

Processing and Property Improvement of Polymeric Composites with Added ZnO Nanoparticles through Microinjection Molding

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ABSTRACT: The use of nanoparticulates in polymeric materials has become a potential alternative for organic-inorganic composite materials because of their versatility in property modification and ease of batch fabrication. This paper investigates the kneading and mechanical properties of polypropylene (PP) with added nano-ZnO powder in sizes of 10–30 nm, through batch kneading and microinjection molding processes. The results show that the PP microgears with added ZnO nanoparticles are well replicated with clear structural def-

inition. The resulting composites with a small amount of nanofiller added exhibit significant improvement in wear resistance and mechanical properties. The possible strengthening and wearing mechanisms is discussed based on the investigation of the worn and fractured surfaces of the composites. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 6009–6016, 2006

Key words: nanofiller; zinc oxide; polypropylene; microgear; microinjection molding; wear

INTRODUCTION

Recently, the use of plastic materials in micropart fabrication has been attractive to processing engineers due to their versatility and ease of the batch fabrication.^{1–3} A number of pure plastics, e.g., LCP (Liquid Crystal Polymer), PC (Polycarbonate), PS (Polystyrene), PP (Polypropylene), PMMA (Polymethyl methacrylate), and POM (Polyoxymethylene or Acetal), have been successfully processed through micromolding methods.^{4–8} However, most of the microparts, such as gears and fans, require high strength, wear resistance, and accuracy. Pure plastic materials alone cannot satisfy these requirements.

Some researchers^{9–11} have produced microparts by the addition of small particulates and fabricating through micropowder injection molding. The reported techniques include blending, molding, debinding, and sintering processes. Some defects, for instance, high shrinkage of microparts, may occur and result in cracking. Through this technique, however, property improvement in strength and wear resistance can be obtained.

Schneider et al.¹² added microfiller to plastics to reinforce their structures and reduce shrinkage. How-

ever, the fillers could not be used successfully in the micromolding process. This was because the fillers, such as glass fibers with a typical diameter of 10 μm and a length of 100–500 μm , were often as big as the molding microparts. Thus, microparts with added nanosize particulates could possibly be used in microinjection molding. However, it was difficult to disperse nanoparticulates uniformly in the polymeric compound through a kneading process. Song et al.¹³ showed their control in the kneading process to manufacture various zirconia feedstocks. The powder agglomeration of the feedstock was retained because of insufficient shear stress. In this case, the agglomeration still existed after parts were sintered.

Wu and Wei^{14–16} conducted a series of the measurements on the homogeneity of submicron-powder in the feedstocks for precision injection molding. The agglomerated powders were shear-kneaded and could be uniformly dispersed in the binder by appropriate kneading control. The results strongly revealed that ceramic feedstocks have good quality only if the kneading process was conducted not only by a strong shear force, but also by effective kneading energy adsorbed by the plastic mixture. However, the properties, e.g., strength and wear, of kneaded polymer/powder mixtures were not investigated.

PP is one of the popular plastics for the parts used in microelectromechanical system (MEMS), such as microgears and microfans in electrical appliances and automotive applications. PP is easily modified with

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blending elastomers and inorganic filler to obtain higher mechanical performances. In the meantime, ZnO, a popular semiconductor material with a high excitonic binding energy, facilitates several optical-electronic behaviors at room temperature. ZnO is also found to be a significantly harder material used to fabricate nanowires and nanotips.^{17–18}

In this study, a homogeneous feedstock with added commercial ZnO nanoparticles and dispersant was produced under the optimum kneading process. The wear and mechanical properties were enhanced by the homogeneous feedstock. In addition, this paper also discusses the reproducibility of the microparts made with feedstock through microinjection molding.

EXPERIMENTAL

Materials

The raw materials used in the study included ZnO nanopowder (Z-tech, Rockville, MD) with sizes of 10–30 nm, polypropylene (PP, Formosa Plastic, Taiwan), and two dispersants, including FP1 (ICI, England) with an ester function group and SA (Nacalai Tesque, Japan) called “stearic acid.” Both dispersants are commonly used as surfactants between ceramic powder and polymer. An optimal amount and combination of the dispersant were chosen based on the results of sedimentation experiments conducted in heptane. The weight content of the ZnO nanoparticle in the polymer compound was 0.5%, 1%, 3%, 5%, and 15%, respectively. The amount of the dispersant added into the polymer compound was between 0.1 wt % to 1 wt %.

Sedimentation and kneading processes

The suspensions for sedimentation experiments were prepared by mixing 54 mL heptane with a specified dispersant and ZnO powder of 1.5 g. The sedimentation heights, H_f (final height) and H_o (original height), were measured after sedimentation for 7 days. The dispersive effect is better when the ratio of H_f/H_o is smaller.

