might provide a useful biocompatible material. Infiltration material used was commercial clear light-cured dental sealant (Dentguard, Thailand) based on a combination of triethylene glycol dimethacrylate (TEGDMA), 2,2-bis[4(2-hydroxy-3 methacryloyloxypropyloxy)-phenyl]propane (Bis-GMA) and urethane dimethacrylate (UDMA).

2.2 Specimen preparation

A mixture of 60% starch, 5% cellulose fiber, 20% gelatin and 15% maltodextrin by weight was prepared by initially stirring in a plastic bag and then thoroughly mixed by a mechanical blender. The mixture was then loaded in the 3DP machine (Z400, Z Corporation). Rectangular bars (80 mm × 10 mm × 4 mm) were printed using a layer thickness of 0.175 mm. Distilled water was used as a binder in all formulations. After building, all the specimens were left in the machine for 2 hours before taken out and then air blowing to remove the unbounded powder.

2.3 Infiltration

Infiltration of 3DP specimens was carried out at room temperature by pouring a liquid infiltrant in the container. The specimens were placed in the liquid and allowed

the infiltrant to enter the specimens naturally by capillary force. Then, the fully infiltrated specimens were light cured by various conditions to solidify the infiltrant portion as following:

- IF-1: Using dental visible light curing unit (Translux EC, Kulzer Co., Ltd) with a probe size of 7.5 mm in diameter to cure repeatedly across the whole specimen on both sides with 40 seconds exposure for each steps.
- IF-2: Leaving the whole specimen in white fluorescent light in the laboratory for 1 hour.
- IF-3: Exposing the whole specimen to direct halogen light bulb (Osram HLX-100 w) without blue filter for 1 hour.
- IF-4: Exposing the whole specimen to direct halogen light bulb without blue filter for 1 hour and heat treated at 100°C for 0.5 hour.

For comparison purpose, pure sealant specimens were prepared by pouring resin in a silicone mould and cured similarly to IF-4 condition. Heat-cured polymethyl methacrylate (Premium Denture Acrylic, Lang Dental Manufacturing Co., Ltd) specimens were also prepared according to the manufacturer instruction.

2.4 Dimension measurement

Dimension of the specimen was measured by a vernier caliper (Mitutoyo) with the reading resolution of 0.01 mm. The measurement was done three times in each direction and the values were then averaged.

2.5 Flexural testing

Flexural tests were performed on a universal testing machine (Instron 4502) equipped with a 10 kN load cell. All tests were carried out according to ASTM D790 at 23°C and 50% RH. using three point bending method with a span length of 64 mm. and a constant crosshead speed of 1.9 mm min^{-1}. The reported data are the average values from five replicates.

2.6 Raman measurement

The light-cured sealant and infiltrated samples were characterized for the degree of conversion using Raman technique. All spectra were obtained with a Perkin-Elmer FT-Raman spectrometer system 2000R supplied with radiation of 1064 nm from Nd^{3+}:YAG laser and InGaAs detector. The power was set at 400 mW and the spectral resolution was 4 cm^{-1}. The degree of conversion (DC) was calculated by the following equation [23, 24]:

$$DC = 100 \times [1 - (R_{polymerized}/R_{unpolymerized})]$$

where R = peak height at 1640 cm^{-1}/peak height at 1610 cm^{-1}.

2.7 Water absorption

Three rectangular specimens for each sample were weighted in air using a precision balance (Precisa XT220A) prior to immersing in water at 22°C for 24 hours. When the desired time was reached, they were then taken out, wiped gently by a dry tissue paper to remove the excess water and re-weighed. The percentage of water absorption was calculated as follows:

$$\text{Water absorption}(\%) = \left[\frac{\text{Wet weight after 24 hours immersion (g)} - \text{initial weight (g)}}{\text{initial weight (g)}}\right] \times 100$$

2.8 Cytotoxicity test

Three pieces of infiltrated sample after curing and post-heated at 100°C for 0.5 hour were tested for toxicity by direct contact method using L-929 mouse fibroblasts following ISO 10993. The incubation period was 24 hours. The morphology of cells was then observed using inverted light microscope after staining the cells with neutral red.

