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Investigation of the strain-rate dependent mechanical behaviour of a photopolymer matrix composite with fumed nano-silica filler

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Abstract

With the evolution of additive manufacturing, there is an increasing demand to produce high strength and stiffness polymers. Photopolymers are very commonly used in Stereo lithography (SLA) and Fused Deposition Modelling (FDM) processes but their application is limited due to their low strength and stiffness values. Nano sized fibers or particles are generally embedded in the polymer matrix to enhance their properties. In this study, we have studied the effect of fumed nano sized silica filler on the elastic and viscoelastic properties of the photopolymer. The uniaxial testing coupons with different concentrations of silica filler have been fabricated via casting. We observed improvement in mechanical properties by the addition of the nano sized filler. As polymers exhibit time dependent mechanical response, we have conducted tensile tests at different strain rates as it is one of the most common modes of deformation, and is commonly used to characterize the parameters of the rate dependent material. We noticed significant dependence of the mechanical properties on the strain rate. Quasi linear viscoelastic (QLV) model, which combines hyper elastic and viscoelastic phenomena, have been employed to capture the response of the material at different strain rates. We found out that the QLV model with Yeoh strain energy density function adequately describes the rate dependent behaviour of the material and has reasonable agreement with the experimental results.

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1. Introduction:

Photopolymers are light sensitive polymeric materials, which changes their chemical and physical properties when exposed to UV light. These photopolymers are very commonly used in additive manufacturing techniques such as Stereolithography (SLA) and Fused Deposition Modelling (FDM). Polymers commonly exhibit weak mechanical properties; for example low stiffness and low strength. In order to improve and expand their applications, fillers such as micro/nano sized silica, carbon nanotubes [1], Al_2O_3 [2] and glass are added. Polymer nanocomposites have demonstrated vast potential to significantly improve the polymers properties by the addition of nano-scale fillers [3]. In the recent past, there are have been serious attempts on the development of more advanced materials by adding nano-fillers on different matrices for improved mechanical and physical properties. Nanocomposites have attracted scientists, engineers, and industrialists with an aim to design and develop nanocomposites having a unique combination of materials, unlike traditional materials. Nanocomposites like traditional composites could have polymeric or ceramic matrices. Generally, polymer matrix composites yield good specific stiffness, fatigue, corrosion resistance, and specific strength than metals. Still, they exhibit weak residual strength and weak impact energy absorption [4-6]. Studies have been conducted in which nano sized fillers with different diameters have been added into polymeric material [7], and it was reported that nano sized filler with lower diameter has a more profound effect on mechanical properties. Recently Asif et al. [8] reported significant improvement in mechanical properties of 3D printed photopolymer with the addition of nano sized silica filler.

An in depth understanding of the mechanical response of polymers over a range of strain rates, temperature and pressure are required in a wide variety of fields e.g. aerospace, automotive and medical devices. The properties are generally governed by not only the composition and microstructure of the materials but also rely on pressure, temperature and strain rate. Researchers have characterized the mechanical response of the polymers (specifically stress-strain relationship) over the past 40 years at strain rates between 10^{-4} and 10^{5} s^{-1} [9-12]. Polymers commonly exhibit time dependent mechanical response as shown by rate dependent yield strength, elastic moduli and post yield behaviour. A range of strain rates and temperature can cause the polymer to change mechanical behaviour from rubbery to ductile plastic to brittle [13-19].

Traditional micromechanical analytical models [20-22] commonly used for micro-sized reinforcement composites, were recently used to predict the overall stiffness of nanocomposites. These conventional theories are based on the observation that the overall mechanical response of composite materials are functions of constituent properties, volume fraction, the shape of inclusion and dispersion, but are not dependent on size. Finite element method [23-25] and molecular mechanics [26, 27] have been recently used to study the behaviour of nanocomposite systems.

There are various types of viscoelastic models which are proposed to predict the rate dependent behaviour of the polymers. Green and Rivlin proposed the early models for capturing the nonlinear response of viscoelastic solids in which stress is expressed as the function of the history of the deformation gradient. For materials with fading memory, Green and Rivlin [28] and Coleman and Noll [29] proposed constitutive models, which demonstrate the point that material response at present time is more strongly dependent on the latest deformations than the those happened in the distant past. Pipkin and Rogers [30] used the history of strain rate rather than the history of strain to express the time dependent stress. In addition, they analysed the likelihood that such integral expressions are also effective when the role of stress and strain are switched. Scharphy [31] analyse the nonlinear viscoelastic behaviour of polymers experiencing small deformations expressed a nonlinear single integral model. In this model, he presented four nonlinear parameters related with instantaneous (elastic), loading rate, transient and accelerated/decorated time-dependent responses. In addition, he discussed dual representations, in which the roles of stress and strain are switched.

