EFFECT OF TEMPERATURE AND FILLER VOLUME FRACTION ON THE STIFFNESS OF PARTICLE REINFORCED POLY-METHYL METHACRYLATE

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ABSTRACT

Particle filled polymer composites are of an increasing scientific and commercial importance due to their economic and technical advantages as opposed to other engineering materials. Since they consist of a physical mixture of reinforcement together with a polymeric matrix, their mechanical properties depend significantly upon the characteristics of the constituent phases. Among the different mechanical properties, the knowledge of the elastic modulus of particle filled polymers represents a convenient way to categorise the materials with respect to their filler contents. In the present study, the stiffness of particle filled poly-methyl methacrylate is determined experimentally and compared with various micromechanical models. The experimental flexural modulus of the composites is found to decrease with temperature (0 ºC - 90 ºC) and increase with particle volume fraction. At lower temperatures there is a good agreement between the experimental and longitudinal Mori-Tanaka [1, 2] analytical results. The Halpin-Tsai [3] predictions for spherical inclusions agree well with the experimental data. At higher temperatures the latter models slightly underpredict the experimental values. Two modifications of the Obakponovwe and Williams model [4] are proposed: (i) the Stapountzi model (S-model) and (ii) the Williams model (W-model). Both models predict the behaviour of the filled composites remarkably well at all temperatures. The microscopy studies give an indication of the particle size and shape. The prediction of stiffness is a complicated task; more information is needed regarding the geometry of the inclusions which seems to play a key role in all the theories.

Introduction

Particle reinforced composites continue to replace other engineering materials in structural and architectural applications. Apart from the cost reduction, the addition of particles to polymers has been proved to be an effective way to control their thermal, optical, and aesthetic properties. However, improvements of the mechanical properties have not generally been established. The scope of the current research is to assess the mechanical behaviour of particle filled solid surface composites (made of poly-methyl methacrylate matrix, PMMA, filled with alumina trihydrate micro-particles, ATH) and to identify the key mechanisms affecting their performance.

A series of three-point flexural tests are performed as a practical way to categorise the materials with respect to their flexural modulus. The elastic behaviour of the composites is assessed as a function of temperature (0 ºC - 90 ºC) and filler volume fraction (29% vol. - 49% vol.). The experimental data are compared with micromechanical models for determining the stiffness of reinforced plastics. Under the assumption of unidirectional orientation of the filler particles, the models of Tandon and Weng [1, 2] and Halpin and Tsai [3] are used. Several studies have attempted to extend the latter theories in order to account for random fiber orientation conditions, which are typical for injection-molded short-fiber-reinforced components [5, 6]; the work by Van Es [6], based on the laminate theory is briefly examined here. Finally, two variations of the Obakponovwe and Williams [4] model are proposed: (i) the Stapountzi model (S-model) and (ii) the Williams model (W-model). Most theories make some basic assumptions; the matrix and inclusions are assumed to be linearly elastic, isotropic and homogeneous. The properties of the constituents are considered to be the same as the properties of the bulk materials [7]. The inclusions are assumed to be evenly distributed in the composite [1, 3]. Perfect bonding is supposed between the components [3, 8].

Theoretical

The theoretical analysis of the stiffness of polymers containing inclusions has been the subject of a number of studies. Tandon and Weng [1] combined the Eshelby’s inclusion model [9] and the average-stress theory of Mori and Tanaka [2] to determine the effective elastic properties of unidirectional short-fiber reinforced composites with different volume fractions. The elastic stress field in and around an ellipsoidal particle surrounded by an infinite medium was studied by Eshelby [9], originally under
the hypothesis of a homogeneous inclusion. Subsequently, Eshelby established equivalence between the homogeneous inclusion and an inhomogeneous inclusion of identical shape [7, 8, and 9]. Eshelby’s solution has been the foundation of a series of theories for short-fiber reinforced composites, amongst them the Mori-Tanaka theory [2]. Mori and Tanaka introduced the idea of mean stress in the matrix considering a non-dilute composite made of unidirectionally aligned spheroidal particles [7, 8]. The Mori-Tanaka mean-field theory has been effectively applied to study the elastic behaviour of fiber-reinforced composites at relatively low concentrations. Tandon and Weng [1] used the Eshelby’s solution and Mori-Tanaka method to analyse the effect of the aspect ratio of the inclusions on the five independent elastic moduli of transversely isotropic composites with non-interacting particles. The numerical solutions involve an iterative procedure to determine the five independent elastic constants. The results for longitudinal, $E_{II}$, and transverse, $E_{T}$, elastic moduli are described by:

