Microstructure Deformation and Fracture Mechanism of Highly Filled Polymer Composites under Large Tensile Deformation

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Abstract. The microstructure deformation and fracture mechanisms of particulate-filled polymer composites were studied based on microstructure observations in this paper. By using in-situ tensile test system under scanning electron microscopy, three different composites composed of polymer binder filled by three different types of particles, namely Al particles, AP particles and HMX particles, with the same total filler content were tested. The roles of initial microstructure damage and particle type on the microstructure deformation and damage are highlighted. The results show that microstructure damage starts with the growth of the initial microvoids within the binders or along the binder/particle interfaces. With the increase of strain, the microstructure damages including debonding at the particle/binder interface and tearing of the binder lead to microvoid coalescence, and finally cause an abrupt fracture of the samples. Coarse particles lead to an increase of debonding at the particle/binder interface both in the initial state and during the loading process, and angular particles promote interface debonding during the loading process.

1. Introduction
The particulate-filled polymeric composites (FPCs) constitute a broad class of structural and functional materials, which are highly packed particulate composite materials containing hard particles embedded in a polymeric binder. Such as the polymer concretes, the dispersion-hardened thermoplastics, syntactic foam and the solid rocket propellants, they are widely used in various engineering fields[1,2].

When the material is strained, irreversible microstructure damage in the form of microvoids in the binder or along the binder/particle interface occurs. As the applied strain increases, the growth of damage takes place as successive nucleation and coalescence of the microvoids or as polymer binder tearing[3]. These damage processes are microstructure dependent, and which is responsible for the microstructure dependence of the macromechanical behaviour of FPCs[4]. In order to develop an accurate analysis method to characterize the macromechanical properties of FPCs, the evolution of different microstructural damage mechanisms of FPCs should be correctly understood and their effects on macromechanical properties should be measured.

During the last decades, several techniques have been developed to directly observe the microstructural damage process of FPCs, such as Moiré interferometry[5, 6], digital speckle
photography[7, 8], white-light digital image cross-correlation (DICC) analysis[9], and in-situ tensile tests under scanning electron microscope(SEM)[10]. Among these techniques, the last one is the most frequently used technique. By using the in-situ SEM observation, Zheng et al[10] investigated the crack initiation, propagation, and termination on the plerosphere/PP composites, and concluded that the toughness and strength of the polymer can be improved due to large numbers of microcracks caused by the particles. Kim and a coworker[11] studied the cavitation in rubber toughened polymers and the debonding in particulate-filled polymers, and found that the cavitation process plays an important role in promoting the shear yielding of the matrix ligaments between microvoids, which is the main mechanism of absorbing the energy. The debonding process has also been studied. Many factors, such as the filler content[13], filler size[13] and interaction between the filler particles and the matrix[12] have been proven to affect the debonding process. The debonding process can affect the mechanical properties of particulate-filled polymers. Homogeneous debonding leads to tough fracture behavior, and local debonding leads to brittle behavior[14].

In this work, a series of quasi-static tests by using the in-situ SEM observation were carried out to study the microstructure deformation and fracture behavior of a propellant simulation material, which is a highly-particle-filled composite in which the total content of the fillers are 74%, with a few percent polymer binder. The short, rectangle-shaped specimens were machined from the original bulk materials. The in-situ SEM observation was used to monitor the process of microstructure deformation to observe the initiation and propagation of microcracks, and reveal the failure mechanisms of the specimens.

2. Materials and Experiments
The particulate-filled polymeric composites (FPCs) used in the experiments are propellant simulation materials consisting three kinds of filler particles, HMX, AP and Al particles. The total content of the filler particles is 74%. The contents and average particle sizes of the fillers are given in table 1.

| sample | Al% (14 μm) | AP%(146 μm) | HMX% (18 μm) |
|--------|-------------|-------------|--------------|
| 1      | 59          | 15          | 0            |
| 2      | 0           | 15          | 59           |
| 3      | 18          | 5           | 51           |

Figure 1. The in-situ loading device DEBEN Microtest-2000 placed in the chamber of Scanning Electron Microscopy(SEM)
In order to investigate the process of microstructure deformation and damage of the propellant simulation material under tensile loading, the in-situ tensile tests under scanning electron microscopy (SEM) is adopt to observe the microstructure evolvement process. As shown in figure 1, the in-situ loading device of DEBEN Microtest-2000 is used to apply tensile loads on samples, and SEM is used to observe the microstructure deformation and damage modes. The correlation between components and microstructural deformation mechanism was investigated with a series of in-situ SEM observation.

