

Advancing 3D Printing Filaments with Carbon Nanotubes for Composite Structures: A Method and Characterization Study

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Abstract

Adding new chemicals, especially nanomaterials, to 3D printing filaments is a promising method for creating unique composite structures. As a result of its adaptability in a wide variety of technical sectors, including mechanical engineering, sensor development, and bioengineering, interest in the prospective uses of carbon nanotubes (CNTs) is consistently on the rise. This 2D carbon nanomaterial has unique properties that may be used with 3D printing to provide novel approaches to the design and manufacture of one-of-a-kind components. This research demonstrates a simple approach to coating a commercial polymeric filament with CNTs, which fused deposition modeling may then employ to create a testing structure. Experimental characterization was carried out to examine the presence, function, and distribution of CNT on the polymer surface to ascertain the process's dependability.

Keywords

Carbon nanotube, 3D printing, Filaments, Polycaprolactone, Composites

Introduction

The research and development of specialized composites is an intriguing and useful possibility to produce one-off structures with several uses. CNTs and other carbon-based nanomaterials can be used as fillers to improve the final composite in a few ways [1, 2].

Many individuals are intrigued by the flexibility of CNTs, which consist of a single layer of sp²-bonded carbon atoms organized in a regular hexagonal lattice [3, 4]. The presence of oxygen functional groups such as epoxides, alcohols, and carboxylic acids in the single-layer sheets of CNT raises the prospect of large-scale, cost-effective chemically modified CNT manufacturing [5]. Because of these groups, CNT is very hydrophilic and can expand and disperse in water with little effort. It has been reported that CNTs may be exfoliated to generate stable aqueous dispersions that are almost totally composed of sheets 1 nm thick by subjecting them to a modest ultrasonic treatment in water [6].

Researchers are exploring CNTs potential in a variety of sectors since it has the potential to be a useful material in many settings, including healthcare. Researchers [7], owing to characteristics like biocompatibility, biodegradability, a high specific surface area, and the propensity to be effectively disseminated in aqueous media. These characteristics point to a broad variety of possible uses; to better bioactivity and drug delivery in bone tissue engineering, for instance, they may help make mesoporous zinc oxide scaffolds covered in CNTs flakes [8, 9]. In addition, research into the cardiac troponin-I protein was conducted to develop a novel label-free impedimetric biosensor for the detection of myocardial infarction [10]. In addition, experiments using a magnetite/CNTs composite to

remove cobalt (II) ions from aqueous solutions demonstrated that CNT might be a viable option. CNT-based materials are being investigated for use in electrochemical sensor building in electroanalytical chemistry [11].

Since the final qualities of a composite are reliant not only on the selected materials but also on the manufacturing procedures, it is vital to account for the latter in this framework [12, 13]. Although several technological approaches exist, 3D printing is rapidly becoming the technique of choice due to the high degree of precision it affords throughout the whole manufacturing process, beginning with the initial concept and ending with the final product [14]. Modeling, selective laser sintering includes a variety of experimental solutions, all of which have a common manufacturing strategy based on the addition of successive layers in a direction perpendicular to the deposition plane to create three-dimensional structures [15, 16]. These methods may be used to treat a wide variety of materials, including metals, polymers, and ceramics, albeit a unique setup may be needed to gather a suitable structure resulting from a specialized design for each kind of material.

This research investigated whether it would be possible to include CNTs into polycaprolactone filaments for usage in FDM 3D printers (FDM). The suggested procedure made it possible to include a second phase into the resultant structure, therefore defining a new method for producing composites. To characterize the CNT-modified polymer, compare it to the plain case, and evaluate the validity of the suggested approach, thermal analysis was performed.

Experimentation

Materials

Go Green Products offered CNTs in powder form (4-10 % oxidation) (Chennai, India). Javanthi Enterprises supplied the polycaprolactone (PCL) filament and the distilled water (Chennai, India).

Filament preparation

For 30 min, CNTs were ultrasonicated in a solution of 0.5% (w/v) bidistilled water. For 3 h at 40 °C, a sample of PCL filament was magnetically stirred in the resulting suspension. The recovered filament was air-dried at 40 °C after treatment and put back into service for 3D printing.