3 Results and discussion

Although the 3DP part that was built using water-based binder is sufficiently strong for general handling purposes, it is still not sufficiently strong for use as biomaterials in the body. Generally, method employed to enhance the strength and integrity of 3DP part is infiltration by a low viscosity liquid material that can be subsequently transformed into solid by various means for example cyanoacrylate adhesive, wax or epoxy resin [25]. However, these infiltrants are not biocompatible for use in medical applications. Therefore, various solutions of biocompatible polymer such as polylactic acid and polycaprolactone were previously investigated as materials for infiltration [15]. Since the viscosity of the polymer solution should be low to aid the penetration into 3DP part, the percentage of the polymer in the solution cannot be high resulting in the limitation in degree of strengthening. In addition, using a polymer solution will make the claim of using water binder to avoid the residual solvent in the part invalid since the residual solvent would remain in the part unavoidably [13, 14].

In indirect fabrication process of implant by RP, heat-cured and self-cured polymethyl methacrylate are frequently used casting materials. However, these materials are viscous

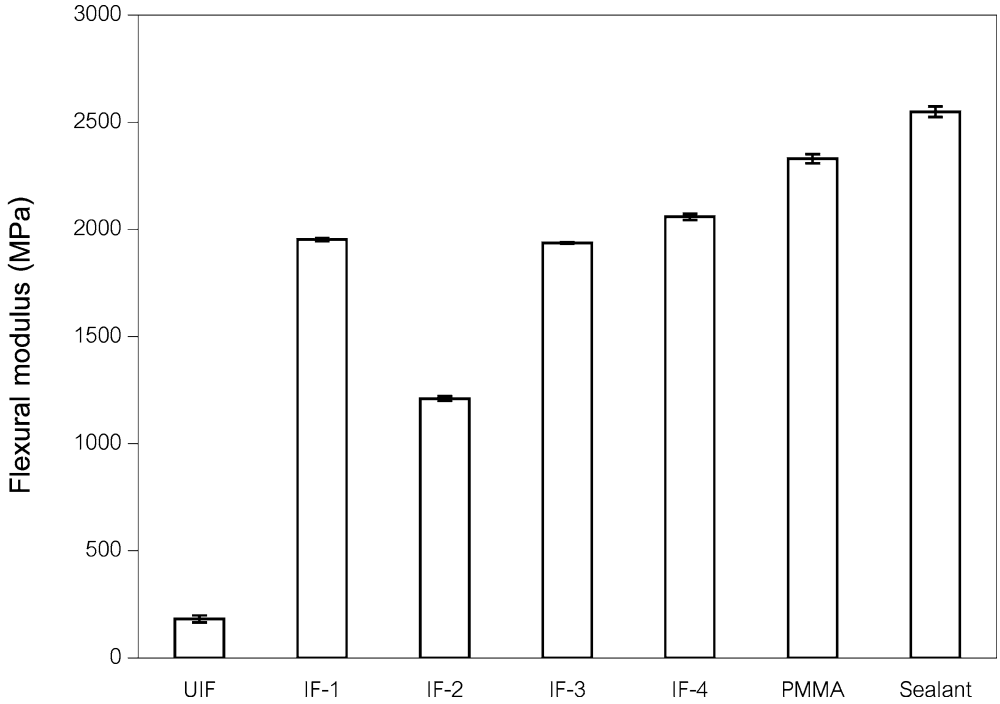

Fig. 2 Comparison of flexural modulus of uninfiltrated and infiltrated samples

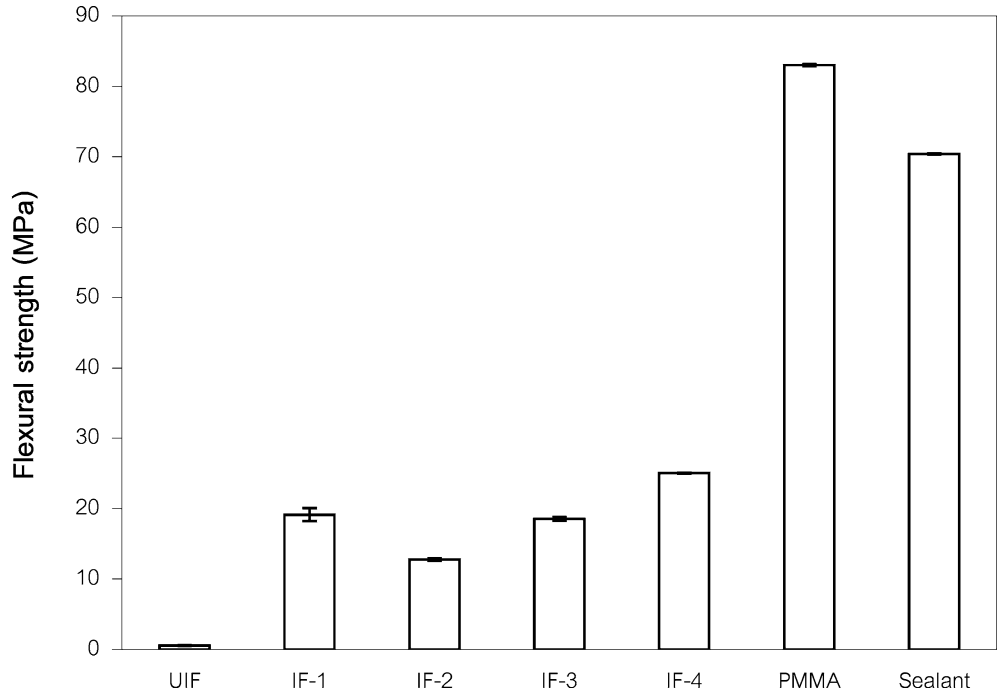

Fig. 3 Comparison of flexural strength of uninfiltrated and infiltrated samples

during mixing process and not suitable for infiltration purpose. Therefore, in this study, light-cured dental sealant was selected as an infiltrant due to its nontoxic, low viscosity and high strength compared to polymethyl methacrylate [26–28]. From the results, it was observed that the sealant could fully penetrate 3DP sample easily and rapidly without the aid of vacuum. After curing, no dimension changes could be detected in all directions and all curing conditions used. Figures 2–4 show a comparison of flexural modulus, strength and strain at break among uninfiltrated and infiltrated specimens. It could be observed that flexural modulus and strength of infiltrated specimens were influenced

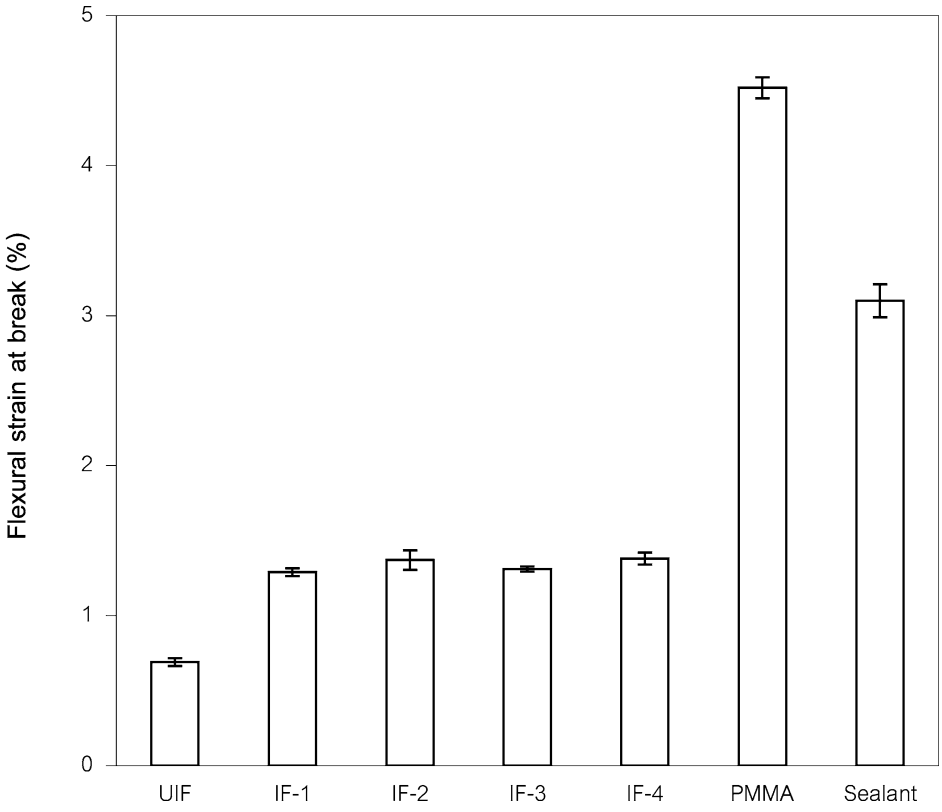

Fig. 4 Comparison of flexural strain at break of uninfiltrated and infiltrated samples