A Z-blade kneader (Ray-E, Tainan, Taiwan) with a 650-mL mixing bowl was used, and operated at a constant rate of 35 rpm. Batch mixing that is different from the small amount kneading in a laboratory was conducted in this study. At the beginning of the kneading process, pure ZnO nanoparticle was preheated to 175°C in the kneader. PP plastic pellets were then added to the powder and kept at 175°C in the kneader. After kneading for 25 min, dispersant was added and the temperature of the kneader was immediately reduced to 160°C and held for 50 min. The dough-type mixture was granulated in the mixing bowl as the temperature of the bowl was reduced to 70°C for 20 min.

Quality evaluation

To measure the homogeneity of the mixtures, a micro-gear with 8 teeth, a thickness of 1.5 mm, and an outer diameter of 1.5 mm was molded through microinjection molding. The made gears were measured with a coordinate measurement instrument (CMM, Poly, Italy). The precision level of the measurement was 1 μm. The reproducibility of the microgears was evaluated as a standard of accuracy. Ten measured microparts were selected from the eleventh to the twentieth molded gears. That is, the first ten pieces were discarded because their quality was unstable. The allowable deviation in the precision of microparts on the market is normally 20 μm. Thus, the level of accuracy achieved here was acceptable with the deviation in the precision of the microparts being less than 20 μm.

To examine the mechanical behavior of the composites with added nano-ZnO, wear, tensile, and flexural tests were conducted in this study. Wear tests were carried out by using a pin-on-disk tester (Micro Phonics, Irvine, CA). Cylindrical specimens with a diameter of 8 mm and a thickness of 10 mm were used in wear tests, following the conditions specified in ASTM G99-04. Round specimens were placed in contact with the disk which had a surface roughness of 0.2 μm (Ra) at a position 37 mm from the center and rotated from 2500 (0.58 km) to 30,000 revolutions (6.97 km) with a step increase of 2500 revolutions at a constant speed of 70 rpm. The vertical load on the pin was 0.5 kgf. Then, the mass of each specimen was measured using an electronic weighing machine (Honeywell, UK). The mass loss (ML) was then calculated as follows:

$$ML = \frac{m - m'}{m} \times 100\%, \quad (1)$$

where m is the mass before wearing and m' is the residual mass after wearing test. To achieve high quality, low mass loss is required. In addition, tensile and flexural specimens were conducted in a universal testing machine (MTS 810) according to ASTM D638 and D790, respectively. The results were averaged from ten specimens.

RESULTS AND DISCUSSION

Dispersive properties in heptane

The sedimentation results of ZnO nanoparticles with different dispersants are shown in Figure 1. The sample with FP1 additive exhibited the least sedimentation height. The height ratio (H_f/H_o) of the ZnO nanoparticles with FP1 decreased to 30% compared with that without surfactant. However, the other two systems, either SA or the combination of FP1 and SA, were shown to be less effective for the dispersion of

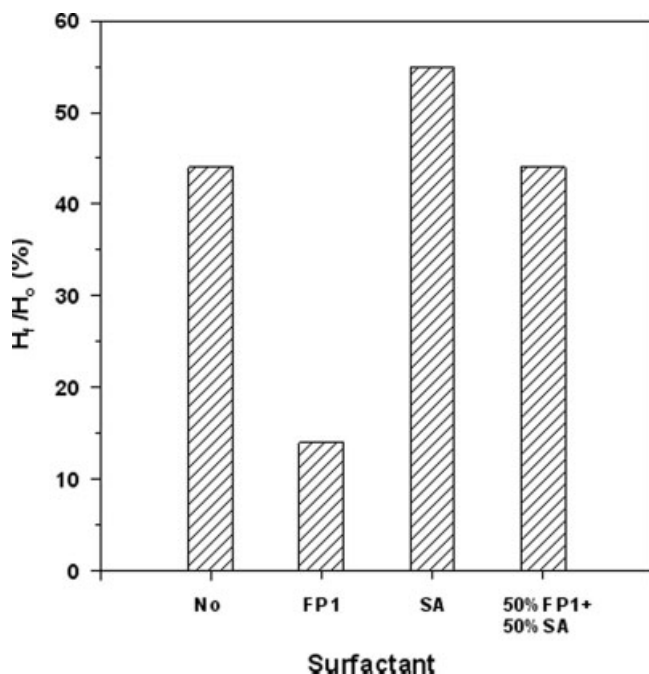


Figure 1 Sedimentation results of the ZnO nanopowder with different surfactants for 7 days.

the nanoparticles. Therefore, FP1 surfactant was used for the samples in following tests.