\[
\frac{E_{II}}{E_m} = \frac{A}{A + V_f (A_1 + 2v_m A_2)} \tag{1}
\]

\[
\frac{E_{T}}{E_m} = \frac{2A}{2A + V_f (-2v_m A_3 + (1 - v_m) A_4 + (1 + v_m) A_5 A_d)} \tag{2}
\]

where

$V_f$ = volume fraction of filler

$v_m$ = Poisson’s ratio of the matrix

The terms $A_1, A_2, A_3, A_4, A_5$, and $A$ appearing in Equations (1) and (2) are functions of the Eshelby’s tensor and the properties of the filler and the matrix [1]. Equations (1) and (2) give solutions for the transverse and longitudinal moduli which depend upon the geometry of the filler particles via the Eshelby’s tensor components. Including the entire range of aspect ratios ($\alpha$) from zero to infinity the results are applicable to disk-shaped (or oblate spheroids) $\alpha<1$, spherical ($\alpha =1$) and fiber-like (or prolate spheroids) reinforcements ($\alpha>1$). For spheroidal inclusions aligned along the direction of the load the components of the Eshelby’s tensor are given in detail in Tandon and Weng [1]. For the classification of the terms oblate and prolate spheroids, see Figure 1.

Halpin and Tsai [3, 10] proposed a set of equations for predicting the stiffness of short-fiber reinforced composites based upon prior work presented by Hill [11] and Hermans [12]. In 1965, Hill [11] developed a self-consistent composite model, in which a single fiber is embedded in an infinite homogeneous medium that has the average properties of the composite [10]. Another similar approach, called the generalized self-consistent theory was adapted by Kerner [13] for spherical particles and by Hermans [12] for cylindrical fiber composites. Halpin and Tsai [3, 10] reduced Hermans’ solution into a simple analytical form which has been widely used for determining the elastic constants of unidirectionally reinforced composites [14]. The Halpin-Tsai model suggests that the composite modulus of a reinforced system could be expressed by a set of equations as:

\[
E = \frac{1 + \zeta \sigma V_f}{1 - \zeta \sigma V_f} E_m \quad \zeta = \left(\frac{E_f}{E_m}\right)^{-1} - 1 \tag{3}
\]

where

$E$ = represents any of the composite moduli

$E_f$ = modulus of the inclusions

$E_m$ = modulus of the matrix

$\sigma$ = shape parameter

Figure 1. Spherical particles (left), prolate (middle) and oblate (right) spheroids: the arrows show the direction of the load

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The factor $\sigma$ depends on the filler geometry, packing geometry and loading conditions [10]. For $\sigma \to 0$ the Halpin-Tsai equations reduce to the inverse rule of mixtures (lower bound), whereas for $\sigma \to \infty$, the Halpin-Tsai theory reduces to the rule of mixtures (upper bound). Assuming that the particles are aligned with the loading direction, Ashton et al. [15], determined $\sigma = 2\alpha$, with $\alpha$ being the aspect ratio of the particles. This was based on a comparison with 2-D finite element solutions based upon Foye’s calculations [16]. Halpin and Kardos [14] found that $\sigma = 2\alpha$ gave good predictions for the longitudinal modulus of short-fiber systems; the modulus in the transverse direction was found be insensitive to the aspect ratio with $\sigma = 2$. Van Es [17] proposed that $\sigma = 2/3\alpha$ may give good agreement with the Mori-Tanaka predictions for the longitudinal modulus of platelet filled polymers [18]. The Halpin-Tsai equations have a semi-empirical nature due to the fact that the equations are identical in form when calculating longitudinal reinforcement for discontinuous cylindrical fibers and lamellar shape reinforcements. The M-T and H-T models assume that the particles are aligned. From a realistic point of view all composites contain some level of filler disorientation. Composites with a random orientation of particles would be expected to give lower modulus values. Van Es et al. [6] used the laminate theory to show that the modulus of particle filled composites with a random orientation of particles is given by [6, 18]:

