Fabrication and Performance of Nanocomposites Containing Zirconia Particles

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Abstract. The discovery of polymer nanocomposites and the achievement of super-toughness polymer are in the most significant advances with the development of new polymer materials. This paper is aimed to study the manufacturing process and mechanical response of the zirconia particle reinforced epoxy-based nanocomposites. The tests of tension and compression were carried out by the zirconia content on different levels. The damage signals were monitored by using the acoustic emission instrument. The results show that the elastic modulus increases gradually with the increase of zirconia particle content both tension and compression. The maximum value of tensile strength of the nanocomposites can be found at 8 wt% zirconia content. Compared with 0 wt% zirconia content, the maximum value of tensile strength has 26% growth. The compressive strength decreases gradually with the increase of zirconia content. And compared with 0 wt% zirconia content, the compressive strength of 15 wt% zirconia content decreases by 9%.

1. Introduction
With the development of nanotechnology and the emergence of new nanomaterials, the research of polymer-based nanocomposites has attracted increasing interest and wide attention from both scientific and industrial circles [1~3]. The rapid development of nano science and technology not only stimulates the research work eagerly, but also accelerates the potential applications in many fields. The non-homogeneous microstructure of composites is of the large differences between constituent properties [4~7]. The interfaces in composite materials are reasons for the complexities of micro-level damage or failure. The damage of composites usually initiates with the cracking in matrix and interface with different scale levels. It has been reported that inorganic nano-sized particles can strongly change the macroscopic properties of the polymer even at very low concentrations [8~10]. The nano-particles have large surface to volume ratio that can increase the interactions between particles and polymer matrix, which leads to great effects on the overall properties of composites. Various studies can be found in the literature regarding the incorporation of these new materials [11~13]. Therefore, inorganic nanoparticles can be employed to prepare different characteristic composites for various applications. The acoustic emission (AE) method can use to detect elastic waves generated by micro-scale destruction in the materials and also to monitor the damage of materials as a non-destructive inspection technique. There are many experimental reports showing the use of AE signal to characterize the damage in materials [14~16]. AE technique has been frequently used during different mechanical tests to monitor damage mechanisms created in various composites. The correlation with a given damage mechanism is often made using a single AE parameter. The present investigation is also for the damage detection of polymer nanocomposites by employing the acoustic emission method, the real-time failure process has been detected and analysed effectively.
2. Experimental procedures

2.1. Materials
The epoxy resin E51 and the hardener A50 modified MXDA were used in this work to form base polymer materials. The micro-sized ZrO$_2$ particles as filled nano-zirconia powder were then added into the matrix materials to form the zirconia-epoxy nanocomposites. They were prepared by means of in-situ synthesis method for better dispersion of the particles in the matrix. At the beginning of the nanocomposite manufacturing process, the predetermined amount of the ZrO$_2$ powder was added into the epoxy resin by mechanical stirring and following by ultrasonic technique for about 1 h at room temperature in order to provide a uniformly dispersed nanoparticle-epoxy uncured mixture. The curing agent A50 was then added into the mixture by appropriate ratio and followed by mechanical stirring and afterward vacuuming for a long time. This step was to remove air-bubbles that were trapped inside the nanocomposites before curing. The mechanical stirring machine is HSFS-S400 high-speed disperser and the ultrasonic apparatus is FS-800N ultrasonic processor as shown in Figure 1 and Figure 2. Several types of sample pieces were made in this study, they were pure epoxy resin (0 wt% zirconia content), and nanocomposites with 3 wt%, 5 wt%, 8 wt%, 10 wt%, and 15 wt% ZrO$_2$ nanoparticles. Figure 3 and Figure 4 show the sample and the SEM micrograph, in which the content of ZrO$_2$-nanoparticles is 8 wt%. The scale length in Figure 4 is 50 μm. It can be seen from the picture that the particles are uniformly dispersive on the whole.

![Figure 1. High-speed disperser](image1)

![Figure 2. Ultrasonic processor](image2)

![Figure 3. Nanocomposite](image3)

![Figure 4. SEM micrograph](image4)

2.2. Experiments
Tensile tests were performed in order to determine the mechanical behaviour of the zirconia epoxy nanocomposites according to GB1040.1-2006-T. DNS-300 testing machine with the additional apparatus was used to measure the monotonic tensile properties. Specimens were cut from the prepared plates by the effective testing dimensions (100×10×4mm$^3$) and the aluminium tabs were bonded with a suitable adhesive for the experiments. Tensile tests were conducted at room temperature with a cross-head rate of 1mm/min, the testing fixture as shown in Figure 5. Strains during the loading
were measured by the glued strain gauges on the specimen surfaces. Therefore, elastic modulus and Poisson ratio of specimens were determined by the measuring data. The tensile modulus is determined by the slope of stress-strain curve from 2000με to 5000με. The ultimate tensile strength is the maximum tensile stress.

