The role of polymer phase in the deformation of highly filled particulate polymer composites

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Introduction

We are investigating the deformation behavior of soft polymer composites filled substantially with a hard phase: such composites potentially have desirable mechanical properties such as high stiffness and high toughness. The concept of composites is of growing interest in different biological materials such as nacre, bone for their exciting properties [1]. For example, nacre has 95% volume of hard minerals and only 5% of soft biopolymer. Geological materials present in the lithosphere are mostly combinations of different hard and soft phases. The common feature in these kinds of materials is the presence of a high volume fraction of hard phase in a soft matrix, enabling strong interaction between the hard phases.

Polymer matrix filled with randomly dispersed spherical metal particles has been used to study the deformation behavior of the composite with a high volume fraction of fillers. Beyond a certain volume fraction, the particles touch neighboring particles and form an infinite cluster that is continuous throughout the sample: this critical volume fraction is termed a percolation threshold. The electrical conductivity of the composite with metallic fillers increases sharply at this volume fraction. For spherical particles, the percolation threshold is near 0.2 [2].

To rule out effect of any special geometrical arrangement of particles we have considered randomly dispersed spherical particles in a polymer matrix. Beyond the percolation threshold, particle-particle interactions increase until a rigidity threshold is reached, where the particle network can support substantial loads. The rigidity threshold for composites filled with spherical inclusions is usually significantly higher than the percolation threshold [3].

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There are important findings related to the tensile strength of particulate composites at very high volume fractions. It has been reported that at higher volume fractions the composites become brittle. The early fracture of highly filled composites has been attributed to stress concentrations near the particles [4], with a decrease in tensile strength at high filler content. There are reports suggesting that compressive strength increases with increasing filler content [5]. Interactions between stress fields around particles have been suggested as a key factor for increasing strength [5]. Uniaxial compression test can capture the effect of strong interaction between the particles at high volume fractions.

Here we are interested in volume fractions close to random close packing of the particles. In such cases particles can transfer load through the contacts with neighboring particles. We examine the role of the polymer phase in the deformation of packed particulate composites.

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Materials and processing

The two phases for the composite have been selected based on their significantly different electrical and mechanical properties. Acrylonitrile butadiene styrene (ABS) polymer has been selected as the matrix phase. Nickel micro-particles have been selected as the filler. The electrical conductivity of the polymer and nickel are in the order of 10^{-13} and 10^{7} Sm^{-1}, respectively. The stiffness of the polymer and nickel are 3 and 200 GPa, respectively.