The samples for micromechanical deformation observations were prepared as follows. The samples with a rectangle section of 10mm×1mm and the length of 20mm were cut out from the bulk materials. Before the samples were fixed on the tester, their surfaces were golden-coated for SEM observations. The failure strain of the tested simulation materials is higher than 250%. Due to the restriction of the space of the test system, the maximum applied displacement of the loading device is only about 10mm, so the effective length for observation is limited to 3mm(the distance between two clamps) to ensure that the samples can be broken in the tensile tests.

Tensile specimens of the simulation materials were stretched in the in-situ loading device at a crosshead speed of 0.4 mm/min. At several given elongations, the crosshead was stopped and sustained for several minutes to scan the deformed regions of the samples by SEM, and the typical SEM pictures were captured for further analysis of the microstructure deformation.

3. Results and Discussions

3.1. Initial microstructures

The initial microstructures of the samples are shown in figure 2. The large particles with smooth surface are AP particles, and their average size is 146μm. The bright spherical particles in figure 2 (a) and (c) are Al particles, and their average size is 14μm. The dark and irregular particles in figure 2 (b) and (c) are HMX particles and their average size is 18μm. It can be observed from the SEM photography that there are two kinds of initial damage in propellant simulation materials mainly shown as follows

- Broken particle: mainly occurred in large AP particles.
- Microcrack and void: mainly appeared at the interfaces among HMX, large AP particles and polymer binder.

![Figure 2. SEM photography of initial microstructure. (a) Sample 1(59% Al, 15% AP), (b) Sample 2 (15% AP, 59% HMX) and (c) Sample 3(18% Al, 5% AP, 51% HMX)](image)

3.2. Tensile fracture process

In the simulation materials, the stiffness and strength of filler materials are much higher than those of the binder material. As results, the deformation mainly takes place in the binder materials, and the
initial defects of microvoids and interface debonding grow obviously even at the initial stage of the tensile test. With the increase of deformation, it is observed that the interfacial debonding firstly occurs along the large AP particles, and then the large irregular HMX particles during the tests for samples containing HMX particles.

Owing to the development of the microvoids in matrix and along the interfaces, the microvoids homogeneously develop over the entire surface of the sample with the increase of deformation in the initial stage of deformation. When the displacement is around 3mm, the microstructures develop into homogeneous void structures over the entire sample. When the displacement attains about 5mm, as shown in figure 3, a local cracklike structure can be observed that crosses to both sides of the samples perpendicular to the loading direction. In the cracklike regions, large deformation of the binder ligaments can be seen, and the interconnected voids have been formed. The deformed binder shows a network structure. Some fractured matrix ligaments that have developed large deformation can also be seen. It can be seen that the debonding along large particle interfaces are comparatively severe. Many voids can be seen on both sides of the particles in the direction parallel to the applied strain that are formed by large deformation of the matrix between particles after the debonding process, especially around the large AP and irregular HMX particles.

![Figure 3](image)

*Figure 3. SEM photography of microstructure at the deformation of 5mm. (a) Sample 1(59% Al, 15% AP), (b) Sample 2(15% AP, 59% HMX) and (c) Sample 3(18% Al, 5% AP, 51% HMX)*

At the last stage of tension, the process of interface debonding is completed and very few interface debonding occurs[15]. The deformation mainly takes place by the growth of voids and stretch of binder ligaments in the cracklike structure. Finally, the fracture of binder ligaments leads to the coalescence of voids and results in the fracture of sample from the cracklike structure regions.

It can be concluded from the above experiment results that, the damage mechanisms of the tested propellant simulation material mainly include the growth and coalescence of initial defects, interfacial debonding along large particles and the fracture of binder ligaments. At low deformation levels, the dominant mechanism of damage accumulation is the growth of initial defects and interfacial debonding. The interface debonding of large irregular particles precedes that of small smooth particles. While at high values of tensile deformation, the dominant mechanism is the fracture of binder ligaments between filler particles.

### 3.3. Effects of filler particles

As shows in figure 3(a) of sample 1, the damage mechanisms are mainly interfacial debonding along the large AP particles, large voids are formed on both sides of the particles in the direction parallel to the applied stress. Al particles are strongly bonded with the polymer binder, and very few interface debonding occurs along the Al particles. The binder ligaments with large deformation are presented...
between Al particles. The stretch and fracture of binder ligaments between Al particles can be observed in the cracklike regions.

For sample 2, large AP particles debonded first, then interfacial debonding around large irregular HMX particles occurred, and debonding appeared first at sharp corners. The binder formed a network structure as shown in figure 3(b).