For the particle reinforced polymer materials, compressive properties must have special attention because the damage phenomenon of the composite is very obvious. So the tests of zirconia-epoxy nanocomposites become an important issue. The compressive tests were performed according to GB/T 1041-2008. The compressive specimens used in these experiments are cut from the repaired panels by regular sizes (30×10×10mm³). The strain gauges were glued on two surfaces of the specimen. The compressive experiment was conducted at room temperature with a cross-head rate of 1mm/min, the testing fixture as shown in Figure 6. The loading method was by controlling the compressive deformation. The strains were measured by the strain gathering system. The compressive properties of specimens were determined by the measuring data. The compressive modulus is determined by the slope of stress-strain curve from 2000με to 5000με. The ultimate compressive strength is the maximum compressive stress. During the tests, the damage signals were monitored by using the acoustic emission instrument (DS2 model) as shown in Figure 7. The testing diagrams were captured from the loading system and AE event counter. And typical curves of nanocomposites with different amounts of ZrO₂-nanoparticles have been plotted in Figure 8. In diagrams, vibrating counts and acoustic emission energy can indicate the damage phenomenon of ZrO₂-epoxy composites in correspond to the compressive force.

![Figure 5. Tensile test fixture](image1)

![Figure 6. Compressive test fixture](image2)

![Figure 7. DS2 model acoustic emission (AE)](image3)
3. Testing results and discussion
The mechanical properties of resin-matrix composites depend mainly on the properties of its constituents, namely the polymer, the reinforcement and the interface as well. For example, the type of the matrix and the quantity can be strongly effective on the properties of the composites. In this work, the effect of zirconia particle content on the mechanical properties of nanocomposites may be very obvious and worthy of careful consideration. On the basis of the results of tensile and compressive tests, the values of Young’s modulus (E) and ultimate strength ($\sigma_{ult}$) can be calculated as listed in Table 1, respectively. It is clearly found that there is a gradually incremental modulus of elasticity both tension and compression with the increase of the content of zirconia particles. The tensile modulus on the whole is little higher than the compressive modulus. From Table 1, it can be found that the strength of tensile specimens varies complexly with the content of ZrO$_2$ nanoparticles, there is a peak value at 8 wt% zirconia content. The ultimate strength of compressive specimens decreased progressively with the increase of zirconia content. This trend can show that the damage of compressive specimen may be influenced more and more severely with the increase of ZrO$_2$ nanoparticles.

### Table 1. Young’s modulus and ultimate strength of nanocomposites

| ZrO$_2$ (wt %) | Tension E (GPa) | $\sigma_{ult}$ (MPa) | Compression E (GPa) | $\sigma_{ult}$ (MPa) |
|----------------|-----------------|----------------------|---------------------|---------------------|
| 0              | 4.95            | 21.6                 | 4.61                | 118                 |
| 3              | 4.97            | 22.5                 | 4.84                | 113                 |
| 5              | 5.12            | 25.6                 | 4.92                | 112                 |
| 8              | 5.29            | 27.2                 | 5.02                | 110                 |
| 10             | 5.52            | 21.6                 | 5.06                | 108                 |
| 15             | 5.66            | 22.7                 | 5.39                | 107                 |

4. Conclusion
The preparatory methods of ZrO$_2$/epoxy nanocomposites were introduced and seven groups of the samples (zirconia content 0%, 3%, 5%, 8%, 10%, 15%) with inclusion of both tensile specimens and compressive specimens were made. The tensile tests and compressive tests were carried out respectively. The damage signals were monitored by using the acoustic emission instrument.

The experimental results show that the ZrO$_2$ nano particles can enhance both the tensile and compressive modulus. The tensile strength can reach the maximum when the zirconia content is at 8 wt%. The compressive strength tends to decrease gradually as the zirconia content increases. The research indicated that within certain limits, the zirconia particles can enhance the mechanical properties of polymer composites.
In this paper, the influence of ZrO$_2$ nano particles on composite is studied, however the mechanism of nanoparticles on composites is not clear. The future work should be focused on the study of the interface between nanoparticles and matrix to further reveal the mechanism.

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6. References
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