by infiltration conditions, but the strain at break showed no difference. In comparison among different curing conditions, the use of fluorescent light (IF-2) was not effective to cure the infiltrated specimen properly which could be seen from the lowest flexural modulus and strength values. Specimens cured by visible light curing unit (IF-1) showed similar level of flexural properties as the specimens cured by general halogen light bulb (IF-3). Post-heated treatment (IF-4) was also observed to further increase the flexural modulus and strength of infiltrated sample. These differences were confirmed by Raman measurement. In this study, the objective of using Raman measurement is to determine degree of conversion. This is done by comparing vibration bands of residual unpolymerized methacrylate C=C stretching band at 1640 cm^{-1} to the aromatic stretching band at 1610 cm^{-1} [23, 24]. The aromatic band was employed as an internal standard to normalize the effect caused by external parameters such as measurement date, instruments or different sample compositions. In addition, the advantage of using Raman is that it is a scattering technique. Clear sealant or opaque infiltrated samples could be measured and compared. The typical Raman spectra of sealant, uninfiltrated and infiltrated samples are shown in Fig. 5. No overlapped bands from uninfiltrated sample are observed in the interested wavelength spectra of infiltrated samples. It was found that degree of conversion varied with curing techniques, Fig. 6, in similar ways to the order in flexural properties. In general, light-cured sealant polymerizes when the initiator (camphoroquinone) in the resin is activated by light. Camphoroquinone activation is effectively initiated by a hue of blue light that has a wavelength within the range of 400 to 500 nm which is the range of halogen light, not for the fluorescent light. Differences in light intensity, wave length and exposure time were previously observed to influence the degree of conversion. Therefore, the effectiveness of conversion from monomer to polymer of the infiltrant is thought to be the cause of the different mechanical properties of infiltrated samples. Figure 7 shows the correlation between degree of conversion and mechanical properties. It could be seen that the relationship between flexural strength and modulus and the degree of conversion is linear on a semi-logarithmic scale. In the case of strain at break, no correlation was observed.

The use of visible light curing (VLC) unit with halogen light source equipped with blue filter is a typical method to cure the sealant in dental practice, but it is impractical for large-sized sample as in this study due to the small tip of the light probe. The specimen had to be cured repeatedly area by area to cover the whole specimen. Alternatively, it was shown that the use of general halogen light bulb without blue filter could also cure and enhance the flexural properties of 3DP specimen similarly to the use of a dental curing unit, but more convenient. Therefore, it would be practical to use halogen light bulb technique for curing the infiltrated 3DP parts.