From the sedimentation results, the H_f/H_o ratio of the ZnO sample with added FP1 was about 14%, which means about 14% nanoparticles cannot be uniformly dispersed in PP polymer. In other words, the nanoparticles may show some degree of particle agglomeration. To reveal the states of the agglomeration, TEM (Transmission Electron Microscopy, JEOL 100CXII, Japan) was used to analyze the morphologies of the nanoparticles. One typical micrograph of the ZnO nanoparticles is shown in Figure 2. The image revealed that the ZnO nanoparticles are apparently agglomerated. The result was that these primary

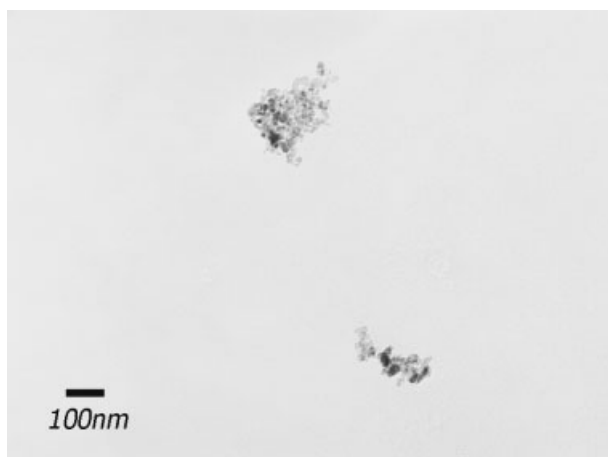


Figure 2 TEM micrograph of ZnO nanoparticles.

nanoparticles could not be 100% dispersed because of strong bonding between particles.

Kneading behavior and dimensional accuracy of microgears

The kneading response of the PP polymer with 1 wt % added nanoparticles was measured by a torque rheometer. The torque profile, as shown in Figure 3, increases in value because one ingredient, PP, changes from solid state to molten state while mixing with the nanoparticles. The peak is so called "loading peak" when the powder and PP polymer are mixed to produce a granular state. The feedstock then turned into a dough state in 50 min and produced consistent properties after another 20 min of kneading after FP1 was added into the admixture. In other words, a homogeneous feedstock was produced when consistent plastic properties were detected. In this experiment, the feedstock was used to fabricate microgears and specimens as described below.

A photograph of the microgears made using the made feedstock with 1 wt % added ZnO nanoparticles through microinjection molding is shown in Figure 4. The molding was conducted under a melt temperature of 190°C, a mold temperature of 80°C, and an injection pressure of 110 MPa. It can be observed from this photograph that the microgears with 8 teeth, a thickness of 1.5 mm, and an outer diameter of 1.5 mm were well formed with clear structural definition. The average part mass is only 2.8 mg.

The reproducibility of microgears is normally evaluated as a standard of accuracy. The standard devia-

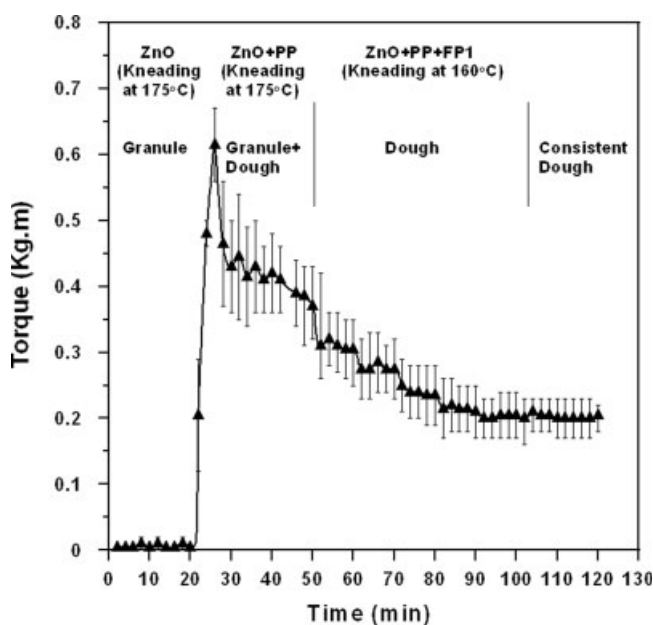


Figure 3 Kneading torque-time profile of the composite with 1 wt % added ZnO nanoparticles.

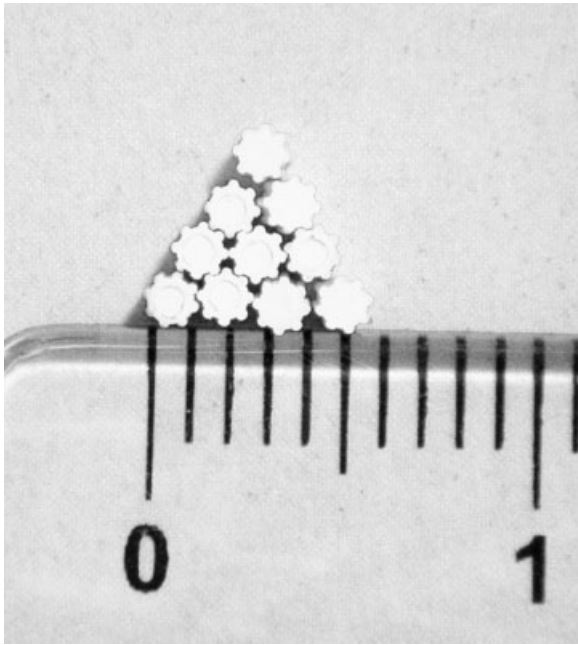


Figure 4 Photograph of microgears with 1 wt % added nanofiller.