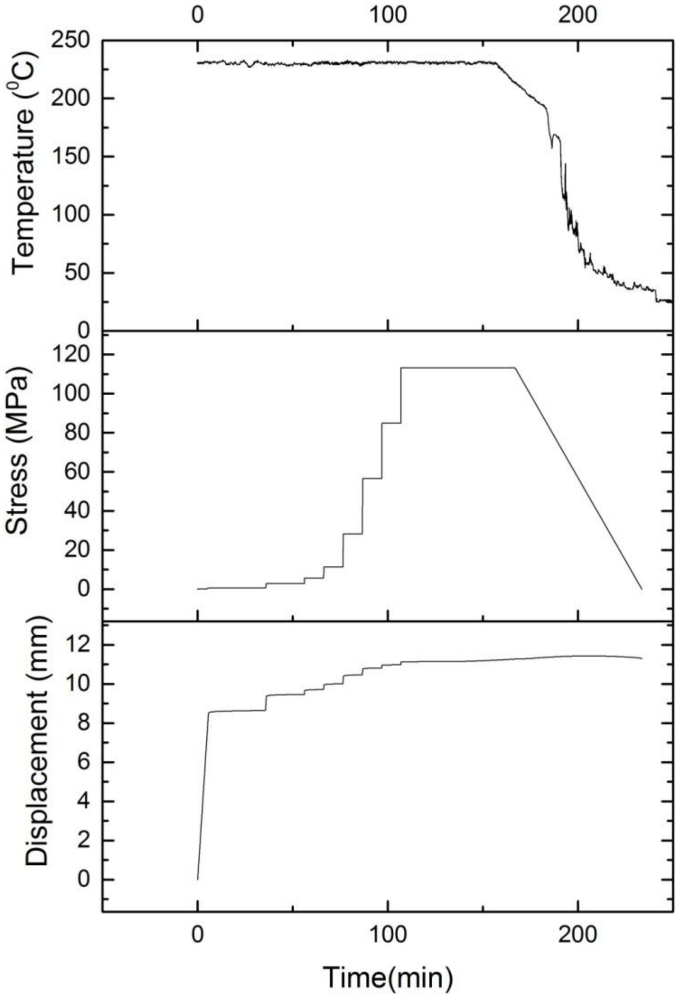

Figure 1. Processing parameters used for compaction

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Absolac 920 grade of ABS from Styrolution has been used together with nickel powder of 10 µm diameter from Alfa Aesar. First, both the as received powders were mixed together with ethanol in a ball-milling chamber at 200 - 300 rpm for 1-2 hours. After mixing, the powder was dried completely and then transferred to compaction die with diameter of 15 mm.

The parameters used for compaction were optimized to get fully dense pellets, with the temperature, pressure and time plots for the compaction process shown in figure1.

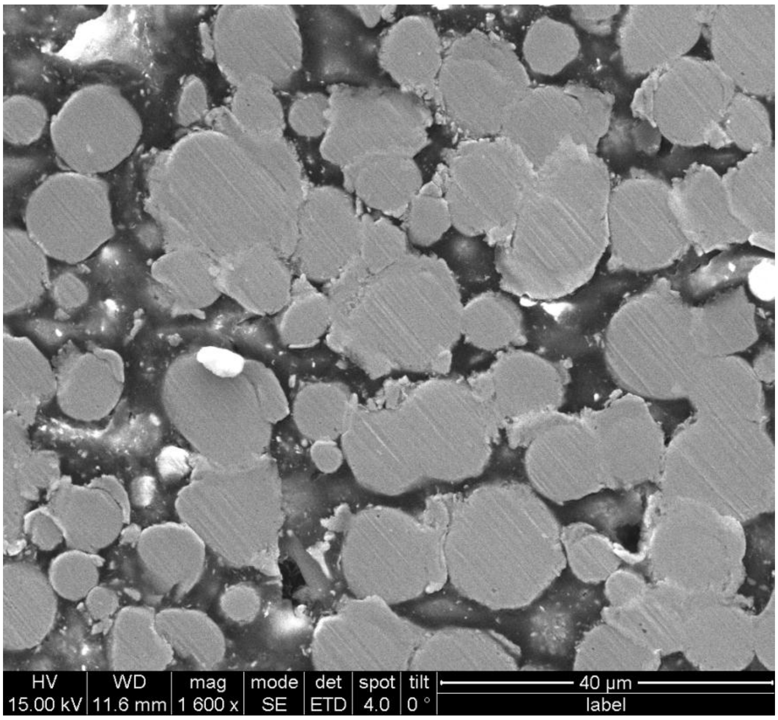

Figure 2. Scanning electron micrograph of the composite of 0.6 volume fraction of Nickel

Figure 2 shows a scanning electron micrograph of the composite with 0.6 volume fraction of nickel: the grey and black contrast correspond to the nickel particles and the polymer matrix, respectively.

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Electrical conductivity

Electrical conductivity was determined using a two probe DC conductivity measurement set up. Silver paste was applied to two opposite surface of the cylindrical pellets for conductivity measurements.

Mechanical testing

Compression samples with a square cross-section of ~ x mm and height of ~ mm were machined from the fully dense pellets, with the compression axis along the hot pressing direction. All compression test was carried out at a strain rate ($\dot{\varepsilon}$) of 10^{-3}, and at temperature from room temperature (298 K) to 393 K.

Results and discussions

The peak compressive strength of the composite with 0.6 Ni volume fraction and the pure polymer at different temperatures is shown in figure 3. The ABS polymer exhibits a glass

