Effect of Interfacial Adhesion on Tensile Strength of 3D Printed Particulate Nanocomposites

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Abstract. Tensile strength of a nanocomposite is dependent on different characteristics such as particle size, particle loading and matrix–particle interfacial adhesion. Matrix–particle interfacial adhesion is one of the main characteristics that affects the mechanical properties. Additive manufacturing have unique and distinct advantages over conventional manufacturing techniques. However, nanocomposites fabricated by additive manufacturing still need a comprehensive study. In this paper we investigated the effect of interfacial adhesion between matrix and filler of samples printed using photopolymer extrusion 3D printing technique. In order to compare the matrix-particle interfacial adhesion of samples printed by this technique, another set of samples have been fabricated using casting technique. Tensile tests on both sets of samples had been conducted and interfacial adhesion parameter models and SEM was used to draw the comparison; consequently, samples fabricated by 3D printing proved to have better mechanical properties than casted samples.

1. Introduction

To overcome the apparent limitations of polymers such as low stiffness and low yield strength, particulate fillers such as micro/nano silica, Al2O3, Mg(OH)2, CaCO3 particles, glass and carbon nanotubes are commonly used to manufacture polymer composites. These fillers diversify the mechanical and physical properties of polymers by introducing their rich mechanical behaviour. By adding either micro or nano particles, Young’s modulus or stiffness can be dramatically improved [1-3]. However strength is heavily dependent on the effective stress transfer between particles and matrix. If the bond between the matrix and particle is good, stress can be effectively transferred from the matrix to the particles. There are several characteristics on which mechanical properties of polymer matrix nanocomposites rely on; i.e. particle size, matrix-particle adhesion, particle distribution and particle loading. Particle loading and matrix–particle interface adhesion affect mechanical properties. For instance, tensile strength of glass bead filled polystyrene composites is dependent on matrix– particle adhesion and increases by improving adhesion [2].

3D printing is an additive manufacturing process in a layer-by-layer additive fashion by either direct material deposition or selective material consolidation within a vat or powder bed. Traditional polymer additive manufacturing techniques such as fused deposition modelling (FDM), fused filament fabrication (FFF) and big area additive manufacturing (BAAM) use thermoplastic material that are liquefied in a heated deposition before being deposited or they used liquid polymers which are cured when exposed to ultraviolet light as in stereolithography (SLA) and polymer jetting. Here, we
investigate the effect of interfacial adhesion and distribution of particles on the mechanical properties of 3D printed polymer-matrix nanocomposite. In order to compare mechanical properties of 3D printed polymer nanocomposites, a comparison is drawn by testing specimens fabricated by casing.

2. Background

2.1 Effect of Matrix-Particle Interfacial Adhesion on Tensile Strength

Considering the stress cannot be transferred from matrix to the filler, in this case strength of polymer-matrix nanocomposite is determined by available effective region of load bearing matrix in the absence of filler. Interfacial layer is unable to transfer stress and the strength of nanocomposite is dependent on effective load bearing cross sectional area portion \((1 - \varphi)\) as

\[
\sigma_c = \sigma_m (1 - \varphi) \quad (1)
\]

where \(\sigma_c\) and \(\sigma_m\) are tensile strength of composite and matrix respectively. Considering \(\varphi\) as a power law function Eq. (1) can be rewritten as:

\[
\sigma_c = \sigma_m (1 - \alpha \varphi^b) \quad (2)
\]

where \(\varphi\) is volume fraction and \((a)\) and \((b)\) are constants depending upon particle shape and arrangement in the composite.

Nicolais and Narkis [4, 5] based on Eq. (2) presented a model to predict the tensile strength of nanocomposite reinforced with spherical filler as:

\[
\sigma_c = \sigma_m (1 - \alpha \varphi^{2/3}) \quad (3)
\]

When particle and matrix possess a good adhesion, a small portion of the stress is transferred by interfacial region, while the deformation of matrix is very small. In this case, stress is effectively transferred and tensile strength is the combination of matrix and filler properties. Therefore, parameter, \(a\) in Eq. 3 becomes smaller than 1.21 indicating strong adhesion.

Another model presented by Kunori and Geil [6] associated the tensile strength of composite with parameter, \(a\) considering it as stress concentration factor as:

\[
\sigma_R = \sigma_m \frac{1 - \varphi}{1 + 2.5\varphi} \exp (B \varphi) \quad (4)
\]

where \(\sigma_R\) is relative tensile strength and expressed as \((\sigma_c / \sigma_m)\). Higher values of parameter, \(a\) indicate higher stress concentration.

