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SYNTHESIS OF A CONDUCTIVE POLYMER FOR POTENTIAL USE IN PRINTING PROSTHETIC HANDS USING FDM TECHNIQUE

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ABSTRACT

Current prosthetic hands are often lacking in feedback mechanism while being very expensive. The Fused Deposition Modelling (FDM) technique provides a cost effective method to directly produce prosthetic hands especially for third-world countries. This study aims to synthesise a conductive composite material with good mechanical properties that could be used to print prosthetic hands using the FDM technique. An ABS/CNT composite material was synthesised via solution processing. The rule of mixtures and Zare’s model were used to analyse the mechanical properties while the percolation threshold theory and excluded volume theory were used for analysing the electrical properties. Results indicate that the material had good dispersion and retained the aspect ratio of CNT, thereby achieving good mechanical and electrical properties.

KEYWORDS

Fused Deposition Modelling, Carbon Nanotube, Conductive Thermoplastic, Prosthetic Hands, Percolation Theory

INTRODUCTION

Upper limb deficiency is a prevalent problem worldwide which imposes catastrophic limitations on individuals to perform activities of daily living (ADLs). However, current hands are unable to meet all the needs of amputees, as seen from the high rejection rates across the globe (Smit & Plettenburg, 2010). Such needs can be summarized in terms of cosmetics, comfort, control, and cost. A major limitation of most current prosthetic hands is a lack of feedback mechanisms. Thus, amputees cannot receive quantifiable feedbacks on their grip, such as grip strength. This leads to frustrating situations, where grasped objects are crushed or dropped. Meanwhile, the commercially available hands with feedback mechanisms are often exceedingly expensive. The cost is further compounded by the need for multiple replacement limbs over a lifetime.

We propose a novel solution to the problem by using the Fused Deposition Modelling (FDM) technique to directly produce customized prosthetic hands with in-built conductive structures. The FDM technique is employed due to its low cost, a critical factor in developing countries. Moreover, it also allows for the direct printing of complicated inbuilt conductive structures, thus removing the need for assembly, especially that of metal wires. Most importantly, the conductive structure allows for a variety of sensor feedback to users, allowing users to receive more information besides visual observation and proprioceptive feedback from the activating muscles, hence enjoying better control of the prosthetic hand. In this study, we aim to synthesise a polymer composite that is conductive, and with mechanical properties suitable for ADL. To allow for durability and usability in ADL, high tensile strength, high elastic modulus and low weight are desired. Among the various polymers commonly used in FDM, Acrylonitrile Butadiene Styrene (ABS) presents an ideal polymer to be incorporated. In addition, ABS has good impact resistance and good chemical resistance, which makes it more durable. However, to compensate for the low conductivity of ABS and to further enhance its mechanical properties, a conductive filler must be added. Carbon nanotubes (CNT) presents an ideal choice to be added to the composite, with high conductivity and superior mechanical properties. Many literature have shown that CNTs are effective conducting fillers for polymers, giving high conductivity at very low concentrations (Moniruzzaman & Winey, 2006). They also significantly improve the strength of polymers, mainly due to their high tensile strength and elastic modulus. There are two main types of CNT, the multi-walled CNT (MWCNT) and single-walled CNT (SWCNT). SWCNT generally has a lower density...
than thicker MWCNT (Gojny et al., 2006). As a lower concentration is needed for higher density nanotube fillers to form a conductive pathway in the insulator, we chose MWCNT for effectiveness and cost considerations.

**METHODOLOGY**

**Materials:** The polymer used in this work was ABS obtained from SABIC (Cycolac EX39, specific gravity = 1.0, MFI = 1 g/10 min). Multiwall carbon nanotubes (MWCNTs) were obtained from Nanocyl S.A. (Nanocyl™ NC7000 nanotubes, Sambreville, Belgium). HPLC grade chloroform, dichloromethane (DCM) and 1, 2-dichloroethane (DCE) were used for the nanocomposites preparation and nanotubes dispersion tests. All solvents were obtained from Fisher Scientific.

**Composite Preparation:** Seven ABS/CNT composites with CNT content from 0.1 wt.% to 10 wt.% (corresponding to 0.06% to 6.1% vol. ratio) were prepared as follows. One gram of ABS pellets was dissolved in 50 ml of DCM under vigorous mixing using a vortex mixer. Meanwhile, 1 milligram of CNT powder was suspended in 20 ml chloroform by sonication at a power of 90W for 8 min. The nanotubes suspension was added to ABS/DCM solution immediately after sonication. The mixture was then sonicated for another 8 min. After sonication, the composite suspension was then dried in a vacuum oven with heating at average 70°C for 3 hours. The procedure was repeated for 5.0, 10.1, 20.4, 41.7, 75.3, and 111.1 mg of CNTs. Separate samples of 0.5g/L CNT/DCE and CNT/chloroform were made by sonication for 8 min and used for dispersibility analysis and UV-Vis spectroscopy.