tion of the diameter of the microgears with 0, 1, 3, 5 wt % added nanoparticles, respectively, was 14, 7, 6, 5 μm , as shown in Figure 5. Higher accuracy was achieved when higher nanoparticle content was added into the PP polymer. This result shows that the reproducibility of the microgears with added nanofillers was outstanding. The shrinkage in PP composites induced those deviations. Pure PP polymer has the highest shrinkage of 0.9%, and PP with 5 wt % added

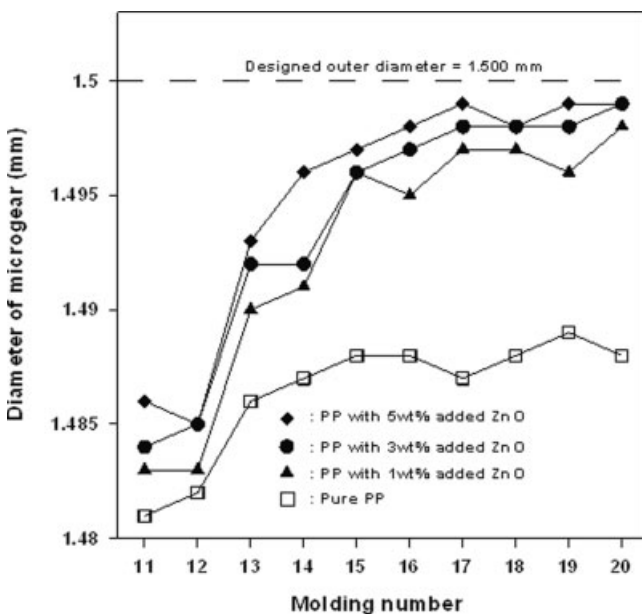


Figure 5 Reproducibility of the microgears through microinjection molding.

nanoparticles has the lowest shrinkage of 0.3%. The shrinkage was reduced when the weight content of the filler was increased.⁸ In this case, the dimensional deviation of PP polymer with 0, 1, 3, and 5 wt % added nanoparticles, respectively, could be reduced if the mold cavity was enlarged beforehand by 0.9%, 0.5%, 0.4%, and 0.3%, to compensate for the shrinkage effects of the polymer.

The measured samples were chosen from the eleventh to the twentieth pieces because the previous pieces were low in quality. Figure 5 also showed that the deviation of microgears after the 15th was stable for every kind of PP composite. Faulty parts were often produced at the beginning because of unstable mold and processing temperatures. That is, high quality parts could only be fabricated when the mold and processing temperatures were stable. The result revealed that the microparts with added nanoparticles can successfully be replicated with microinjection molding.

Wear behavior of parts with nanoceramic filler

The mass loss of polymer with different contents of nanoceramic powder is shown in Figure 6. The mass loss increased significantly when the specimens were contact-worn for up to 3 km. However, the mass loss steadily increased when the specimens were rotated more than 3 km. Polymer with 1 wt % added nanoparticles exhibited the lowest wear result, while a part with 15 wt % added nanoparticles exhibited the highest wear result. In addition, the mass loss of the composites with 0.5 wt %, 1 wt %, and 3 wt % added nano-

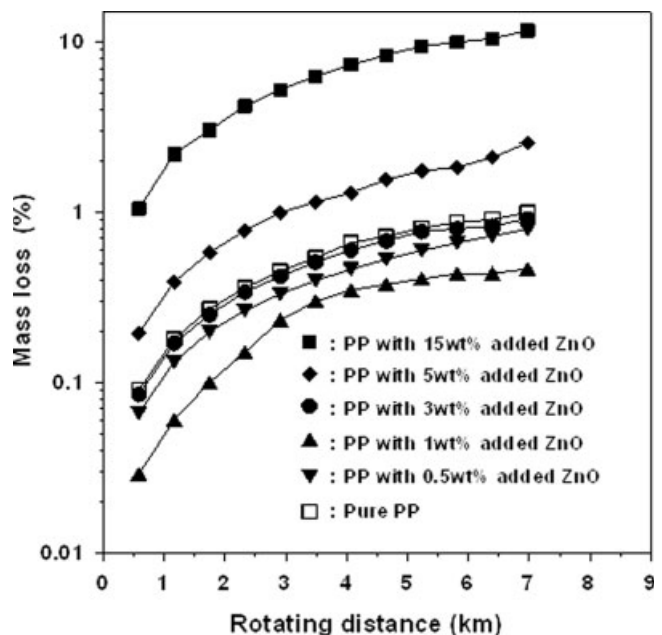


Figure 6 Mass loss of wear tests for PP composites with various contents of ZnO nanoparticles.