Statistics

The results are shown as a mean \pm SD. At least triplicates of each assay were conducted, and non-parametric tests were used to analyze the results. There were two stages of statistical analysis used to compare the groups. The Kruskal-Wallis test employed to analyse the data where appropriate, and the Mann-Whitney U test was employed to analyze each group independently if statistically significant differences were found. The significant threshold was set at 0.05.

Scaffold printing

Scaffolds for testing PCL-CNTs were made using a N2 FFF 3D printer. Z-slices were made from the imported

geometric model file in idea maker. A temperature of 160 °C was applied to the nozzle (diameter 0.4 mm), while the temperature of the construction platform was 20 °C. Scaffolds ($8 \times 8 \times 3.2 \text{ mm}^3$) were made by alternately stacking polymeric layers in the 0 and 90 °C.

Raman characterization

CNT deposition on the scaffold surface was investigated using a Raman spectroscopic evaluation [17, 18]. Readings were taken using a Raman microscope, with samples including CNT powder, unmodified PCL, and PCL-CNT 3D printed structures. A 790 nm laser was used to capture the spectra, with a 10-second exposure time and three accumulations.

To evaluate CNT distribution along the filaments of the 3D printed devices, Raman maps were acquired at numerous, randomly selected sites. This was accomplished by focusing on a fixed area of 150 mm \times 30 mm (step 2.5 mm) at 790 nm for 2 seconds each exposure and 2 accumulations per spectral acquisition. 3D printed PCL-CNT spectra make it easy to observe the 1580 cm^{-1} intensity peak that was used to generate the following maps. This peak is indicative of the CNTs G band.

In all cases, the spectra underwent just basic processing to fix the baseline and filter out any cosmic rays.

Analysis on thermal properties

The thermal characteristics of 3D-printed PCL structures were studied using differential scanning calorimetry with and without carbon nanotube loading (DSC). All samples were heated to a steady 10 °C per minute in aluminium pans using a differential scanning calorimeter linked to a thermal analysis data system. Nitrogen was used for the DSC measurements, which were done at temperatures ranging from -200 to +100 °C. A bare aluminum baking sheet filled in for it.

Thermal stability and CNT residual content were analyzed using thermogravimetric analysis (TGA) to learn more about the composite material. Under a nitrogen environment, readings were taken from 25 to 800 °C at a scan rate of 10 °C per minute.

Results and Discussion

Electrospinning, solvent casting, and foaming are only some of the ways that may be used to fabricate composites containing carbon nanofillers, with the most appropriate method depending on the intended use of the final product [19]. However, such experimental methods may necessitate the use of hazardous solvents and do not permit the fine-tuning of data. The potential for 3D printing to revolutionize the fabrication of unique buildings remains despite these concerns. Pre-processing of chosen materials can create suitable composites for use in 3D printing.

The strategy may be readily applied to FDM printing filament, which is normally made by combining the polymer with a nanomaterial before being extruded [20]. As evidence, the authors say that they were among the first to try 3D printing a composite of CNTs with acrylonitrile, butadiene, and styrene. By first homogenizing precursors in methyl pyrrolidone, the

composite was precipitated, and then the composite was extruded from a single-screw extruder into a filament with a diameter of 1.75 mm. This experimental method often involves a lengthy period of preparation and may need sophisticated technological instruments that are not always easily accessible. As such, the suggested method here may be seen to circumvent these potential limitations, as it proposes a simple procedure for handling a composite structure.

Thermal investigation

Table 1 summarizes the collected results; nevertheless, there were no notable differences between the clean and CNT-modified PCL scaffolds in the DSC study (Figure 1). Since no discernible changes in melting point were discovered amongst the settings examined, it is safe to presume that they are comparable. When compared to PCL filament, the printed structures had lower enthalpy values (as measured by the region under the endothermic peak). The manufacturing conditions, which involved heating the deposited filament over the PCL's usual melting point and then rapidly cooling it, are a likely culprit in the filament's inability to recover its crystalline structure. As shown by the estimated enthalpy values, the PCL-CNT structure is not more likely to nucleate than the plain 3D structure [21]. In contrast, the traditional method necessitates adding the nanofiller to a polymer solution before printing the resulting composite. CNTs may modify the polymer chain, which may then affect the crystal structure, however there is little evidence to support this claim. To deposit a second unique substance on the surface of a 3D-printed object, the loading operation is only a covering method for the filament, designed to have minimal effect on the polymer's particular characteristics.