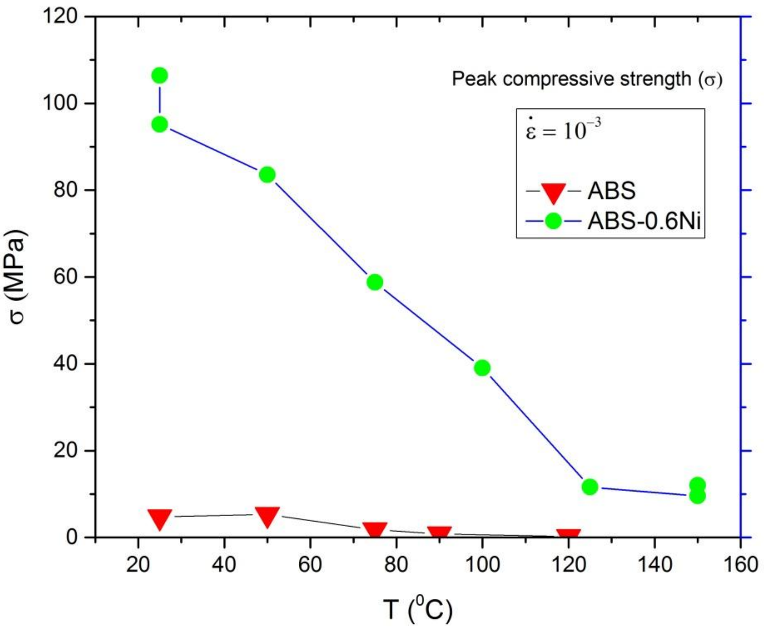

Figure 3. Strength of polymer (ABS) and the composite of 0.6 volume fraction of Nickel at different temperatures

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transition at T~373 K, which leads to a substantial reduction in the strength of the polymer from ~ 5 MPa at 298 K to < 1 MPa at 398 K. It is evident that the room temperature strength of the composite is substantially higher than the strength at 120^{0}C. Neither the arrangement of particles nor the mechanical properties of the individual particles are expected to change in this temperature range, suggesting that the strength of the polymer play a key role in the observed behavior. The high compressive strength at room temperature of the composite requires load to be transferred to the particles either through particle-particle contacts or polymer-particle interface, or a combination of both. Room temperature uniaxial compression tests on the particle network, after burning off the polymer, shown in figure 4 reveal that the particle network cannot take sufficient load. Therefore, significant load transfer must occur through the polymer particle interface.

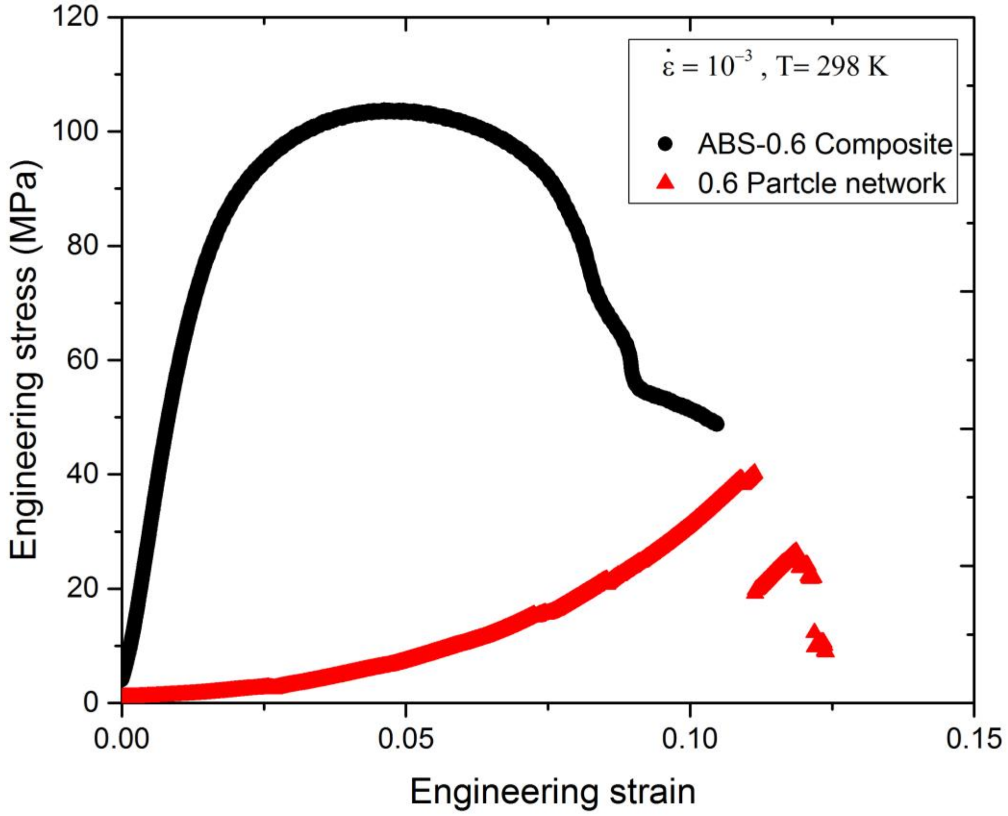

Figure 4. Comparison of compressive strength between the composite (0.6 volume fraction of nickel) and the left over particle network after burning off the polymer

