Effect of Three-dimensional Printing with Nanotubes on Impact Resistance

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Research article

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Abstract

The types of biomedical devices that can be three-dimensional printed (3DP) is limited by the mechanical properties of the resulting materials. As a result, much research has focused on adding carbon nanotubes (CNT) to these photocurable polymers to make them stronger. However, there is little to no data on how CNTs affect the impact resistance of these polymers, an important property when designing and manufacturing lower limb prosthetics. The objective of this study was to expand the use of 3DP to prosthetics by testing the hypothesis that adding CNTs to a stereolithographic (SLA) photocurable resin will result in a cured polymer with increased impact resistance. Twenty-six total specimens: 13 with nanotubes and 13 without nanotubes, were printed on a Form2 SLA printer. Once all the specimens were printed, washed, and cured, the impact resistance was quantified using a pendulum impact tester in a notched Izod configuration. Contrary to the hypothesis, the specimens with SWCNTs (0.312 ± 0.036 ft*lb/in) had a significantly lower impact resistance compared to the non-SWCNT specimens (0.364 ± 0.055 ft*lb/in), $U = 34.0$, $p = 0.004$. This decreased impact resistance may be due to voids in the printed polymer around the aggregated nanotubes. Thus, SLA polymers still do not have the impact strength needed to be used for a full lower limb prosthetic.

Introduction

Three-dimensional printing (3DP) has grown in popularity as a method to manufacture personalized biomedical devices [1], [2]. For example, bionic hand prostheses have been made via 3DP for children with traumatic and congenital hand amputations or reductions [3]. The 3DP technology allowed the researchers to manufacture custom prostheses that were functionally equivalent, both in size and range of motion, to the intact hand. Invisalign braces are another successful example of using 3DP to create uniquely fitted biomedical devices to straighten teeth [4]. Also, 99% of hearing aids that fit in the ear are custom made using 3DP [5].

The most common technologies used in the 3DP of biomedical devices are fused deposition modeling (FDM), selective laser sintering (SLS), and stereolithography (SLA) [1], [6]. FDM printers create parts by using a nozzle to deposit a heat-softened polymer one layer at a time. This method is most commonly used in consumer printers. Although, these FDM printers lack resolution and hence make them unsuitable for the manufacturing of medical applications. SLS creates devices with a metal (titanium or stainless steel) or nylon powder. A laser sinters this powder one small layer at a time to create the part. SLS printers are best suited for metal implants that require sterilization. However, metal is not always desirable for biomedical devices due to its weight. SLA printers create parts by using a laser to cure photocurable polymers one thin layer at a time. These printers are the most commonly used for biomedical devices since SLA printers can utilize a wide range of materials ranging from brittle, glasslike materials to rubbers. These printers also have the highest resolution of the printing technologies, making them ideal for fine features (e.g. bone implants with intricate blood vessel canal systems) [7].

The types of biomedical devices that can be 3DP with SLA printers is limited by the mechanical properties of the resulting materials [8]. Polymers resulting from SLA printers tend to be brittle with a low modulus of elasticity and low ultimate tensile strength. As a result, much research has focused on adding nanoparticles (e.g. SiO_2) and carbon nanotubes (CNT) to these photocurable polymers to make them stronger [7]. Multiwalled carbon nanotubes (MWCNT) can increase the ultimate tensile strength by 17%; although, adding these tubes also decreases the elongation at failure by 13% [9]. Adding nanosilica has been shown to increase the ultimate tensile strength by 20.6% and the elastic modulus by 65.1% [10]. Singlewalled carbon nanotubes (SWCNT) have been shown to increase tensile strength by 24% while reducing elongation at failure by 21% [11]. While these additives create similar increases in ultimate tensile strength, CNTs are the most commonly used due to their unique electrical properties with future implications for integrated circuits (e.g. circuitry of hearing aids).