The 3D printed composite structure's thermal stability and CNT residual content were analyzed using thermogravimetric analysis (TGA) (Figure 2 shows the collected thermograms). Both the PCL and PCL-CNT constructions saw similar weight loss between 450 and 600 °C, which can be attributed to the extensive heat breakdown of the polymer chains. Within the measured temperature range, CNT powder lost only around 5.2% of its weight at 700 °C. When both 3D printed objects were kept at the same temperature, the difference in weight between them was around 0.3%, an amount that may be taken as roughly indicative of the nanofiller content.

Spectroscopic evaluation

CNT powder, pure polycaprolactone, and polycaprolactone-CNT 3D pattern is depicted in their respective Raman spectra in figure 3. As reported by the authors [22, 23], the PCL spectrum has well-defined peaks below its melting point, beginning with the C-COO stretch at around 800 - 950 cm⁻¹, followed by the C-C and C-O stretches at around 1100 - 1240 cm⁻¹, the CH₂ twist at 1350 - 1440 cm⁻¹, the CH₂ band at around 1420 - 1610 cm⁻¹, and finally the C-O stretch at around 1720 - 1810 cm⁻¹. Both the 1410 cm⁻¹ (D band) and 1630 cm⁻¹ (G band) peaks anticipated for CNTs were observed in the PCL-CNT spectra, with the latter being easily discernible despite the former's impact of increasing the peak area centred at around 1300 cm⁻¹ (owing to superimposition of signals in that region).

Table 1: Thermal characteristics of polycaprolactone initial and afterwards 3D printing.

	Melting temperature (°C)	Enthalpy (J/g)
PCL structure	67.9 ± 1.2	61.9 ± 6.1
PCL-CNT structure	66.3 ± 3.2	56.9 ± 6.4
PCL filament	67.4 ± 0.3	85.4 ± 0.9

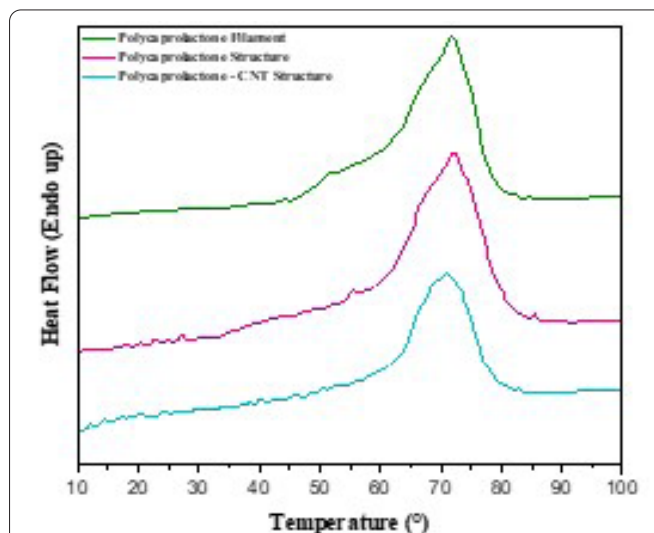


Figure 1: PCL filament, 3D printed PCL, and PCL-CNT thermal analysis using DSC.