**Tensile strength and Elastic Modulus Characterisation:** Tensile strength and elastic modulus of the ABS/CNT composites were measured using standard ASTM D638 dog-bone-shaped specimens on a universal tensile machine 5567 Twin Column (Instron, U.S.A.).

**Electrical properties measurement:** Electrical properties measurement was done using the van der Pauw’s method. Details are shown in Appendix A.

**RESULTS AND DATA ANALYSIS**

**CNT Dispersion and Solvent Selection:** The CNT/DCE and CNT/chloroform solution were visually examined after sonication. It was observed that both suspensions showed a uniform black color without major aggregation and precipitation of the CNT 3 hours after sonication, which indicates good CNT dispersion. However, a very small amount of swollen nanotubes were observed in the DCE solution after standing for 24 hours, which meant that aggregated nanotubes were present. Thus, DCE may not be as effective as chloroform in dispersing CNT.

Figure 1. UV-Vis spectroscopy of CNT dispersed in DCE and chloroform solution

Using UV-Vis spectroscopy, we obtained qualitative indication for the relative degrees of CNT dispersion in different solvents. From Figure 2, absorption peaks can be observed for both solvents at a wavelength region of 260 nm. The peaks indicate a dominant amount of individual CNTs because individual exfoliated CNTs exhibit characteristic sharp absorption peaks due to additional absorption due to 1D van Hove singularities (Yu et al., 2007). Thus, this indicates good dispersion in both solvents. On the other hand, bundled CNTs are hardly active in the wavelength region between 200 to 1200 nm (Yu et al., 2007). Thus bundled CNTs exhibit only monotonously decreasing absorbance with increasing wavelength. Another absorption peak can also be seen at 800nm, which could possibly correspond to another transition between different energy bands of van Hove singularities. Moreover, it can be seen that area below the line for absorbance for CNT-Chloroform is slightly larger than that for CNT-DCE, and the distance between the two lines is especially large at around 260nm. This means a higher amount of exfoliated CNTs is present in chloroform. This further confirms that chloroform is a better dispersing agent and thus chloroform was used in synthesizing the composite. In addition, analysis using Hansen solubility parameters is done in Appendix B.
Tensile Strength and Elastic Modulus: To analyse mechanical properties in the CNT/ABS composites, we first use the rule of mixtures with correction factors as a basis for investigation of tensile strength $\sigma_{\text{composite}}$ and elastic modulus $E_{\text{composite}}$ of the composite (Loos, 2014).

$$\sigma_{\text{composite}} = \left( \eta_s \sigma_{\text{CNT}} + \eta_o \sigma_{\text{ABS}} \right) \phi + \sigma_{\text{ABS}}$$

$$E_{\text{composite}} = \left( \eta_o \eta_1 E_{\text{CNT}} + E_{\text{ABS}} \right) \phi + E_{\text{ABS}}$$

where $\sigma_{\text{CNT}}$ and $E_{\text{CNT}}$ are the CNT tensile strength and elastic modulus respectively, $\sigma_{\text{ABS}}$ and $E_{\text{ABS}}$ are the ABS tensile strength and elastic modulus respectively, $\phi$ is the CNT volume fraction, $\eta_s$ is strength efficiency factor decided by CNT length, $\eta_o$ is the orientation efficiency factor depending on CNT orientation, and $\eta_1$ is the length efficiency factor decided by CNT aspect ratio. Details of calculation are shown in Appendix C. The best fit lines of both equations give an estimate of a CNT aspect ratio of around 110. The aspect ratio is lower than that provided by the manufacturers, though their measurements were most probably done on pristine CNT. Both equations (1) and (2) show a relatively close fit and thus supports the inclusion of these correction factors for making an accurate prediction. The aspect ratios are similar to that reported in other studies using the same CNT type, and thus indicating a limited reduction in aspect ratio.