Currently, 3DP is not a widely used manufacturing method for custom lower limb prosthetics and orthotics because the polymers cannot handle impact [12]. When the leg contacts the ground during normal walking, a force 1.5 times body weight is felt on the foot [13]. This results in up to 1.17 J of impact kinetic energy [14]. To dissipate this energy, traditional prosthetics and orthotics are made of materials with a notched Izod impact resistance of 1.3—18 ft-lbf/in [15]. This impact loading during walking would shatter traditional, brittle SLA polymers that only absorb approximately 0.46 ft-lbf/in of energy (Formlabs Inc., Somerville, MA). The addition of SiO_2 nanoparticles to SLA resin has been shown to increase impact resistance from 0.59 to 0.67 ft-lbf/in [16]. However, this increase is still not enough to make 3DP with SLA a viable option for lower limb prosthetics and orthotics. CNTs have superior tensile strength compared to nanoparticles and thus may increase this impact property enough for prosthetic and orthotic use. Therefore, the objective of this work was to test the hypothesis that adding SWCNTs to SLA 3DP resin will result in a cured polymer with increased impact resistance suitable for later use in manufacturing lower limb prosthetics and orthotics.

Methods

Twenty-six notched Izod specimens [17] were printed: 13 with nanotubes and 13 without nanotubes. GPower [18] was used a priori to determine the number of specimens needed to detect a moderate effect size (Cohen $d = 0.5$) with a reasonable statistical power ($\alpha = 0.05$, $\beta = 0.8$) in a two-tail, independent t-test. All of these notched Izod specimens were printed using the Clear V4 photocurable polymer (i.e. resin) on a Form2 printer (Formlabs Inc., Somerville, MA) (Figure 1). This is a commercially available SLA printer that utilizes digital light projection and a continuous liquid interface [19]. The mechanical properties of the resin are available from the manufacturer (i.e. elongation at failure, elastic modulus, ultimate tensile strength, and impact resistance); although the exact chemical composition of the resin is proprietary, the general components are methacrylated oligomers, monomers, and photoinitiators. The clear resin was used since this is the least viscous polymer offered by the manufacturer, and SWCNTs mix best in less viscous resins. After the specimens were printed, they were washed in a FormWash for ten minutes (per the manufacturer's instructions). This washing station used >90% isopropyl alcohol (IPA) to remove uncured resin from the specimens. Subsequently, a FormCure was used to expose these specimens to a 405 nm light at 60C for 30 minutes (per the manufacturer's instructions). This curing process was done to completely harden the resin and provide the highest mechanical properties (i.e. increase ultimate tensile strength) [20].

CNTs are the most common additive, compared to nanoparticles, due to their high tensile strength. While MWCNT are the most utilized CNT, SWCNTs provide superior resolution in the final part [21]. Hence, SWCNTs of purity >90%, diameter 0.6—1.2 nm, and length 400—2000 nm from Adnano Technologies were used in this study. A 0.10% (weight/volume) solution of resin was created by adding 1 gram of these SWCNTs to 1000 mL of Clear V4 resin. Previous studies have used a range of 0.05% to 1.5% for adding CNTs to SLA polymers [21]. A lower, conservative concentration was used in this study since higher concentrations can result in aggregation of the nanotubes that the laser would not be able to penetrate, thereby resulting in uncured resin. The SWCNTs were dispersed in the resin by shaking (i.e. shear dispersion). Once mixed, the resin was immediately used to create the specimens with nanotubes, thereby reducing any effects due to settling of the SWCNTs.

Once all the specimens were printed, washed, and cured, the impact resistance was quantified using a pendulum impact tester in a notched Izod configuration. The data was analyzed using custom Python code [22]. First, statistical outliers were removed from the data (Figure 2). A statistical outlier was defined using the standard deviation method [23]. Then, the impact data was tested for homogeneity of variance with the Levene's test. Data that failed the Levene's test was adjusted using transformations (e.g. taking the log of all data points [23]). Next, the normality of this transformed data was quantified with the Kolmogorov–Smirnov test. The normally distributed data was compared via the independent t-test to assess the impact resistance between groups. Non-normally distributed data, however, was compared using the Mann–Whitney test (i.e. the non-parametric version of the independent t-test). The impact resistance of the two groups was deemed statistically different if the result of the t-test (or Mann-Whitney) was $p < 0.05$.

To assess if this difference is clinically relevant, the effect size and minimal detectable change (MDC) were also calculated [24]. The effect size (also called Cohen's d) quantified the difference between two groups while removing confounding effects due to sample size [25], [26]. The interpretation of this effect size was then whether a difference was small ($0.2 < d < 0.5$), medium ($0.5 < d < 0.8$), or large ($0.8 < d$). The MDC quantified the amount of change that could realistically be measured between two groups, given the reliability and uncertainty inherent in the equipment. The MDC was quantified according to [27] assuming intraclass correlation coefficients of 0.8 [28]. A statistically significant difference in impact resistance between with and without nanotube groups (i.e. $p < 0.05$ result from t-test) was considered clinically meaningful if the effect size was greater than 0.55 (i.e. a moderate effect size) and the difference between groups was greater than the MDC [24]. This clinical relevance was important to establish as this showed if there was a practical, as opposed to purely mathematical or a statistical anomaly, increase in impact resistance from SWCNTs.