In order to capture the viscoelastic behaviour of biological materials, Fung [32] proposed the QLV model. In the QLV model, stress relaxation function is modelled by separating it into two functions i.e. reduced (normalized) time functions and nonlinear elastic function. The nonlinear elastic function can be derived from strain energy density function [33-35]. The benefit of using the QLV model is that it has mathematical and experimental advantages as it is easy to resolve the constitutive equations and material parameter characterization. The reduced relaxation function is not special and any function that is continuous, positive and monotonically decreasing with time is acceptable.

Muliana et al [36] presented a modified form of QLV models in which they expressed strain as an integral of a nonlinear measure of the stress. They predicted the behaviour of elastomers [37] and light activated shape memory polymers using these models [38]. The QLV model is commonly employed nowadays because it provides the simplest way to include both nonlinearity (dependence of properties of load or strain) and time dependence (viscoelasticity) in a simplified integral model. Apart from biomedical applications [39], the QLV model has also been employed to model materials such as elastomeric polymers, rubbers and composites [37, 40].

In order to study the rate dependent behaviour of our chosen photopolymer, we have conducted tensile tests at different loading rates to characterize the rate dependency of the material. We have used fumed silica as a nano filler to enhance the mechanical properties. Different concentration by weight have been added in to the polymer and dog-bone samples have been fabricated by casting. Quasi Linear Viscoelastic model which combines hyper elastic and viscoelastic phenomena have been implemented by developing a MATLAB script to capture the rate dependent mechanical response of the polymer and of different filler concentrations. The QLV model with Yeoh strain energy density function shows remarkable agreement with the experimental results as it adequately captures the behaviour of all four filler concentrations and of the polymer.

2. Materials and Methods

2.1 Preparation of UV Curable Resin and Casting of Samples

The photopolymer resin (UV Dome 58) used was purchased from Whitehall Technical Services Ltd, Auckland, New Zealand. It is based on an epoxy urethane that was mixed with fumed silica as the filler. Fumed silica has nanoparticles with a very large surface area and a low bulk density. Generally, it appears in the solid state in the form of a white powder. With an adequate homogenization, silica nanoparticle can be mixed with another chemical component. Silica nanoparticles have a spherical shape with a diameter ranging between 25 to 30 nm (Fig 1). Silica nanoparticles appear to make long chains or form agglomerates.

To investigate the effect of different filler concentrations on mechanical properties, samples of different concentrations of silica filler (by weight) were mixed into the resin. In order to have the same aging, samples were prepared the same day inside a photolithography room. A total of 100 g of the mixture was made for each concentration for instance for 4% by weight of filler, 96 g of the resin was mixed with 4.0 g of fumed silica. After a 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 minutes at 20 kHz of ultrasound frequency and 130 W of intensity. Finally, in order to reduce air bubbles in the mixture, samples were degassed in a vacuum for 45 minutes at 65^0C.

Samples were prepared using a mould of the type V (ASTM D638) dog-bone specimen as shown in Fig 2. The mixture was manually casted into a mould using a syringe and placed under a UV light box for 3 minutes. UV light box consists of the UV exposure system of 4 x 15W (5mW/cm^2) having UV light source of 405 nm wavelength. Six samples for the polymer, 4%, 8%, 9% and 10% filler concentrations were fabricated.

3. Results and Discussion

3.1 Uniaxial Tensile Tests at Different Strain Rates

Stress relaxation, creep, uniaxial tension etc are a different set of experiments normally conducted to demonstrate the material properties of the rate dependent material. However, the uniaxial tensile test is considered to be the most common mode of deformation. Uniaxial tension tests at different strain rates could provide plausible information about the viscoelastic behaviour of the rate dependent material [41-43]. Therefore, we considered this mode to study the mechanical behaviour of the photopolymer (UV Dome 58) with four different filler concentrations e.g. 4%, 8% 9% and 10%. Tensile tests were conducted on dog-bone sample of specific dimensions (following ASTM D638 standard type V) as shown in Fig 3 (a) of polymer and Fig 3 (b) (with silica filler) with different strain rates e.g. $1.3x10^{-2}$ s^{-1}, $1.3x10^{-3}$ s^{-1} and $1.3x10^{-4}$ s^{-1}. In order to capture the localized strain in gauge part of the sample a commercial digital image correlation (DIC) open source software GOM Correlate® was used, a video camera was mounted in front of the tensile testing machine to record the test. Before the tests, random speckle pattern was created on the samples with the combination of white and black spray paint as shown in Fig 3 (c). After the tests, recorded videos were post processed in GOM to obtain the strain in the gauge part of the specimen. Fig 4 (a, b & c) shows the DIC images captured during localized strain measurement at gauge part of the specimen.