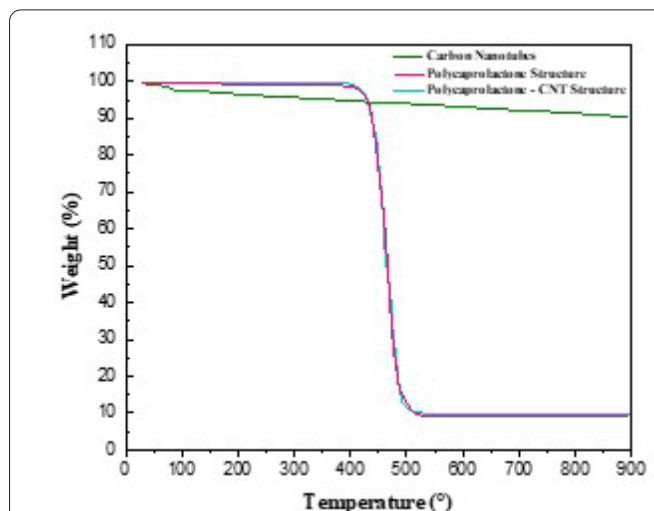


Figure 2: Thermogravimetric analyses (TGA) of 3D-printed PCL and PCLCNT structures and CNTs.

Lack of significant peak shifting in Raman spectra further supported the conclusion that the interaction between PCL and CNT was simply physical and not chemical. The authors also 3D printed a PCL/multi-walled carbon nanotube composite and saw the same result [24]. Raman spectroscopy was used to study several different aspects of CNT, including its quality, the association between the quantity of MWCNT and the intensity of the G and D bands, and the examination of electrochemically energy storage devices made from a PLA/CNT filament.

Scanners were used to evaluate the random distribution of CNTs over the 3D printed structures. The suggested ap-

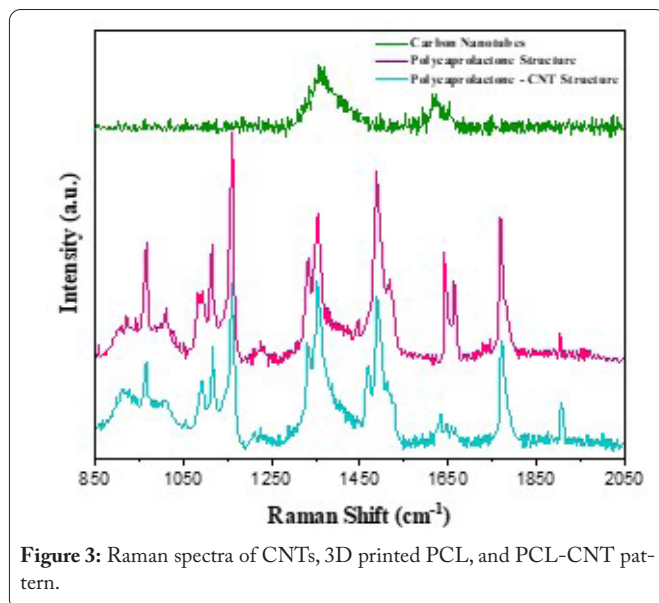


Figure 3: Raman spectra of CNTs, 3D printed PCL, and PCL-CNT pattern.

proach for modifying a PCL filament is successful, as seen by the rather even dispersion of the carbon nanomaterial.

Conclusions

This research presents a simple strategy for incorporating CNTs into 3D printing filament made of polycaprolactone. This method eliminates the need for considerable processing of the parent materials, as all that is required to make composite filament for 3D printing is to mix the two materials together. Evaluations of the suggested method's viability revealed that the carbon nanomaterial was present in the final 3D printed construction and was distributed evenly. One possible drawback of this method, however, is that the desired weight ratio of the combined elements is not regulated until the manufacturing process is finished (things must be checked directly as well, so that the filler content may be compared to its stated value).

The loading method did not have any discernible effect on the morphology of the polymer, as shown by thermal analysis of the 3D printed objects made from PCL filament, which highlights the importance of processing conditions during the deposition stage. Spectroscopic analysis confirmed the existence of CNTs on the printed surface and found that they were distributed rather uniformly, lending credence to the method's promise and providing a dependable new means of producing composites.

The experimental technique will be further refined in subsequent research with the goal of increasing and modulating carbon nanomaterial deposition on the filament surface and then evaluating the resultant scaffolds for targeted applications.

Acknowledgements

None.

Conflict of Interest

None.

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