$$E_{\text{fibers}}^{\text{random 3D}} = 0.184E_X + 0.816E_T$$

$$E_{\text{platelets}}^{\text{random 3D}} = 0.49E_X + 0.51E_T$$

where

- $E_{\text{fibers}}$ = composite modulus, parallel (longitudinal) to the major axis of the filler
- $E_T$ = composite modulus, perpendicular (transverse) to the major axis of the filler

In recent work, Obakponovwe and Williams [4] presented a set of equations for the prediction of particle filled polymer composites with relatively high filler contents. The Obakponovwe-Williams equations suggest that the elastic behaviour of the composites could be described by assuming a unit cell of reinforcement with volume fraction $V_f$ connected in series with the matrix with volume fraction $1-V_f$. The modulus of the filler is supposed to be much higher than the modulus of the matrix constraining the polymer in transverse directions [4]. However, the Obakponovwe-Williams equations do not account for the entire range of filler volume fractions sufficiently, as they overestimate the composite modulus in low filler concentrations. Two modifications of these equations are proposed here: the Stapountzi model (S-model) and the Williams model (W-model). In order to account for the geometry of the inclusions, they both bring in a shape factor, namely $\alpha$ (aspect ratio) and $W$, respectively. In the Stapountzi model (S-model) the elastic behaviour of the composites is described by Equation (6) as follows:

$$E = \frac{E_m E_f}{(1-V_f) \left[ 1 - \frac{2V_m \alpha}{1 - V_m} \right] E_f + V_f E_m}$$

where $\alpha$ = aspect ratio of the particles

In the Williams model (W-model), under the assumption of perfect bonding between the constituents, the stiffness of the composites is given by Equation 7 below:

$$E = \frac{E_m}{(1-V_f)} \left[ 1 + 3V_m \left( \frac{1-V_m}{1+V_m} \right) W^2 \left( \frac{V_f}{1-V_f} \right)^2 \right]$$

where $W$ = shape factor describes the ratio of the radius to the length of inclusions
Experimental

Three-point flexural tests were carried out in conjunction with method (I) - procedure (A) of the ASTM D790M-93 standards for plastics [19], utilizing simple beam specimens with rectangular cross sections and dimensions in accordance with the protocol. The samples were made of poly-methyl methacrylate matrix filled with alumina trihydrate micro-particles with a range of volume fractions (29% vol. - 49% vol.). The flexural performance of the composites was assessed as a function of temperature (0 ºC - 90 ºC) and filler contents. Testing was performed on an Instron mechanical test system (Model 4411 with a 5 kN load cell), using an oven and a thermocouple for temperature control. A liquid nitrogen, N₂, tank was connected to the temperature cabinet for tests at 0°C - 10°C. A minimum of five replicates were used for each test.

The prediction of the stiffness of particle filled polymer composites requires the information about the relevant properties of the constituents, i.e., the unfilled matrix material and the filler particles. The Young’s modulus of PMMA was measured in tension according to the ASTM D638M-84 standard [20] using an Instron mechanical system and metal-foil strain gauges. The Poisson’s ratio of PMMA was determined using the same tensile test technique (i.e., using metal-foil strain gauges) in order to monitor the axial and transverse strains. The data for the stiffness and Poisson’s ratio of the alumina trihydrate filler were taken from the literature concerning hard reinforcing particles [21]. They were assumed to be equal to 150 GPa and 0.24 for $E_f$ and $v_f$ respectively, and uniform with temperature. The particles either as powder or embedded in the composite could be indented in an Atomic Force Microscope (AFM) to cross-check these values and such work is planned.