A model developed by Pukanszky talks about the spontaneous formation of interphase in the nanocomposite considering variation of tensile strength as a function of composition [7]. The model can be written as:

\[
\sigma_R = \sigma_m \left(1 - \frac{\varphi}{1 + 2.5\varphi} \exp (B \varphi) \right) \quad (5)
\]

Parameter, \(B\) is expressed as the load carried by the dispersed phase based on its interaction, which can be considered as a measure of matrix-filler adhesion, higher values of \(B\) shows good adhesion. The parameter, \(B\) can be written as:

\[
B = (1 + A \rho l) \ln \left( \frac{c_l}{\sigma_m} \right) \quad (6)
\]

where \(A\) is surface area of particles, \(\rho\) is the density of particle, \(l\) and \(\sigma_i\) are thickness and strength of interphase, respectively.

A model developed by Sato and Furukawa [8] for Young’s modulus of nanocomposites containing an adhesion parameter \(\zeta\) can be written as:

\[
E = \left[ 1 + \frac{0.5 \varphi}{1 - \varphi} \left(1 - \psi \zeta \right) - \frac{\varphi^{1/3} \psi^{2/3}}{(1 - \varphi^{1/3}) \varphi} \right] \quad (7)
\]

\[
\psi = \left( \frac{\varphi}{3} \right) \frac{1 + \varphi^{1/3} - \varphi^{2/3}}{1 - \varphi^{1/3} + \varphi^{2/3}} \quad (8)
\]

where \(\zeta\) of 1 and 0 shows poor adhesion and perfect adhesion respectively.
3. Materials and Methods

3.1 Samples Printed using a Photopolymer Extrusion 3D Printing Technique.
A photopolymer extrusion (PPE) 3D printing technique is used to print the samples, Figure 1 shows the PPE printing technique. The entire 3D printing system includes a UV curing system using two UV laser diodes, an extrusion system consists of a peristaltic pump and a nozzle, and a platform with 3 linear motions (x, y and z) and 2 rotary motions (A and B).

![Figure 1: Photopolymer Extrusion 3D Printing Technique](image)

3.2 Samples Fabricated using Casting Technique
In order to compare the mechanical properties of 3D printed samples, samples were prepared using a mould of the type V dog-bone specimen as shown in Figure 2. UV curable resin prepared as discussed in section 3.3 was manually poured into the mould using a syringe and placed under UV light box for 3 minutes. Samples with 8%, 9% and 10% concentrations of the filler were fabricated and tested. Figure below shows the mould used to fabricate cast samples.

![Figure 2. Mould of type V dog-bone specimens.](image)

3.3 Preparation of UV Curable Resin
The photopolymer resin being extruded is made from a commercial polymer named UV Dome 58 (Whitehall Technical Services Ltd) based on an epoxy acrylate that was mixed with fumed silica as filler. In this study fumed silica is used as a reinforcing filler in the resin. For investigation of the mechanical properties of 3D printed samples and samples made by casting, samples were prepared with different concentrations of the silica filler (by weight) mixed into the resin. Mixtures were prepared the same day to have samples with the same aging and were prepared inside a photolithography room. A total of 100 g of mixture was made for each concentration, for instance for 2% by weight of filler, 98 g of the resin was mixed with 2.0 g of fumed silica. After slow manual stirring for 5-10 minutes with a thin spatula, the mixture was mixed with an ultrasonic homogenizer. An ultrasonic homogenizer from Sonics and Materials Inc was used for 2 x 1 minute at 20 kHz of ultrasound frequency and 130 W of intensity. Finally, to reduce air bubbles in the mixture, samples were left to stand in a vacuum oven for 45 minutes at 65°C.

4. Experimental Procedure

4.1 Tensile Test
In order to characterize and compare the mechanical properties (e.g. tensile strength and Young’s modulus) of 8%, 9%, 10% and pure resin (UV Dome 58) samples, tensile tests were conducted, three dog-bone samples of each concentration of specific dimensions (following ASTM D638 standard type V) were fabricated in accordance with the methodologies discussed in section 3.1 and 3.2. 8%, 9% and 10% filler concentrations were used to print and cast the samples. As the viscosity of the pure resin is too low to be extruded through nozzle, pure resin samples were first cast and then tested. Pure resin has ultimate tensile strength of 7.3 MPa and Young’s modulus of 71.6 MPa. Table 1 shows tensile properties of printed and cast samples and Figure 3 shows printed and cast specimen after test.

