Effects of Particle Type on Thermal and Mechanical Properties of Polyoxymethylene Nanocomposites

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ABSTRACT: The effects of particle size of titanium dioxide (TiO_2) on mechanical, thermal, and morphological properties of pure polyoxymethylene (POM) and POM/TiO_2 nanocomposites were investigated and compared with the results for nanoparticle ZnO in the same matrix, reported in a previous paper. POM/TiO_2 nanocomposites with varying concentration of TiO_2 were prepared by the melt mixing technique in a twin screw extruder, the same method that used for blending the homogeneous ZnO nanocomposites. The dispersion of TiO_2 particles in POM nanocomposites was studied by scanning electron microscopy (SEM). The agglomeration, as observed by the mechanical properties of TiO_2 particles in the polymer matrix, increased with increasing TiO_2 content, a result not found for ZnO even at lower particle sizes. Increasing the filler content of POM/TD32.4 and POM/TD130 (130 nm) nanocomposites resulted in a decrease in tensile strength. The Young modulus, stress at break and impact strength of TiO_2 nanocomposite did not improve with increasing filler contents, in opposition to the better agglomeration conditions of ZnO nanocomposite even at lower particle sizes. Because of agglomeration, the POM/TD32.4 nanocomposites had lower mechanical properties and lower degradation temperature than the POM/TD130 ones. The sizes of nanoparticles determined the agglomeration, but however, the agglomeration also depended on the type of nanoparticles, even when using the same matrix (POM) and the same mixing method. TiO_2 nanoparticles were more difficult to mix and were more agglomerated in the POM matrix as compared to ZnO nanoparticles, regardless of the size of the nanoparticles. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 123: 3217–3224, 2012

Key words: agglomeration; polymer nanocomposites; polyoxymethylene; titanium dioxide

INTRODUCTION

Polymer nanocomposites have attracted considerable interest in the past decade.[1–5] Polymer nanocomposite is a polymer matrix with a reinforcing phase consisting of particles with one dimension in the nanosize regime.[6] Many researchers have reported that the incorporation of very small amounts of inorganic particles into a polymer matrix can significantly improve their thermal and mechanical properties, well above those of traditional filled polymers.[7–10] The properties of particulate filled polymer composites depended on the particle size, shape, loading, the dispersion of the nanoparticles in the polymer matrix, and good adhesion at the interface surfaces.[11–14] Among the various mineral fillers, calcium carbonate ($CaCO_3$),[15–20] zinc oxide (ZnO),[21–24] and titanium dioxide (TiO_2)[25–29] have been among the most utilized nanomaterials. $CaCO_3$ has been used because of its low cost, and TiO_2 has been mainly used as a white pigment, due to its brightness. In addition, TiO_2 can act as a flame retardant or antioxidant that may help improve the thermal stability of the final products.[29] POM is one of the major engineering thermoplastics because of its high strength, stiffness, and excellent chemical resistance. However, its poor impact resistance limits its range of applications.[30]

Ma et al.[23] investigated the effect of nanoscale ZnO on the electrical and physical characteristics of polystyrene (PS) nanocomposites. It was reported that the addition of ZnO nanopowder increased the flexural modulus and reduced the flexural strength. The glass-transition and thermal degradation temperatures of the ZnO/PS nanocomposites increased with ZnO content. Chae et al.[31] investigated the effect of ZnO nanoparticles on the physical properties of PS and PS/ZnO nanocomposites prepared by solution mixing. They found that the thermal stability of PS was enhanced with increasing ZnO content.

Wacharawichanant et al.[24] investigated the effect of particle size of zinc oxide (ZnO) on the mechanical, thermal, and morphological properties of pure polyoxymethylene (POM) and POM/ZnO nanocomposites with varying concentration of ZnO, by a melt mixing technique in a twin screw extruder. The results showed that Young's modulus and stress at break of POM/ZnO71 (71 nm) and POM/ZnO250 (250 nm) nanocomposites increased with increasing filler contents. The method used for blending ZnO was the same as for blending TiO_2, as described in this manuscript. The degradation temperature of POM/ZnO71 nanocomposites was higher than that of POM/ZnO250 nanocomposites. After blending, the ZnO nanocomposites were quite homogeneous and showed good dispersion characteristics.

It's well known that the size of nanoparticle affects the agglomeration characteristics of the nanocomposite. A recent article by Bravet[32] showed that the surface treatment of nanoparticles also affected the mixing properties in polypropylene matrix and the properties of the nanocomposite, which depended on the agglomeration degree. No information has been published reporting the influence of the type and characteristic of the nanoparticles on the mixing properties in the same matrix, when using the same mixing methodology.

In this work, we report the influence of particle sizes of TiO_2 on the morphology, mechanical, and thermal properties of POM/TiO_2 nanocomposites compared with ZnO nanopaticles in the same POM matrix.[24] POM/TiO_2 nanocomposites with varying concentration of TiO_2 were prepared by a melt mixing technique in a twin screw extruder, using the same methods used for blending the ZnO.[24]

EXPERIMENTAL

Materials

POM was supplied by Polyplastics, under the trade name of "DURACON M90-44." The melting temperature of the POM was around 165°C. Melt flow rate of POM equal to 9.2 g/10 min at 190°C, and specific gravity of 1.41 g/cm^3. TiO_2 in the form of a white powder with average particle sizes of 32.4 nm (TD32.4) and 130 nm (TD130) was purchased from Aldrich and Ajax Finechem, respectively.