Apart from the elastic constants, extra information is required for the filler material (i.e., the alumina trihydrate particles or ATH), related to the geometry of the inclusions and their preferred, if there is one, orientation in the composite. Optical and scanning electron microscopy studies were performed on both the filler powder and the composite materials. The size of the particles was studied using Laser Light Scattering.

Results and discussion

The values of the elastic modulus and Poisson’s ratio of PMMA measured in the tensile tests are presented in Figures 2 and 3, respectively. Due to the inherent difficulty to record the transverse strain under tension, there was some scatter in the Poisson’s ratio data, mainly at higher temperatures. The data are compared to the values calculated from a previous study [22] on PMMA, where a pressure-volume-temperature (PVT) technique was used and the results are found to be similar (Figure 3).

![Figure 2](image)

**Figure 2.** Elastic modulus of the PMMA matrix ($E_m$) determined as a function of temperature.

The results for the elastic modulus of the ATH filled PMMA composites determined by the three-point flexural tests are presented against the predictions of the different analytical models in Figures 4, 5, 6, 7 and 8, for the M-T (Equation 1), M-T random3D-fibers (Equation 4), H-T (Equation 3), S-model (Equation 6) and W-model (Equation 7) models, respectively. In general, the elastic modulus of the composites shows a decrease with temperature (0 ºC - 90 ºC) and an increase with particle volume fraction, 29% vol. - 49% vol.
Figure 3. Poisson’s ratio of the PMMA matrix \( (v_m) \) determined as a function of temperature; also PVT data [22] are shown for comparison.

More specifically, in Figures 4 and 5, the experimental flexural modulus results at different temperatures (2 °C, 23 °C, 60 °C and 90 °C) are plotted against the Tandon and Weng (M-T) longitudinal solutions for aspect ratios \( \alpha=1.5 \) (fiber-like reinforcement) and the M-T random3D-fibers moduli predictions for aspect ratios \( \alpha=4 \), respectively. In this study, different scenarios for the particle geometry were examined varying from spherical particles to prolate spheroids with two different aspect ratios, \( \alpha=\ell/d=1.5 \) and \( \alpha=\ell/d=4 \) and oblate spheroids. The two cases which better described the experimental data (i.e. M-T with \( \alpha=1.5 \) and M-T random3D-fibers with \( \alpha=4 \)) are presented in Figures 4 and 5. From the plots there are two possible suggestions: either i.) there is a preferable orientation of the particles: the results are indicative of a fiber-like spheroidal shape of the inclusions with aspect ratios around \( \alpha=1.5 \), and aligned along the direction of the load in all cases, or ii) there is random orientation of the particles: the particles would be described as fiber-like spheroidal in this case with higher aspect ratio \( \alpha=4 \).

A divergent behaviour is observed at low volume fractions of 29 % vol. This could be attributed to the fact that the low volume fraction sample has an increased number of voids compared to all the other samples or it is possible that the 29 % vol. specimens (material sheets) were cut along a different direction - not the mould direction. Specimens will be cut along perpendicular directions from the same plates to investigate the presence of particle alignment.

Figure 4. M-T longitudinal (II) moduli predictions for \( \alpha=1.5 \) (fiber-like spheroidal inclusions) and comparison with experimental flexural modulus data at different temperatures.
From Figures 4 and 5 it can also be seen that at lower temperatures (2°C and 23 °C) there is a good agreement between the experimental and analytical results. At higher temperatures, the models slightly underpredict the experimental values. This could be due to inadequate temperature control throughout the experiments at higher temperatures. To check the latter assumption a thermocouple was placed into a dummy sample which was left in the oven for up to 6 hours; although the oven temperature was set at 90 °C the temperature of the specimen had not reached the value of 90 °C during this period (but reached 84 °C). The tests at higher temperatures will be repeated with thermocouples checking the temperature at each volume fraction separately to check if the heat transfer is the same in all materials.