From Figure 2 and Figure 3, it can be seen that a small increase in CNT content does significantly increase both the tensile strength and elastic modulus of the composite, thus reducing the amount of CNT needed for enhancing the mechanical properties of the CNT/ABS composite. This is attributed to well dispersion and retention of aspect ratio.

$$E_{\text{composite}} = m \phi^{2/3} E_{\text{polymer}} + E_{\text{polymer}}$$

where $E_{\text{polymer}} = E_{\text{ABS}}$ in this case and $\phi$ is CNT volume fraction. Equation 3 implies that too much CNT content does not cause a large improvement of elastic modulus in CNT/polymer composite, possibly due to high agglomeration, poor dispersion, and high waviness of highly incorporated CNT in the polymer matrix. A higher value of $m$ may be indicative of good dispersion of CNT in the polymer matrix along with strong adhesion at the interface. The best fit curve gives a value of $m = 8$ for our experimental data. Comparing the $m$ parameter in this study to that in other studies, this study’s results show a high value. Thus, this empirical model indicates that the degree of dispersion is relatively high. It should be noted that the estimated errors in the mechanical properties are due to difficulties in synthesizing multiple identical specimens, as the melting of the composites may have incurred during the heating process.

Electrical Conductivity: To transfer from the insulating state to the conductive state, polymer composites require a critical concentration of conductive filler known as the electrical percolation threshold (Al-Saleh et al., 2013). Firstly, we used the excluded volume concept to predict percolation threshold (Balberg et al., 1986). CNTs are modelled as capped long cylinders with length L and a half sphere of diameter W/2 at each end. Their average excluded volumes can then be calculated by:
\[ V_{ex} = \frac{2}{3} W^3 + \frac{2}{3} W^3 + \frac{2}{3} W^3 \sin \gamma \mu \]  

where \( \langle \sin \gamma \rangle \mu \) denotes the average of angles between CNT rods and \( \sin \gamma \mu = \frac{4}{3} \) in this case. It was proposed by Balberg et al. (1986) that:

\[ \phi_c = 1 - \frac{V_{ex}}{V_{ex}} \]  

where \( V_e \) is the total excluded volume, \( V_{ex} \) is the average excluded volume, \( V \) is the actual volume of CNT rod, and \( \phi_c \) is the critical volume threshold. From a Monte Carlo study in 3D space (Celzard et al., 1996), \( V_e = 1.4 \) for continuous, randomly oriented, infinitely thin rods, \( V_e = 2.8 \) for continuous deformable spheres or parallel objects.

\[ V_{ex} \leq \phi_c \leq 1 - \frac{V_{ex}}{V} \]  

It can be seen that the percolation threshold is lower for rods than for spheres. This predicts the threshold to be between 0.4332 vol.% and 0.8646 vol.%.

From Figure 4, the graph can be roughly divided into three zones. In the first zone from 0.0% to 0.6%, a small increase in CNT content brings a significant increase in electrical conductivity. This is characteristic of the percolation threshold, with a sharp jump in the conductivity by many orders of magnitude. It can be predominantly attributed to the formation of a three-dimensional conductive network of the fillers within the matrix, and thus bringing an onset of electricity. In the second zone between 0.6% and 4.2%, a relatively moderate increase in electrical conductivity with increasing CNT concentration is observed. This behaviour can possibly be explained by the tunneling mechanism, which argues that besides direct contact, tunneling between filler particles can also act as an important conduction mechanism. The mechanism can be identified by studying the current-voltage (I-V) relationship at 1.2 vol.% (Strumpler & Glatz-reichenbach, 1999). Figure 5 indicates that the conductive behaviour follows an exponential trend, which is characteristic of conduction by tunneling. On the other hand, conductance by direct contact between the CNT particles is characterized by linear I-V relation. Tunneling occurs when the applied electric field is big enough to allow the electron wave function to penetrate through a thin potential barrier into the conduction band of the dielectric, and when CNT particles are less than 10nm apart. Thus, the increase in conductivity after around 0.6% can be attributed to both the formation of direct contacts and an increase in tunneling. In the third zone after 4.2%, an only marginal increase in electrical conductivity was obtained, even though CNT content more than doubles. This can be explained by the air inclusions caused during composite processing, which counters any increase in electrical conductivity with further increased solids content after the percolation threshold is reached. Alternatively, the formation of CNT aggregates at high concentration may also contribute to the leveling off of electrical conductivity.