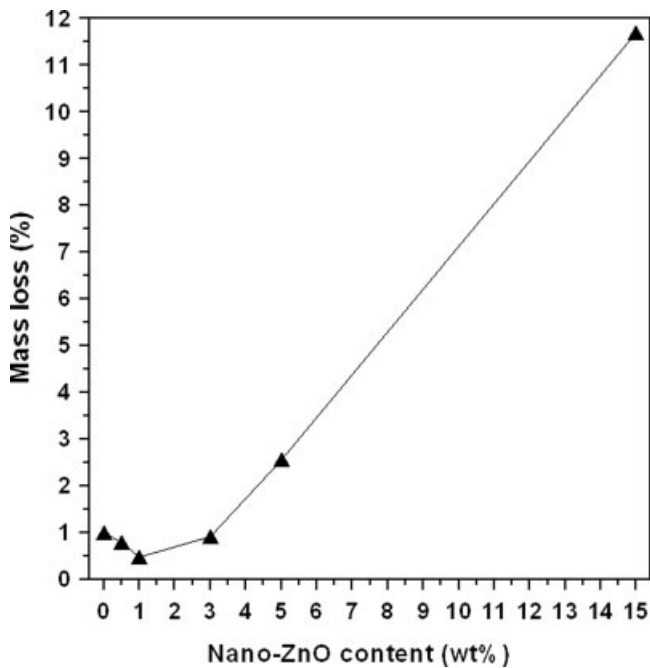


Figure 7 Mass loss of the composite tested after 6.97 km wearing plotted against the content of ZnO nanoparticles.

particle showed 20.2%, 53.1%, and 0.1%, respectively, lower than that of a pure PP. The composite with 1 wt % added nanoparticles exhibited an optimum wear resistance.

The wear result of the composites tested after rotating 6.97 km is shown in Figure 7. The wear dramatically increased as the nanofiller content exceeded 3 wt %. The results contradicted the intuition that a composite with more abrasive powder resisted contact-wearing. To find the reasons, SEM images of the composites with added nanoparticle were shown in Figure 8. In the case of the composite with 1 wt % added nanoparticles, the particles were slightly agglomerated, as shown in Figure 8(a). Several nanoparticles agglomerated to form a particle cluster in a size of 60 nm. However, most nanoparticles were uniformly distributed in the polymer compound.

The wear resistance was effectively improved when 1 wt % nanoparticle was added in PP. During wearing, the polymer was removed, leaving only the ceramic powders, which were much harder than the neighboring polymeric substrate and resisted abrasive wear. After the particles were removed, the neighboring polymeric matrix continued to wear. Thus, the composite, although it contained only 1 wt % nanoparticle, could significantly increase the resistance.

However, the PP with 5 wt % added nanoparticle revealed apparent agglomeration state, as shown in Figure 8(b). The resistance was significantly weakened because the nanoparticles were not uniformly distributed in the matrix. The ZnO nanoparticles could not be fully dispersed because of the agglomeration, as

concluded in the *Results and Discussions* section. The other reason was due to the kneading machine, which was not effective in dispersing nanoparticles in the polymer when more nanoparticles were added. The composite with 15 wt % added nanoparticle revealed