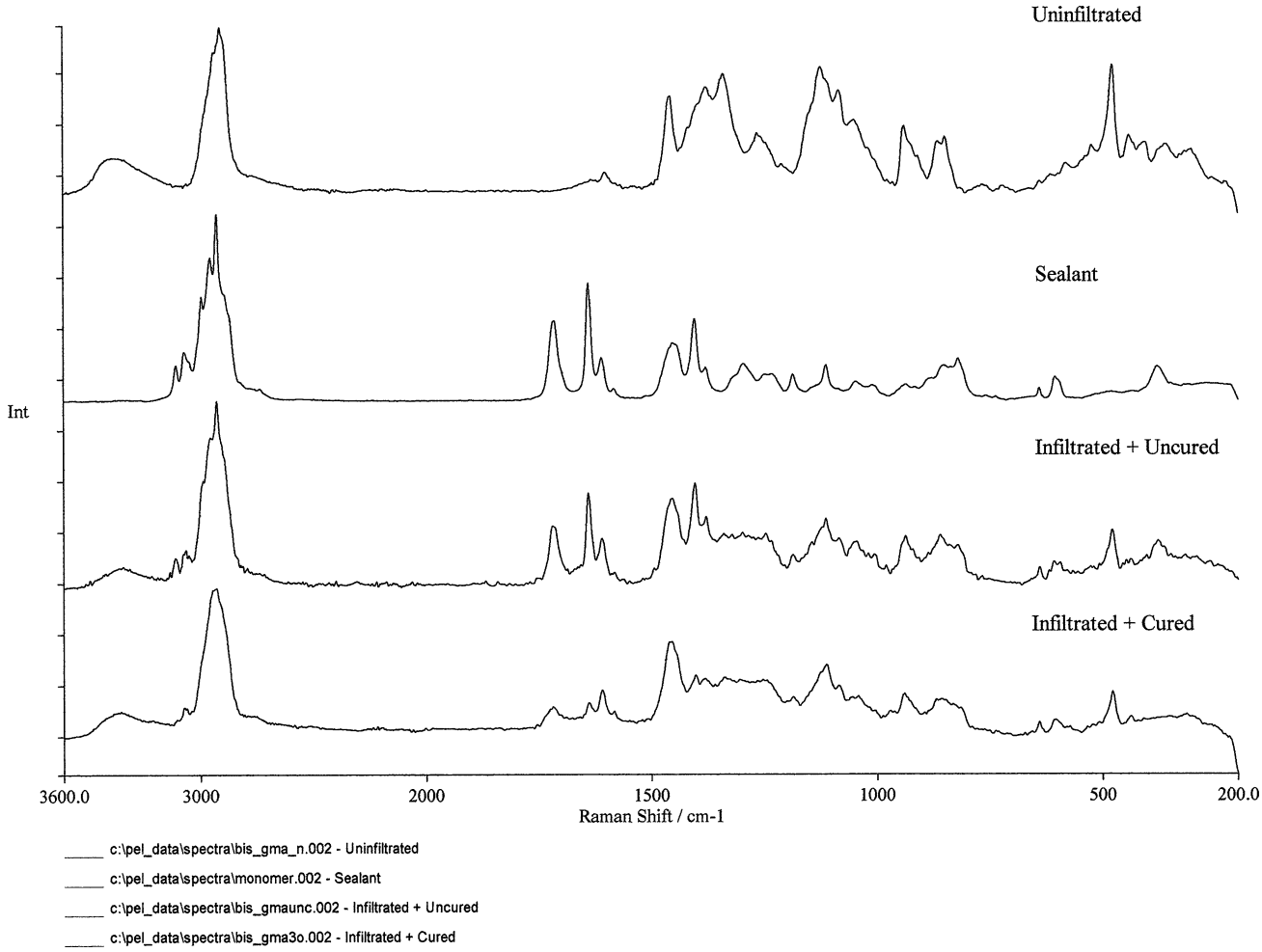

Fig. 5 Raman spectra of pure sealant, uninfiltrated sample, uncured infiltrated sample and cured infiltrated sample

It can be observed that infiltration greatly enhance the modulus and strength of specimens well over 10 times and 20 times respectively comparing to original uninfiltrated 3DP samples. Although the modulus of infiltrated samples increased to approach 80% of the values of polymethyl methacrylate and sealant, but the strength of the infiltrated specimen could only reach approximately one third of the values. Structurally, it can be envisaged that infiltrated 3DP specimens have structures similar to composite systems that consist of low strength natural polymer powders and voids in stronger infiltrant resin matrix. In general, modulus is resulted from the strongest part in material while strength is resulted from the weakest part. Therefore, the modulus of the infiltrated samples would be mainly resulted from the resistance to deformation of infiltrant portion which had modulus similar to pure sealant. The presence of low modulus natural polymers in the system did not affect significantly. In the case of strength, since the natural polymers and the natural polymers/infiltrant interface were much weaker than the resin, these areas would be starting points of rupture upon loading. Once this occurred, the load was amplified and transferred to the areas of infiltrant resin within the composite causing them to be under greater load. Thus, the infiltrated samples were much weaker than the pure sealant resin. This could also be seen from similar values of strain at break of infiltrated samples regardless the curing conditions and much lower values comparing to pure sealant.