To obtain the percolation threshold \( \phi_c \), we used the percolation theory, which predicts for the dependence of conductivity \( \kappa \) on filler concentration \( \phi \) a scaling law of the form \( \kappa = k (\phi - \phi_c)^t \) for
The critical exponent $t$ value for the ABS/CNT composite is at 2.42, which is within prediction, as it is expected to depend on the system dimensionality with calculation values of $t \approx 1.33$ in two and $t \approx 2$ in three dimensions. From Figure 6, the percolation threshold is at 0.23%, and it is evident that the threshold value is much lower than the predicted threshold volume fraction. Although it can be attributed to the high aspect ratio and well-dispersion, the presence of a lower kinetic percolation threshold than the statistical threshold predicted is also possible. In addition, errors arising from uncertainties in measuring small conductivities are possible, though this is possibly minimized by the van der Pauw method.

CONCLUSION

This study successfully synthesised an ABS/CNT conductive composite material for potential use as prosthetic hands. High mechanical and electrical properties were attained using the solution processing method. The results indicate that the material had good dispersion and retained the aspect ratio of CNT. This study also has huge potential to be used in many other applications due to its combination of conductivity, high mechanical properties and low cost. In future studies, the impact of the FDM technique on material properties will be investigated.

REFERENCES


Appendix A

Electrical conductivity measurements were conducted using the van der Pauw method. The prepared samples were cut into shapes shown in Fig. A1 to minimize effects from contact resistance. Measurements were repeated with different amounts of current, polarities of current, and opposite sides of the sample. Average values of the vertical resistance $R_{vert}$ and horizontal resistance $R_{hor}$ were calculated. Whether a side is vertical or horizontal is decided arbitrarily. The sheet resistance $R_{sheet}$ of the each sample was estimated by using the following formula:

$$R_{sheet} = \frac{R_{vert} R_{hor}}{R_{hor} - R_{vert}}$$  \hspace{1cm} (A1)

Thickness $d$ of each sample was measured and the resistivity $\rho$ of each sample is estimated with the following formula:

$$\rho = R_{sheet}d$$  \hspace{1cm} (A2)
Appendix B

For a qualitative investigation of CNT dispersion, Hansen solubility parameters were used. The total solubility parameter

\[ \delta_t^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \]  

(B1)

and the distance \( R \) in Hansen 3D space between the CNT and the solvent solubility parameters

\[ R = \sqrt{\delta_{CNT}^2 - \delta_{d,S}^2 + \delta_{p,CNT}^2 - \delta_{d,S}^2 + \delta_{h,CNT}^2 - \delta_{d,S}^2} \]  

(B2)

are used, where \( \delta_d \) is the dispersion component, \( \delta_p \) is the polar component and \( \delta_h \) the hydrogen bonding component. It is estimated that the value of the total Hansen solubility parameters for a similar type of CNT as used in this study is 21.1. The solubility parameters for chloroform and DCE are estimated to be 19.0 and 20.9 respectively. Moreover, the \( R \) value for chloroform is estimated to be 3.9 while that for DCE is estimated to be 1.4.

Appendix C

For Eq. (C1), \( \eta_s = 1 - \frac{l}{l_c} \) is CNT fibre length, and \( l_c \) is the critical length. In the case of a hollow cylinder such as CNT particle, \( l_c \) is given by

\[ l_c = \frac{\sigma_{CNT} D^2}{2 \tau} \]  

(C1)

where \( D \) and \( D_i \) are the external and internal CNT diameters, respectively, and \( \tau \) denotes the interfacial sheer stress between ABS and CNT, which is also key to effectively enhance ABS properties using CNT fillers. Eq. (C1) is fitted to the experiment graph to find \( \eta_s \). The best-fit line of the tensile strength data gives a ratio between actual length and critical length of 3.33. In order to strengthen the material to its maximum potential, this ratio must be bigger than one because the stress transferred to the fibre reaches the maximum value (\( \sigma_{CNT} \)) at a length \( l_c \) from the end of the fiber. Therefore, it can be seen that in the composite, an optimal stress transfer can be achieved. The best-fit line of the tensile strength data gives \( l \approx 1000 \) nm, and thus the CNT aspect ratio of around 110.

For Eq. (C2), \( \eta_o \) is the orientation efficiency factor, with \( \eta_o = 0.2 \) for randomly aligned fibers. Also, \( \eta_l \) is the length efficiency factor, which is given by

\[ \eta_l = 1 - \frac{\tan \theta}{2} \]  

(C2)

where

\[ a = \frac{3a_0}{2\delta_{CNT} \delta_{d}} \]  

(C3)

From the best fit line, it gives an aspect ratio \( \frac{l}{D} \) of around 110–120, which is close to that predicted above.