For sample 3, large AP particles tended to interfacial debonding first, followed with a large amount of interface debonding along HMX particles. In some regions with severe damage, HMX particles were almost apart from the binder completely. In this sample, due to the contact of Al particles and HMX particles, a small quantity of Al particles debonded from the contact places as shown in figure 3(c). It indicates the HMX particles may affect the polymer binder coating of Al particle and the dedonded particles are not fully coated by the polymer binder.

By comparison, the interfaces along large AP particles easily debonded. For samples with high volume fraction of AP (sample 1 and 2), it is easy to cause severe local damage which act as the fracture source leading to sample failure. For samples with comparatively low volume fraction of AP, the development of deformation inside the sample is comparatively uniform under large range of deformation, the polymer binder around the small particles can deform more fully, which leads to homogeneous interfacial debonding of small particles as shown in figure 3(b), especially for irregular HMX particles.

Figure 4 illustrates the fracture photographs. For all samples, the surfaces of AP particles were quite smooth without residual binder, which indicates the wettability and adherence of the polymer binder and AP particles are insufficient, and interfacial debonding can occur completely. For AP particles, the debonding is also highly related to particle distribution and surface coating. Although the surface of AP particle is smooth, some large AP particles clustered or the surfaces were not coated by binder, which lead to the debonding of AP particles completely. The debonding of small Al and HMX particles is invisible during the overall tensile process, which showed that these particles were well coated by polymer binder, and the bonding strength was comparatively high. The shape of HMX particles is extremely irregular, large HMX particles debonding started from sharp corners. The homogenous debonding of large quantity of HMX particles leads to the uniform deformation of sample and improve the fracture toughness.

3.4. Force-displacement curves
Figure 5 shows the typical load-displacement curves recorded during the tensile process. The fluctuation of the curve in figure 5 (a) caused by the pause of tension for SEM observation. It can be seen that for each time of crosshead suspension, it could lead to stress relaxation. But after certain
deformation when it started to reload, the loads can recover to the original magnitude measured by continuous loading as shown in figure 5(b), which is the load-displacement curve measured by continuous tensile loading

![Load-displacement curves](image_url)

**Figure 5.** Typical load-displacement curves of sample 3. (a) Recorded with crosshead suspension for SEM observation, (b) Recorded by continuous loading

The load-displacement curves in figure 5 can be divided into two stages: the nonlinear elastic stage and hardening stage. In elastic stage, the damage was mainly the elastic expansion of initial voids, and it can recover after unloading. While at the beginning of hardening stage, the interface debonding of large particles and inelastic expansion of voids (or the inelastic deformation and damage of binder) occurs. With the increasing of deformation, the damages continuously accumulated and the microcracks began to expand, which cause the degradation of mechanical properties of the stimulation materials. But the loading capacity of sample still slowly increases due to the strengthening effect of particles and strengthening deformation of binder. When the deformation reached the maximum magnitude, the sample cracked immediately due to the macrocracks caused by the fracture of local matrix tearing.

It should be noted that during the tensile process, obvious deformation and sliding occur near the clamps due to large deformation of the samples, thus the recorded displacement-time curve is not precise, only the record of loads is accurate. Thus, these tests cannot be used directly to calculate the stress-strain curves of samples. The macroscale experiments are still needed to investigate the effect of particle fraction and types on the mechanical properties of the simulation materials.

4. Conclusions

The in-situ tensile tests under SEM is adopt to observe the microstructure evolvement of the propellant simulation materials under tensile loading, and the effect of particle characters on the microstructure damage mechanisms are analyzed. Three different composites composed of polymer binder filled with the same filler content of Al particles, AP particles and HMX particles were tested. The results show that at low deformation levels, the dominant damage mechanism is the growth of initial defects, and then the interfacial debonding along the large AP particles. While at the large deformation, the dominant mechanism is the fracture of binder ligaments between filler particles. Al particles are strongly bonded with the polymer binder, and very few interface dedonding occurs along the Al particles. The wettability and adherence of the polymer binder and AP particles are insufficient. The interfacial debonding can occur completely along AP particles and large voids are formed on both sides of the particles in the direction parallel to the applied strain. The shape of HMX particles is extremely irregular, large HMX particles debonding started from sharp corners. In the sample with high content of HMX, the debonding of large quantity of HMX particles leads to the uniform deformation and improvement of the fracture toughness. While in this sample, the contact of Al particles and HMX particles causes a small quantity of Al particles debonded from the contact places.
Acknowledgments
This work was supported by the National Natural Science Foundation of China under Grant No. 11202154, the Fundamental Research Funds for the Central Universities of China under Grant Nos. 2012-Ia-021 and 2011-IV-090, and by Open Foundation of State Key Laboratory of Explosion Science and Technology (Beijing Institute of Technology, China) under Grant No. KFJJ11-9Y.

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