Results

Statistical Check of Data

There were no statistical outliers in either group of the impact data. The variances of the data were equal between groups, $F(1, 24) = 0.92$, $p = 0.35$. The non-CNT data was not normally distributed, $D(13) = 0.60$, $p < 0.001$. The SWCNT impact data also proved to be non-normally distributed, $D(13) = 0.59$, $p < 0.001$.

Comparison between Groups

The specimens with SWCNTs (0.312 ± 0.036 ft*lb/in) had a significantly lower impact resistance compared to the non-SWCNT specimens (0.364 ± 0.055 ft*lb/in) by 14%, Mann-Whitney $U = 34.0$, $p = 0.004$ (Figure 3). This difference of 0.053 ft*lb/in was greater than the minimal detectable change of the equipment, 0.003 ft*lb/in. This resulted in a large effect size of $d = 1.13$.

Discussion

SLA is not commonly used to 3DP lower limb prosthetics due to the inadequate impact resistance of the resulting materials. The objective of this study was to investigate the use of SWCNTs to increase the impact strength of an SLA polymer. Contrary to the hypothesis, these CNTs decreased the impact resistance by 14%. This may be a result of the lack of chemical interaction between the polymer and nanotubes.

The nanotubes were added to the viscous polymer through shaking, as done in other studies [9]. As the parts were cured layer by layer in the printer, the nanotubes and polymer chains did not cross-link as nanotubes have no inherent functional groups that can attach to the polymer chains [29]. Previous studies have shown that slippage occurs between the nanotubes and polymer matrix, which limits stress transfer between these materials [30]. This lack of stress transfer is theorized to arise from a mismatch in coefficients of thermal expansion between nanotubes and the polymer matrix [30]. This lack of covalent bonding and stress transfer is likely what contributed to the decreased impact resistance of the material. As the nanotube-resin polymer undergoes impact loading, local fractures likely occur at these nanotube-polymer chain interfaces, similar to what has been shown in tensile testing simulations of nanotube-polymer composites [31]. Although, these local fractures could not be confirmed in the nanotube-polymer composite of this study as scanning electron imaging does not provide adequate depth to capture images of embedded nanotubes [32]. Hence, computational modeling has been used in the literature to explain these types of phenomena [31].

The overall goal of this work is to determine how to alter SLA polymers to make them impact resistant enough for manufacturing of personalized lower limb prosthetics. According to the literature and results of the current study, SLA polymers do not yet provide the impact resistance needed for a complete lower limb prosthetic. Although, the results of this study do provide useful information towards this goal. The mere presence of SWCNTs, a nanomaterial with a high tensile strength, is not enough to increase the impact functionalization groups and method on impact strength. There is a paucity of research on how functionalization affects these impact properties.

There are some study design factors to consider when interpreting the results of this study. First, a single polymer from FormLabs was considered in this study. FormLabs provides many other options. However, the current study was limited to one polymer to isolate the effect of SWCNTs on impact strength without the confounding effects of polymer types. Second, a single type of SWCNT was used. This was chosen for a similar reason, to isolate the effect of SWCNT on impact resistance without the confounding factors of SWCNT length and diameter. I would hypothesize to see similar results where SWCNTs of various sizes would decrease the impact resistance of other polymers; although the difference would be quantitatively different. Third, some studies mix nanotubes into composites via ultrasonic dispersion [9]. However, this method was not used in the current study as sonification may damage the nanotubes [33].

In conclusion, adding SWCNTs to SLA polymers through shear dispersion decreased the impact resistance of the material by 14%. Thus, SLA polymers are still not a viable option for manufacturing lower limb prosthetics. This decrease may have been a result of local fractures that occur at the nanotube-polymer chain interfaces. Functionalizing the nanotubes for better stress transfer between the nanotubes and polymer chains may change this in future studies.

Declarations

Ethics: Not applicable since no human subjects were used.

Consent for Publication: Not applicable since no identifiable data was collected or presented.