In addition, the differences in the flexural properties of infiltrated samples and pure sealant could be further explained by the differences in degree of conversion. From Raman studies, it was shown that pure sealant had greater degree of conversion than infiltrated samples. This is due to the fact that pure sealant is more transparent than infiltrated samples. Thus, the intensity of light that can pass through the material during curing is greater for initiating polymerization and resulting in a stronger resin. Although infiltrated specimen is still weaker than polymethyl methacrylate, it is stronger than previously reported biomedical 3DP parts which showed modulus of ∼60–600 MPa and strength of ∼1.7–14 MPa [13, 15]. The values are still in the range of

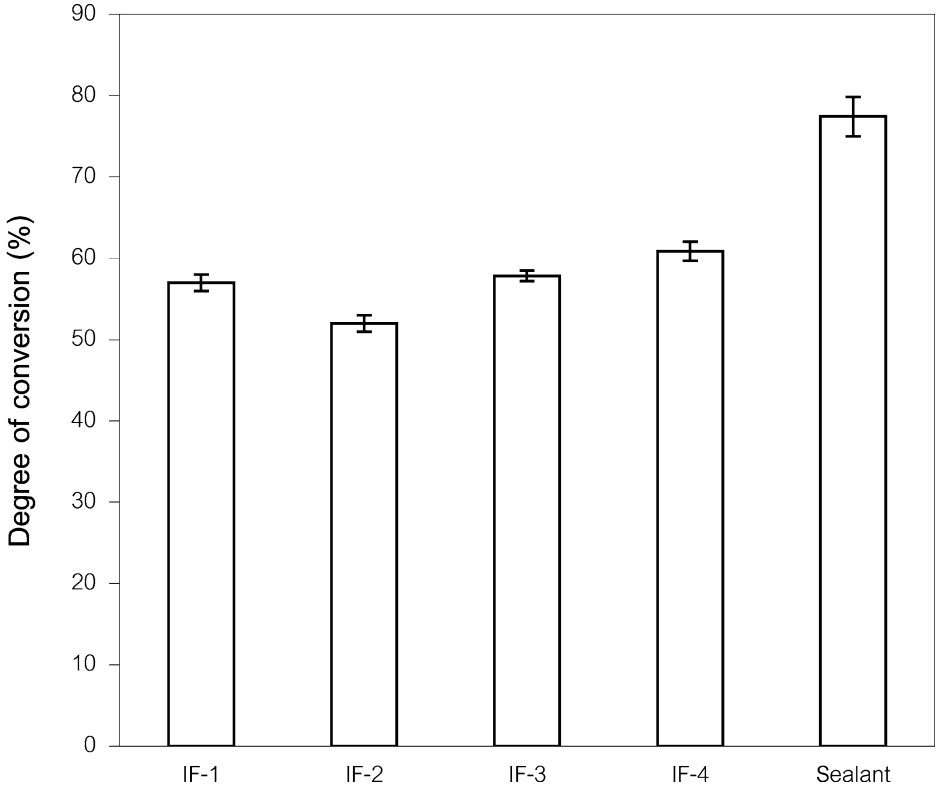

Fig. 6 Influence of curing conditions on degree of conversion determined by Raman technique