Fig 5 (a, b & c) shows the stress-strain curves obtained for the polymer, 4%, 8%, 9% and 10% filler concentrations with the loading rates discussed above. As most rate dependent materials exhibit a stronger response to faster loading rate, the tensile strength of the polymer as well as of all four filler concentrations increases by increasing the strain rate. Tensile strength of polymer is significantly increased by the addition of nano sized silica filler, tensile strength of

4% filler concentration is higher than 8%, 9% and 10% filler concentrations at all loading rates, this is because by increasing the filler concentration diameter of the nanoparticles increases and the surface area decreases resulting in a weak matrix-particle interfacial adhesion. Nanoparticles with higher surface area provide more enhanced matrix-particle interfacial adhesion. Increasing filler content increase the diameter of the filler and thereby decreasing the surface area, which results in poor matrix-particle interfacial adhesion, the particles are unable to carry any part of the externally applied load. Therefore, the strength of the composite cannot be higher than the neat polymer matrix [44]. As seen in Figure 5, 4% filler concentration has stronger mechanical properties compared to 8%, 9%, and 10%. It can be established that 4% filler content is the maximum amount of filler at which photopolymer (UV Dome 58) exhibits a stronger response. At 1.3×10^{-2} s^{-1} adding filler content decreased the strain to failure of the material except for 4%. With 8% and 4% filler, the nanocomposite was found to have almost the same strain to failure as of the pure polymer exhibiting more ductile behaviour than other filler concentrations. At 1.3×10^{-3} s^{-1} pure polymer is found to exhibit more brittle behaviour compared to all the filler concentrations used, while 4% filler showing high strain to failure demonstrating more ductile behaviour. At 1.3×10^{-4} s^{-1} pure polymer has low strain to failure compared to all filler concentrations used; 4% and 8% filler content exhibited almost similar strain to failure.

Nanocomposites could overcome the problems such as a uniform dispersion of nano fillers in the matrix if a suitable processing method is selected. Local stress concentration arises with in the nanocomposite structure when aggregation is formed in the nano filler. While strength is heavily dependent on the effective stress transfer between particles and matrix. If the bond between the matrix and particle is weak, stress cannot be effectively transferred from the matrix to particles. These results in a premature failure of the polymer reducing its strength and strain to failure. To create a strong interface, a suitable nano filler that is compatible with the polymer matrix is essential. A Significant amount of research has been conducted using particulate nanocomposites and promising results have been obtained especially for the improvement of mechanical and dynamic properties [45, 46].

3.2 Application of QLV Model with Yeoh Strain Energy Density Function

Viscoelasticity is the property of the materials that exhibit both viscous and elastic characteristics when undergoing deformation where after the load is applied there is an instantaneous elastic deformation, and the viscous part occurs with respect to time. Fung [32] first proposed the Quasi-Linear Viscoelastic (QLV) model which is frequently used to study the behaviour of soft biological tissues. The QLV is capable of capturing elastic non-linearties of soft tissues. The Cauchy stress for QLV model is represented as

$$\boldsymbol{\sigma}(t) = -p\boldsymbol{I} + F(t)\left\{\boldsymbol{S^e}[\boldsymbol{C}(t)] + \int_0^t \boldsymbol{S^e}[\boldsymbol{C}(t)]\frac{\partial G(t-s)}{\partial(t-s)}ds\right\}\boldsymbol{F(t)}^T \qquad (1)$$

where, $\boldsymbol{\sigma}(t)$ is the Cauchy stress tensor, $\boldsymbol{F}$ is the deformation gradient, $\boldsymbol{C} = \boldsymbol{F^T F}$ is the right Cauchy-Green tensor, p is Lagrange multiplayer and $\boldsymbol{I}$ is identity tensor. The term $\boldsymbol{S^e}[\boldsymbol{C}(t)]$ can be taken as effective (instantaneous) second Piola Kirchhoff elastic stress tensor [47].

Recently, Slesarenko and Rudykh [41] demonstrated QLV model by combining Yeoh strain energy density function and Neo Hooken strain energy density function to study the behaviour of a soft rubber like digital materials used in Polyjet multi-material 3D printing. They reported that the QLV model with Yeoh strain energy density function successfully captures the behaviour of most of the soft digital materials.