Availability of Data: The raw data can be made available upon request.

Competing Interests: There are no conflicts of interest to disclose.

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Nomenclature

3DP

Three-dimensional printing

FDM

Fused deposition modeling

SLS

Selective laser sintering

SLA

Stereolithographic

CNT

Carbon nanotube

MWCNT

Multiwalled carbon nanotube

SWCNT

Singlewalled carbon nanotube

IPA

Isopropyl alcohol

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Figures

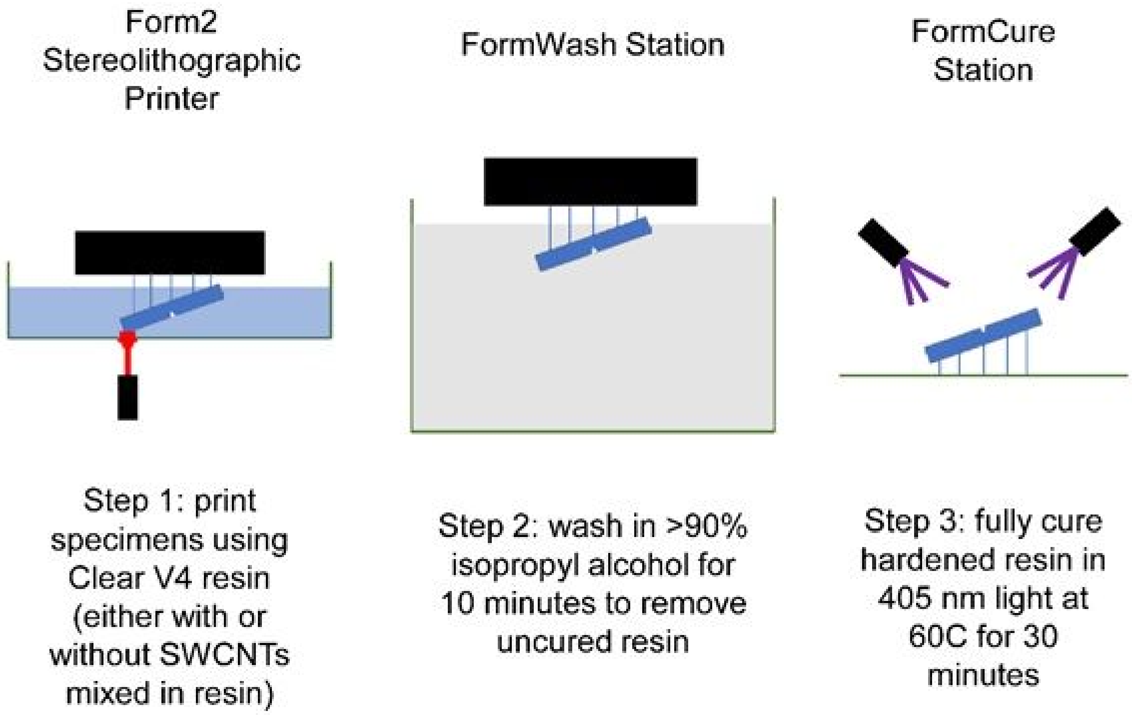

Figure 1

Figure 1: Impact specimens were printed with an SLA printer, washed in isopropyl alcohol, and cured with UV light.