Table 1. Tensile properties of 8%, 9% and 10% 3D printed samples

| Filler Concentration | Sample | Ultimate Tensile Strength (MPa) | Young’s Modulus (MPa) | Filler Concentration | Sample | Ultimate Tensile Strength (MPa) | Young’s Modulus (MPa) |
|----------------------|--------|-------------------------------|----------------------|----------------------|--------|-------------------------------|----------------------|
| 8%                   | a      | 32.5                          | 535                  | 8%                   | a      | 7.5                           | 195.4                |
|                      | b      | 28                            | 422                  |                      | b      | 12.0                          | 250                  |
|                      | c      | 16.7                          | 209                  |                      | c      | 13.5                          | 308                  |
| 9%                   | a      | 22.2                          | 507                  | 9%                   | a      | 10.3                          | 141.5                |
|                      | b      | 34.6                          | 617                  |                      | b      | 19.3                          | 256                  |
|                      | c      | 27.6                          | 623                  |                      | c      | 11.8                          | 259                  |
| 10%                  | a      | 28.5                          | 443                  | 10%                  | a      | 12.9                          | 231                  |
|                      | b      | 23.6                          | 386                  |                      | b      | 9.9                           | 184.4                |
|                      | c      | 25.4                          | 448                  |                      | c      | 13.0                          | 249                  |

Figure 3. (a) 3D printed specimen after tensile test (b) Cast sample after tensile test

5 Results and Discussion

5.1 Application of Interfacial Adhesion Parameter Models

3D printed and cast samples were fabricated and tested as discussed in section 3 and 4. Nicolais and Narkis model Eq. (3), Kunori and Giel model Eq. (4), Pukanszky Model Eq. (5) and Sato and Furukawa model Eq. (7) were applied to investigate and compare the interfacial adhesion parameters of 3D printed and cast samples. In order to convert the weight fraction into volume fraction density of filler (fumed silica) and UV dome 58 (polymer) is taken as 0.18 g/cm³ and 1.1 g/cm³ respectively. Volume fractions (\( \phi \)) 0.347, 0.376 and 0.404 were calculated for 8%, 9% and 10% weight fractions respectively. Figure 4 (a, b & c) represents the boxplots of the calculated interfacial adhesion parameters for 8%, 9% and 10% filler concentrations respectively based on Eq. (3), Eq. (4), Eq. (5) and Eq. (7)
From Figure 4, it can clearly be seen that all four models predict very strong interfacial adhesion for 3D printed samples, when seen on the scale defined by each model for perfect and weak adhesion. Cast samples exhibit weak interfacial adhesion as their interfacial adhesion parameters are weaker when compared with 3D printed samples. 3D printed samples for 8%, 9% and 10% filler concentrations exhibit much stronger bond between filler and matrix resulting in higher ultimate tensile strength.

In order to further investigate this behaviour of 3D printed samples and to elaborate the reason behind stronger interfacial adhesion, scanning electron microscopy (SEM) was used to study the distribution of the filler at subsurface in both 3D printed and cast samples.

### 5.2 Scanning Electron Microscopy (SEM)

Figure 5 shows SEM images of the 3D printed and cast samples, it is quite evident from the SEM images that the distribution of the filler in 3D printed samples is more homogenous and the filler is well distributed throughout the image, compared to casted sample where the distribution is not
homogenous and clear absence of filler can be seen. This is the reason why the casted samples have weak interfacial adhesion and non homogenous distribution of filler resulted in weak bond between filler and matrix in casted samples. Homogenous distribution of filler in 3D printed samples results in a strong matrix–filler adhesion providing strong bond and ultimately higher interfacial adhesion and mechanical properties.

![Figure 5](image)

**Figure 5:** (a & c) SEM image of 3D printed sample (b & d) SEM image of cast samples

6. **Conclusion**

In this work, interfacial adhesion parameters of 3D printed and casted samples were investigated with the aid of interfacial adhesion parameter models and scanning electron microscopy (SEM). Tensile tests have been conducted and it was found that 3D printed samples exhibit stronger bond between matrix and filler than casted samples as the distribution of the filler is more homogenous in 3D printed samples.

**References**

[1] Zi-Kang, Z., et al., J. Appl. Poly. Sci., (1999). 73(14): p. 2977-2984.
[2] J., D.M.E. and H. D., J. Appl. Poly. Sci., (1983). 28(12): p. 3809-3815.
[3] Fu, S.-Y. and B. Lauke, Comp. Part A: Appl. Sci. and Manuf., (1998). 29(5): p. 575-583.
[4] Nicolais, L. and L. Nicodemo, Inter. J. Poly. Mate. and Polym. Biomat., (1974). 3(3): p. 229-243.
[5] E., L.R., N. L., and N. M., J. Appl. Poly. Sci., (1973). 17(4): p. 1173-1185.
[6] Kunori, T. and P.H. Geil, J. Macrom. Sci., Part B, (1980). 18(1): p. 135-175.
[7] Pukánszky, B., Comp., (1990). 21(3): p. 255-262.
[8] Sato, Y. and J. Furukawa, Rubb. Chem. and Tech., (1963). 36(4): p. 1081-1106.