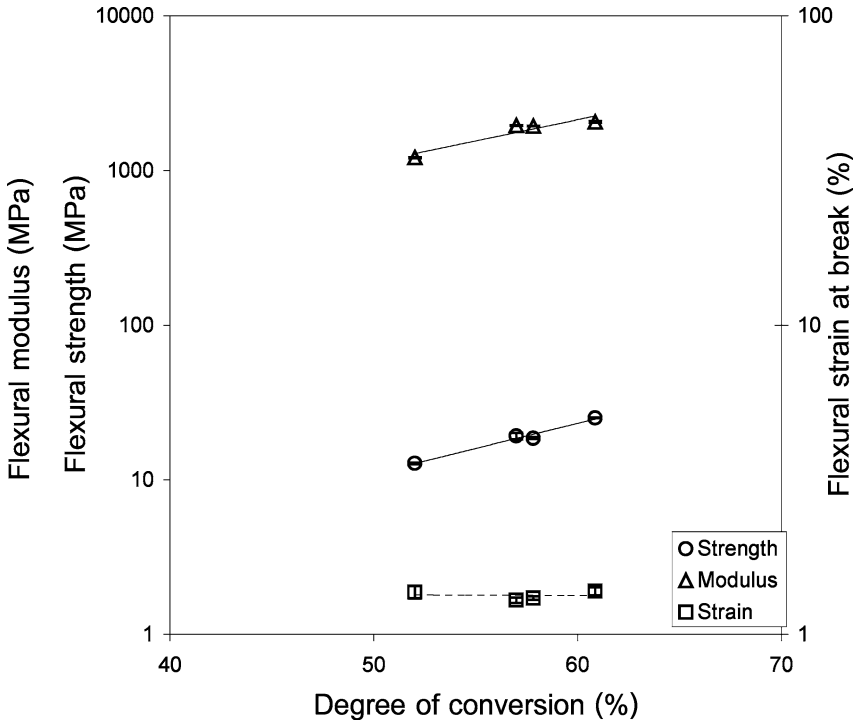

Fig. 7 Semi-logarithmic correlation between degree of conversion and mechanical properties

trabecular bone and some synthetic materials that are normally employed as an implant for reconstructive surgery for example porous polyethylene and silicone [30–32]. The ability of infiltrated sample to withstand a drilling force without breakage is also shown in Fig. 8. In case of toxicity, preliminary *in vitro* toxicity test of infiltrated 3DP parts, IF4, using L-929 cells showed that the cells which were in contact with samples were healthy. No inhibition zone was observed.

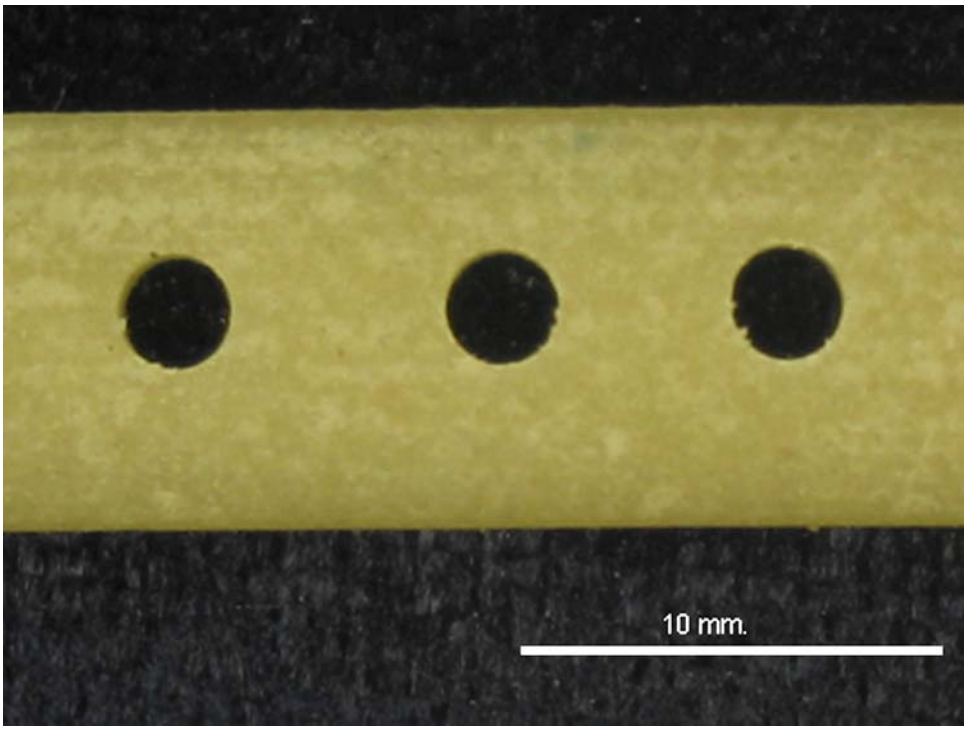

Fig. 8 Demonstration of drilling holes on infiltrated sample

4 Conclusions

In this study, an alternative method for increasing strength of large 3DP parts without using toxic solvent was demonstrated. The use of light-cured acrylate resin as an infiltrant was observed to enhance flexural modulus and flexural strength of natural polymers based three dimensional printing (3DP) part to be closed to generally used polymethyl methacrylate resin. In addition, infiltration also helps in maintaining the structural integrity of 3DP parts when contacting water. Preliminary *in vitro* toxicity test showed that infiltrated sample was not toxic. From the results of mechanical and physical properties, this post-processing technique would increase the possibility of directly using 3DP samples for fabrication of implants for reconstructive applications.

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