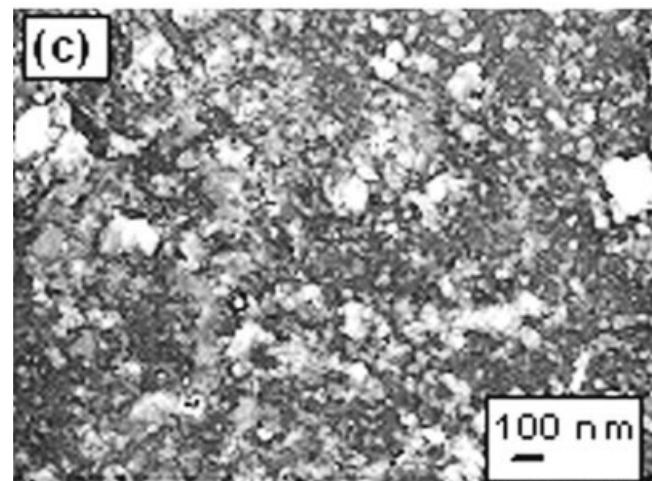
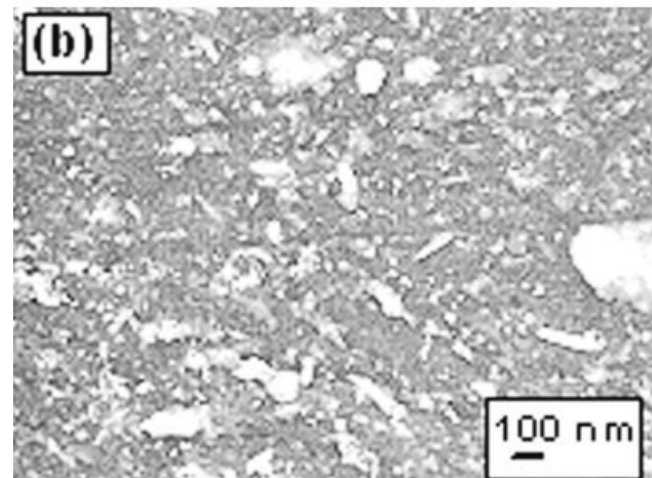
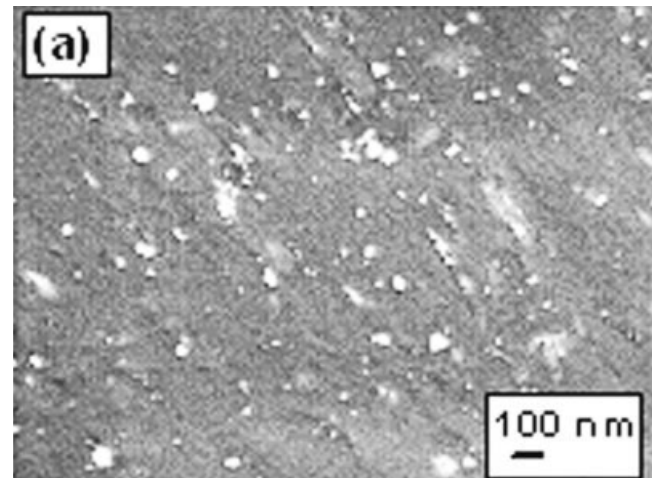


Figure 8 SEM image of polished surface of PP polymer with added ZnO nanoparticles, (a) 1 wt %, (b) 5 wt %, and (c) 15 wt %.

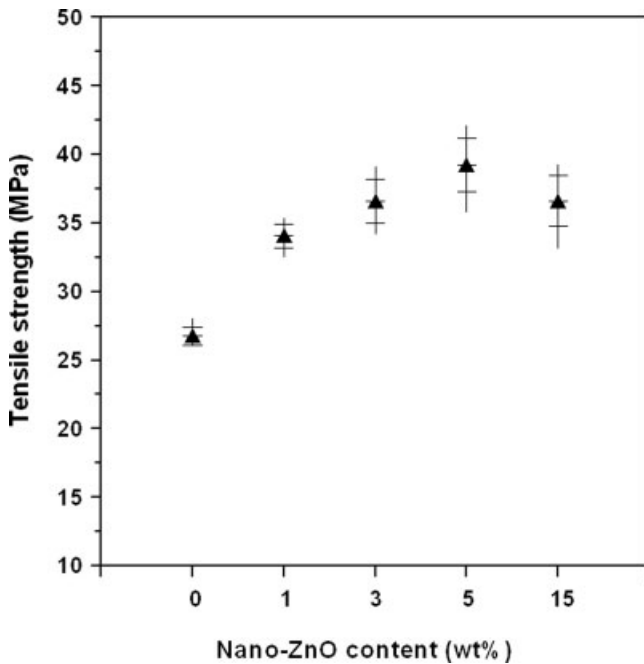


Figure 9 Tensile strength of the molded composite samples as a function of the content of added ZnO nanoparticles.

serious agglomeration, as shown in Figure 8(c), resulting in greater mass loss. The micrograph showed that the nanoparticles could not be firmly embedded in PP substrate. The nanoparticles lost the function of reinforcement because of a lack of coupling force by the substrate. The results indicated that uniform distribution of nanofillers and firm combination with the polymeric matrix was very important for the production of reinforced composites.

Crystallization temperature and mechanical properties of nanocomposites

To understand the relationship between the crystallization temperature and mechanical properties of nanocomposites, the crystallization temperatures of PP with different added nanoparticles were measured by differential scanning calorimetry (DSC, TOLEDO, Sweden). The crystallization temperatures of PP with 0, 1, 3, 5, and 15 wt % added nanoparticles, respectively, were 110.6, 111.8, 113.2, 114.1, and 114.5°C. The crystallization temperatures of PP composites were increased with increasing nanoparticle content. Tang et al.¹⁹ has also observed that after the incorporation of 2 wt % of ZnO nanoparticles, the crystallization temperature of PP was increased from 111 to 114°C. Zhao and Li²⁰ have also showed that the crystallization temperature of PP composites increased with increasing the nanoparticle content. In addition, this research also showed that polymer composites with higher crystallization temperatures have better mechanical properties.