Similar trends are observed when the experimental results at different temperatures are plotted against the Halpin-Tsai solutions for spherical particles, $\alpha=1$ ($\sigma=2$), see Figure 6. The Halpin and Tsai equations are uniform for cylindrical fibers and platelet inclusions [3]. This means that the length across a disk-shaped particle is assumed to be constant, i.e., disk-shaped particles are treated as rectangular platelets. In the Halpin-Tsai theory the transverse modulus is thought to be independent of aspect ratio and is always taken as $\sigma=2$ [14]. As in the M-T case, different aspect ratios were also examined but spherical reinforcement (or shape factor $\sigma=2$) seemed to be giving the best prediction.

Finally, the results of the Stapountzi and Williams models are shown in Figures 7 and 8, respectively. Both the latter models describe the behaviour of the filled composites remarkably well at all temperatures. The aspect ratio used in the S-model was $\alpha=2$, which indeed fit the experimental data at all temperatures. The $W$ shape factor in the W-model was chosen equal to $W=4$. 

![Figure 5. M-T random3D-fibers moduli predictions for $\alpha=4$ (fiber-like spheroidal inclusions) and comparison with experimental flexural modulus data at different temperatures](image1)

![Figure 6. H-T moduli predictions for $\alpha=1$ and comparison with experimental flexural modulus data at different temperatures](image2)
Optical and scanning electron microscopy studies performed on both the filler powder and the composite materials provided an indication of the geometry of the filler particles. From the pictures in Figure 9, the particles seem to be close to spherical especially at lower volume fractions, with sizes varying from 1.5 to 100 microns. According to the results of Laser Light Scattering the particles have a weighted mean diameter around 33 microns. Preliminary statistical studies indicate that the morphological parameter commonly used to characterize the shape of inclusions, known as the aspect ratio of the particles is in the range between $1<\alpha<4$, with mean values around $\alpha=2$. The aspect ratio of the particles is going to be further investigated in the near future. The study will also be extended to fracture properties.

Figure 7. S-model predictions for $\alpha=2$ and comparison with experimental flexural modulus data at different temperatures

Figure 8. W-model predictions for $W=4$ and comparison with experimental flexural modulus data at different temperatures

Conclusions

The knowledge of the stiffness of particle filled polymers represents a practical way to study and categorise the materials. The elastic modulus of the particle filled PMMA composites determined experimentally shows an increase with particle volume fraction and a decrease with temperature (0 °C - 90 °C). The prediction of the elastic modulus is a complex process; essential information regarding the geometry of the filler particles seems to play a key role in all analytical models. The Mori-Tanaka and the Halpin-Tsai theories are indicative of filler particles with aspect ratios, $\alpha$, in the range of $1\leq\alpha<4$. There are some differences between the Mori-Tanaka and the Halpin-Tsai theories mainly due to the way they account for the geometry of the filler particles. At lower temperatures (2, 23 °C), there is a very good agreement between the experimental and longitudinal M-T
analytical results. The Halpin-Tsai predictions for spherical reinforcement are in good agreement with the experimental data. At higher temperatures, both models slightly underpredict the experimental values. The Stapountzi (S=2) and Williams (W=4) models describe the behaviour of the filled composites remarkably well at all temperatures. It is necessary in future work to assess the implication of the geometry of the particles in the analytical modeling. It is also essential to validate the value of the aspect ratio that best describes the composite stiffness data from independent experimental observations.

Figure 9. Optical microscopy photos of ATH filled PMMA composites with 29% vol. (top left), 33% vol. (top right), 45% vol. (bottom left), 49% vol. filler contents (bottom right).

Acknowledgments

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