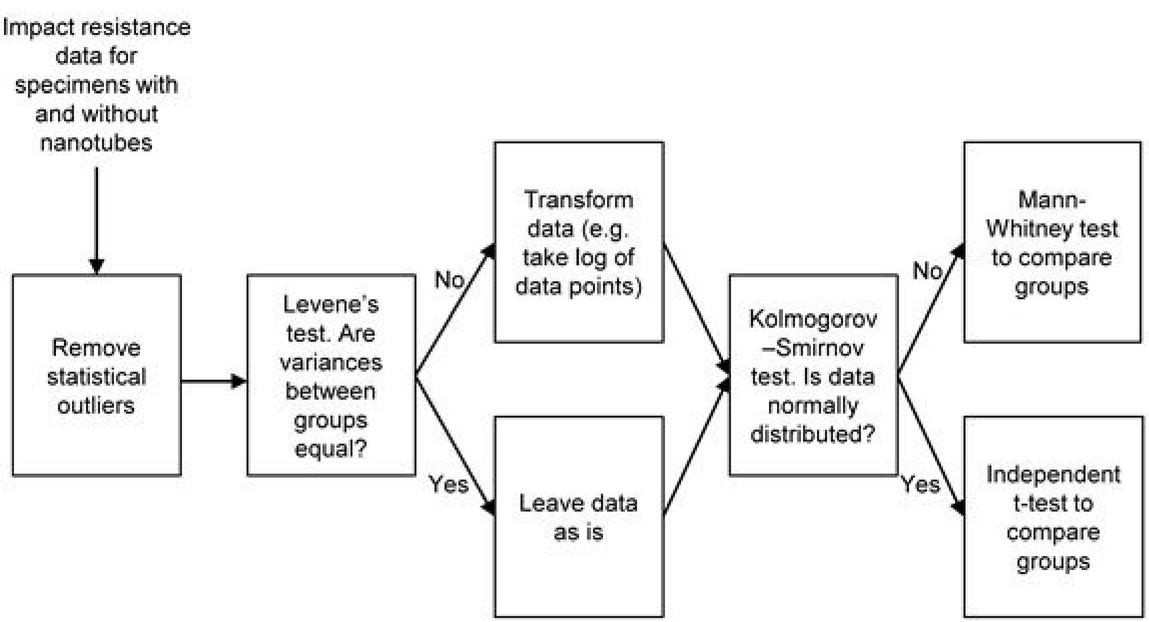

Figure 2

Figure 2: Method used to statistically compare the impact resistance of the two groups: specimens printed without SWCNTs and those printed with SWCNTs.

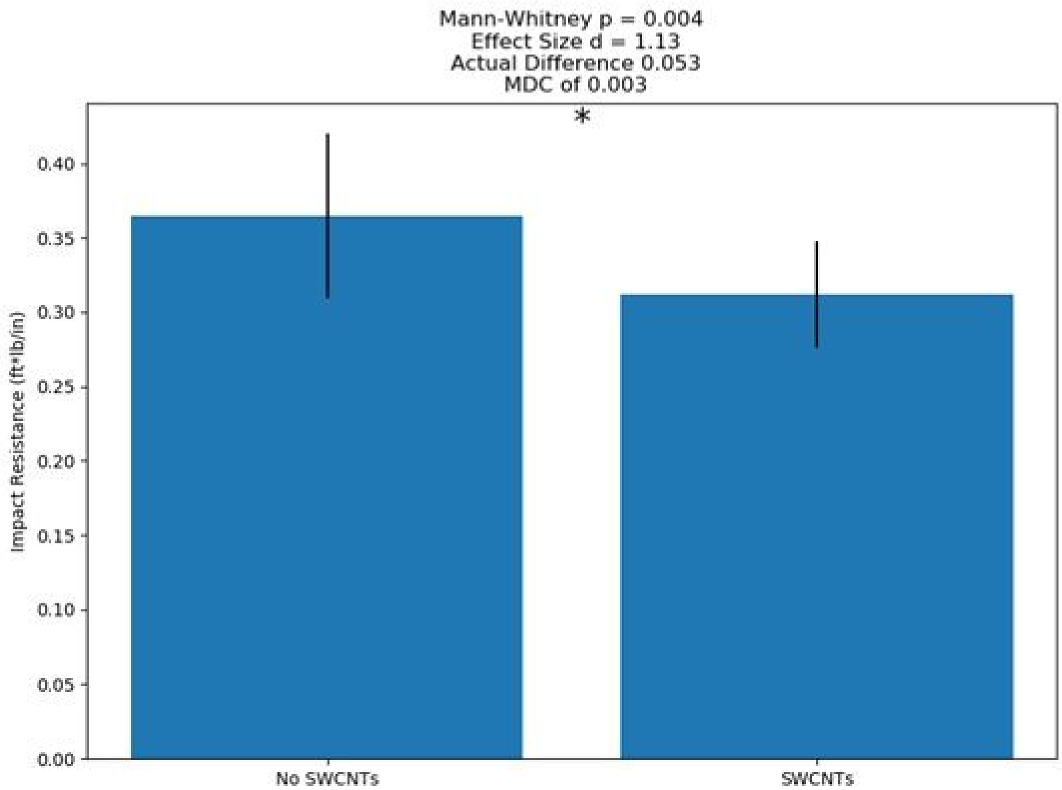

Figure 3

Figure 3: SWCNTs significantly decreased the impact resistance of the SLA printed specimens.