Theoretically, polymer composites with higher crystallization temperatures have better mechanical properties. This is expected owing to the stiffness improvement effect of inorganic ceramic particles. To confirm this important result, the tensile strength of PP composites was measured, as shown in Figure 9. The tensile strength increased linearly when the nanoparticle content was increased to 5 wt % in the composites. In addition, the flexural strength and modulus of PP composites were measured, as shown in Figure 10(a,b). Both properties increased line-

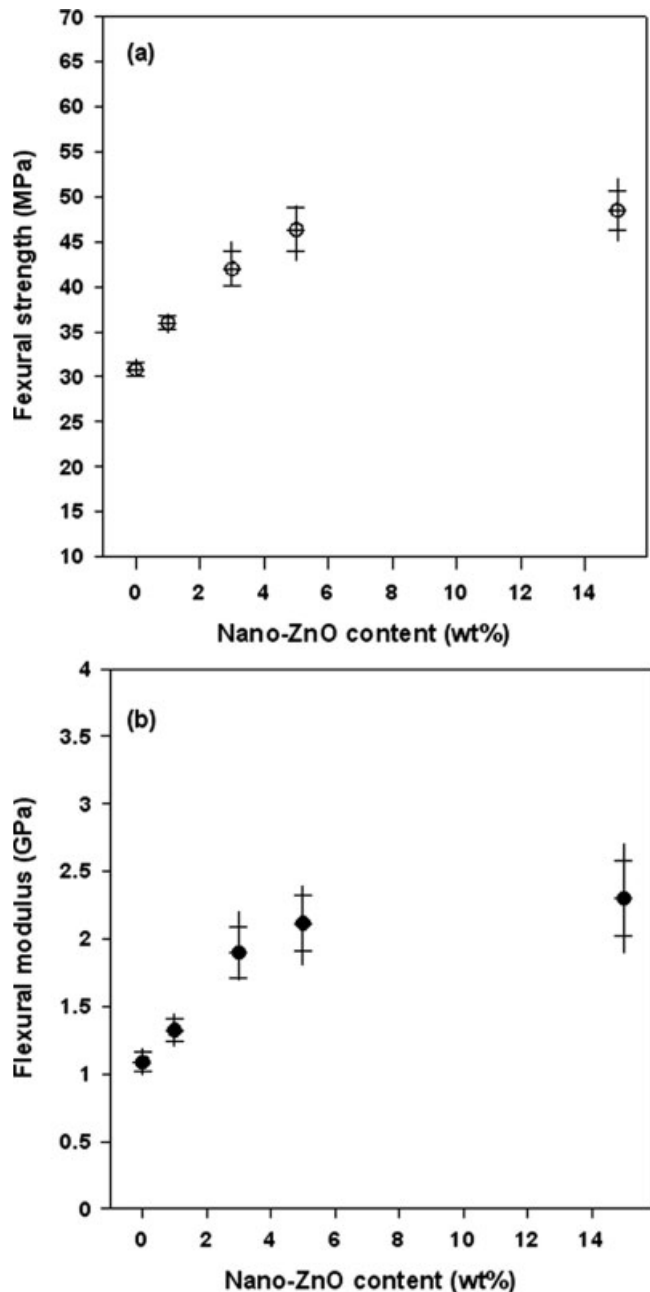


Figure 10 Flexural properties of the molded composite samples as a function of the content of added ZnO nanoparticles. (a) Flexural strength and (b) flexural modulus.