In this study, we employed a similar hyper-viscoelastic approach using QLV model with Yeoh strain energy density function to model the behaviour of our chosen material under uniaxial tension. Equation (3) represents the QLV model with Yeoh strain energy density function, for the detailed theoretical background of the model readers are recommended to read the work of Slesarenko and Rudykh [41] and references therein.

Strain energy density function for classical two-term Yeoh model [48] can be defined as

$$W = \frac{\mu}{2}\left[(I_1 - 3) + \frac{\alpha}{2}(I_1 - 3)^2\right] \qquad (2)$$

where μ is the instantaneous shear modulus, α is a constant.

The Cauchy stress component for QLV model with Yeoh strain energy density function can be represented as

$$\sigma_{11}(t) = [\alpha\lambda^3(t) + (1-3\alpha)\lambda(t) + 2\alpha][\lambda(t) - \lambda^{-2}(t)] + \mu \int_0^t D'(t-s)[\alpha\lambda^3(s) + (1-3\alpha)\lambda(s) + 2\alpha]\left[\frac{2}{3}\lambda^2(t)\{\lambda^{-1}(s) - \lambda^{-4}(s)\} + \frac{1}{3}\lambda^{-1}(t)\{\lambda^2(s) - \lambda^{-1}(s)\}\right] ds \qquad (3)$$

Stress relaxation function $D(t)$ defines the influence of current stress state in QLV model, which is represented here by the Prony series as

$$D(t) = 1 - \sum_{i=1}^{n} \gamma_i \left(1 - e^{-\frac{t}{\tau_i}}\right) \qquad (4)$$

γ_i and τ_i relaxation coefficients and represents relaxation times respectively.

We used 5 term Prony series with relaxation times τ = 0.01, 0.1, 1, 10 and 100 s considering relaxation occurs at different time scales and one term Prony series is normally insufficient to adequately define the material response different rates. The experimental stress strain curves with different strain rates have been fitted with MATLAB script using trust region reflective algorithm with non-linear least square criterion. Fig 6 (a, b, c, d & e) exhibits the fitting results of the QLV model with Yeoh strain energy density function Eq. (3), it can be clearly seen that the model shows exceptional agreement with experimental results of polymer and filler concentrations having filler concentrations 4%, 8%, 9% and 10%. Table 1 shows the calibrated material parameters of the QLV model with Yeoh strain energy density function for the polymer, 4%, 8%, 9% and 10% filler concentrations. As seen in Table 1 instantaneous shear modulus μ increases with an increase in the filler concentration up to 8%, For 9% and 10% it is found to be decreasing. This is because with higher filler concentration particles tends to form agglomerates, which results in weak matrix-particle interfacial adhesion. Homogenous dispersion of nanoparticles helps to decreases the agglomeration and improve the mechanical properties. However, it is very challenging to homogeneously disperse the nano-filler because of the strong tendency of nanoparticles to agglomeration [49, 50]. In addition, as discussed in section 3.1 adding higher filler content decreases the surface area of the particles leading to weak interfacial adhesion, which is also a major contributor to weak mechanical properties.

4. Conclusion

In this study, we have studied the rate dependent behaviour of photopolymer nanocomposite by conducting tensile tests at different strain rates. Fumed silica is used as a reinforcement and different concentrations of filler have been added to enhance the mechanical properties. We found out that the ultimate yield strength is significantly affected by the strain rate, for example, tensile strength of the photopolymer is 2.2 times higher at $1.3\text{x}10^{-2}$ s^{-1}compared to the tensile strength at $1.3\text{x}10^{-4}$ s^{-1}. Adding silica filler enhanced the mechanical properties of the photopolymer, for example with 4% filler content tensile strength is 2.25, 2.38 and 2.42 times higher than the tensile strength of the polymer at $1.3\text{x}10^{-2}$ s^{-1}, $1.3\text{x}10^{-3}$ s^{-1} and $1.3\text{x}10^{-4}$ s^{-1} respectively. QLV model combining hyper and viscoelastic phenomena have been used to capture the rate dependent non-linear behaviour of the material. We selected the uniaxial tension test scheme with three different strain rates to calibrate and capture the viscoelastic parameters and time dependent response respectively. We have successfully demonstrated the capability of the QLV model with hyper-viscoelastic phenomena to capture the behaviour of the material. In this work, the QLV model with Yeoh strain energy density function bears very good agreement with the experimental results.

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