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As derived by Woodcock [6], the average edge to edge inter-particle spacing (h) between the first nearest particle in a randomly dispersed particulate system decreases with increasing volume fraction according to equation 1.

$$\frac{h}{d} = \left[\left(\frac{1}{3\pi\phi} + \frac{5}{6}\right)^{1/2} - 1\right] \tag{1}$$

where d is the average diameter of particles and φ is the volume fraction of particles.

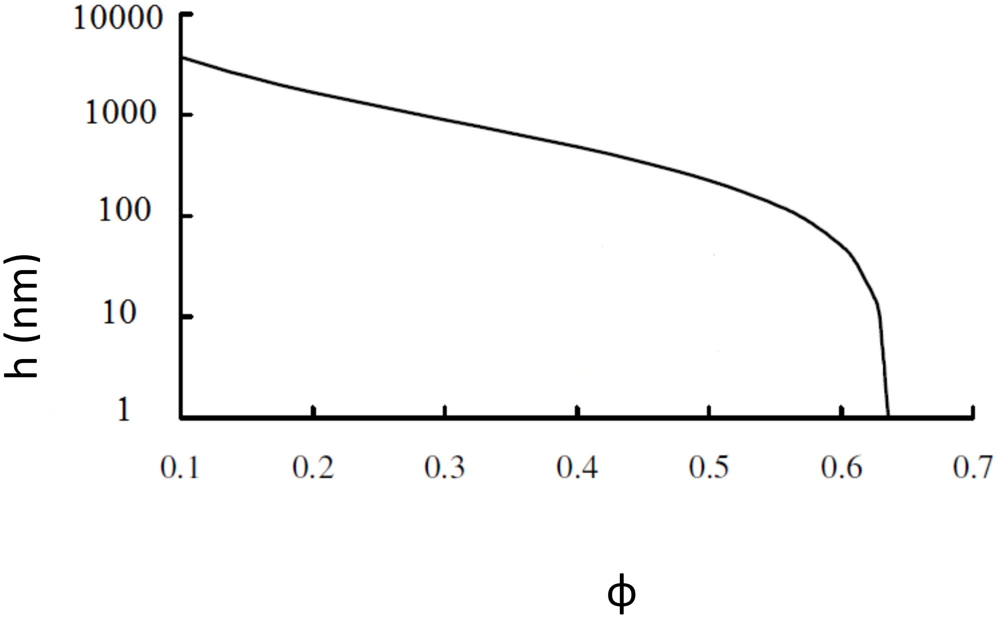

Figure 5. Average inter particle spacing (h) between two nearest particles of 10 µm diameter with volume fraction(ϕ) of particles (reproduced from [7])

The relation between h and φ for particle size of 10 µm has been plotted in figure 5 [7]. The average distance between the nearest particles becomes < 100 nm for a volume fraction of > 0.6.

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We propose that the polymer flow stress is very high in the presence of narrow confining interfaces at $T<<T_g$, leading to high strengths in the composite. However, at higher temperatures in the vicinity of T_g, the polymer can relax very fast and thus does not support load, leading to a drastic reduction in the strength of the composite.

Conclusions

The rheological behavior of a polymer phase has been found to play a key role even at very high volume fraction of particles in a composite, near the random close packing of particles. At room temperature, assuming that the polymer layer thickness reduces to a very small value of <100 nm when volume fraction of fillers is 0.6, the flow stress of the polymer is enhanced due to a confining influence of neighboring hard particles. However, at temperatures close to T_g, the easy flow of the polymer relaxes the confinement effect to reduce the strength of the composite. Further detailed studies are necessary to clarify the effect of confinement at different thickness of polymer layer at different temperatures.

Acknowledgment

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