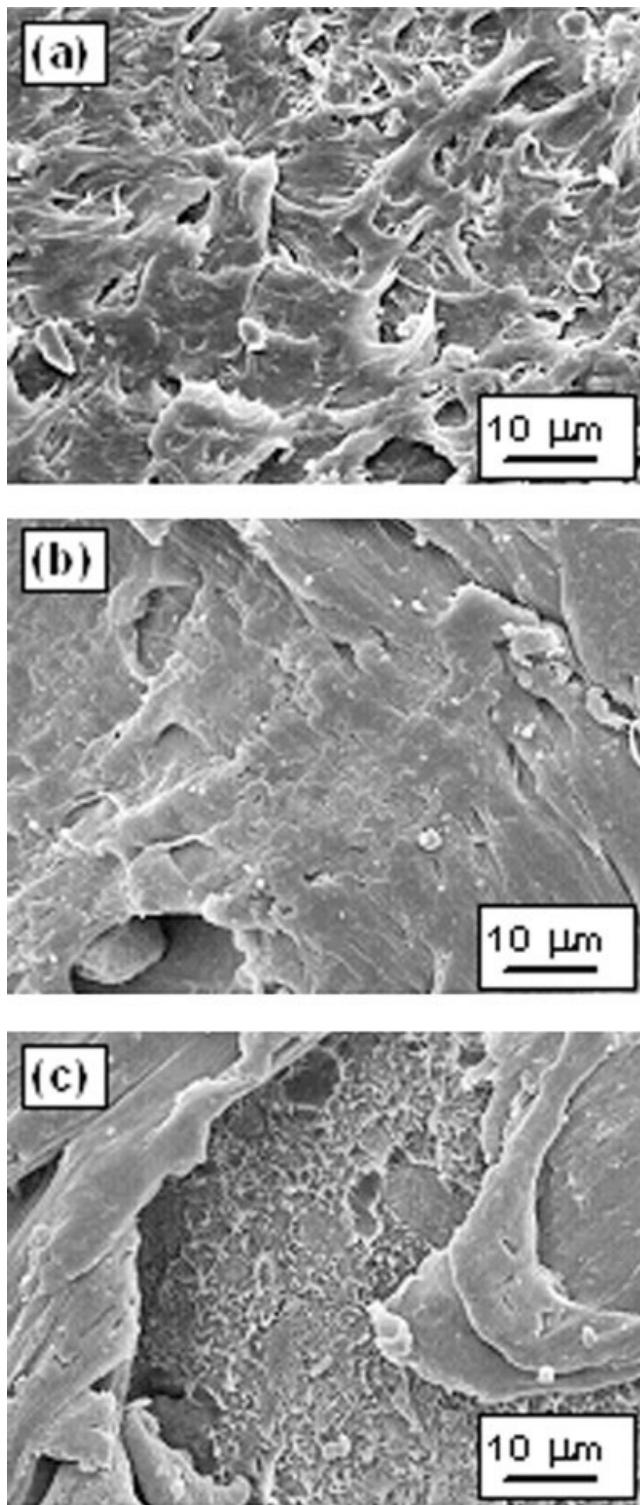


Figure 11 SEM images of the cross-sectional fracture surface of PP with added nanoparticles in (a) 1 wt %, (b) 5 wt %, and (c) 15 wt %.

arly when the nanoparticle content was increased to 5 wt % in the composites. The results showed that the mechanical properties of the PP were effectively improved by the ZnO nanofillers. The results also showed that the mechanical properties increased with

increasing the crystallization temperature when the nanoparticle content was increased to 5 wt % in the composites.

Compared to PP with 5 wt % added nanoparticles, both flexural strength and modulus were slightly increased, but tensile strength was decreased when 15 wt % nanoparticle content was added into PP polymer. The crystallization temperature of PP with 15 wt % added particles was only higher 0.4°C to that of PP with 5 wt % added particles. The possible reason is the serious agglomeration occurring in PP with 15 wt % added nanoparticles. Thus, uniform distribution of nanoparticles in matrix is the best way to prevent such a decrease in strength.

SEM images of the fractured surface of the tensile specimens are shown in Figure 11. The nanoparticles could resist the extension of cracks when the specimens were subjected to applied force. In addition, the nanoparticles could absorb energy to resist mechanical forces. Smaller cracks were easily formed in the worn surfaces of the specimens of the composite with 1 wt % added nanofiller, as shown in Figure 11(a). The small amount of the filler could not stop the crack extension when the specimens were pulled. However, the polymer with added 5 wt % content could stop the crack extension, resulting in larger tensile strength, as shown in Figure 11(b). Serious cracks on the worn surface of the specimen for PP with 15 wt % added nanoparticles are shown in Figure 11(c). The cracks continually extended among the nanoparticle clusters because the nanoparticles were in agglomeration when more than 5% nanoparticles were added into the polymer.

CONCLUSIONS

A homogeneous feedstock with added nanofillers and dispersant was produced under the optimal kneading process. Microparts made with feedstock could be successfully manufactured through microinjection molding. The standard deviation of the diameter of microparts was decreased with an increase in the nanofiller content in PP polymer. The results showed that the reproducibility of the microinjection molding using the composites with added nanofiller was outstanding. In addition, high quality parts could only be fabricated when the mold and processing temperatures were stable.

Only a small amount (1 wt %) of the nanofiller needed to be added to PP to increase wear resistance. Larger amounts (>5 wt %) of the nanofillers in the polymeric matrix resulted in less resistance to contact wearing than pure polymer. The nanoparticles in 1 wt % were effectively dispersed in the matrix, but ≥ 5 wt % of nanoparticles were agglomerated in the substrate and resulting in a poor wear resistance.

The mechanical properties increased with increasing the crystallization temperature when the nanoparticle content was increased to 5 wt % in the composites. The mechanical strength of the PP polymer can be effectively improved by adding small amount of the nanofiller. However, the composite with ≥ 15 wt % nanoparticles showed weaker strength. Suitable quantity of the nanoparticles added in PP and uniform distribution of the nanoparticles are important factors for producing high quality parts.

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