Sample preparation

POM pellets and TiO_2 particles were dried in an oven at 100°C for 3 h before melt extrusion. The POM/TiO_2 nanocomposites were melt-compounded in the desired compositions in a twin screw extruder (Thermo Haake Polylab System, model PTW16/25D, Germany; HAAKE Rheocord RC300p and Rheomex PTW16/25D, Germany) at temperatures in a range of 170–200°C and a screw speed of 50 rpm (the same method that used for blending homogeneous ZnO[24]). Screw barrel temperatures were 170, 180, 180, 190, 200°C in each zone. After compounding, the nanocomposites were compression-molded into standard dumb-bell tensile bars and rectangular bars at temperature 190°C and pressure 5000 psi for 20 min.

Sample characterization

Tensile tests were conducted according to ASTM D 638 (ISO 527) using a universal tensile testing machine LR 50k from Lloyd instruments. The tensile tests were performed at a crosshead speed of 50.8 mm/min. Charpy impact strength tests were performed according to ASTM D 256 at room temperature. Each value reported, represented the average of five samples.

Differential scanning calorimetry (DSC) characterization (model DSC, Pyris I, Perkin–Elmer, USA) was performed to investigate the crystallization and the melting behaviors of the nanocomposites. The heating (and cooling) rate used was 10°C/min in a nitrogen atmosphere for both heating and cooling scans. The crystallinity for unfilled POM and the POM matrix of the POM/TiO_2 nanocomposites was calculated according to the DSC data from the heating scan. The temperatures of melting (T_m) of POM for the different nanocomposites were measured by DSC and the enthalpy of melting for 100% crystalline POM is 326.3 J/g.[33]

The thermal stability of POM/TiO_2 nanocomposites was measured by thermogravimetric analysis (TGA) (Model Diamond Thermogravimetric/Differential Thermal Analyzer, TG/DTA, Perkin–Elmer, USA) The sample weights were 2–5 mg; the temperature was in the range of 50–600°C at a heating rate of 10°C/min with nitrogen purge flow rate of 50 mL/min.

The morphology of the impact fracture surfaces of the POM/TiO_2 nanocomposites and the dispersion quality of the TiO_2 particles was determined by scanning electron microscopy (SEM) (Model Maxim 2000S, CamScan Analytical, England). All specimens were coated with gold before SEM study.

RESULTS AND DISCUSSION

Effect of particle type on mechanical properties

The tensile strength and stress at break of the nanocomposites of POM/TD130 and POM/TD32.4 as a function of nanocomposite compositions are represented in Figures 1–4. It is seen that in the range of 2 to 4% addition of nanoparticles of TiO_2, the
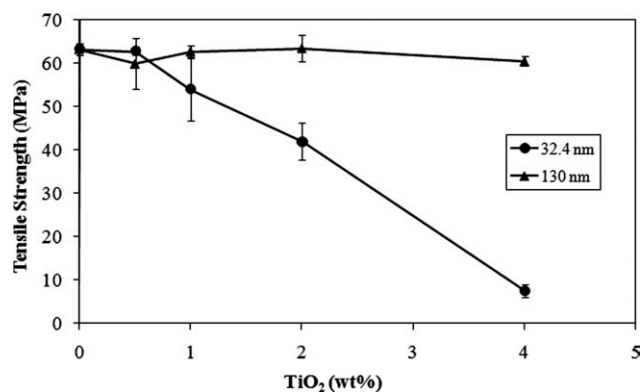
Figure 1 Tensile strength of pure POM and POM/TiO$_2$ nanocomposites at various particle sizes of TiO$_2$.

TD32.4 samples have inferior mechanical properties than those of TD130. The method for blending TiO$_2$ in this research was as that used for blending ZnO particles sized 71 and 250 nm.[24] For addition of TiO$_2$ particles, the similar trend of mechanical properties for the TD32.4 and TD130 in the range below 1% addition was observed as that of ZnO in the whole concentration range (1–8% addition) in the same matrix.[24] A possible explanation for this result is the fact that the methods used for blending TD32.4 and TD130 above 2% resulted in a severe agglomeration, a phenomenon that did not take place when using ZnO nanoparticles. The mixing method used was unable to overcome the interfacial bonding between TiO$_2$ particles, as it does when using it with nanoparticles ZnO size 71 or 250 nm[24] in the same matrix at the high composition range.

Figure 1 illustrates the variations of the tensile strength of POM/TiO$_2$ nanocomposites at various particle sizes of TiO$_2$. The tensile strength of TD130 did not significantly change with composition as in the case of ZnO size 71 and 250 nm[24]; TiO$_2$ did not significantly improve the tensile strength of POM specimens (which where prepared by compression molding). A possible explanation is the slightly
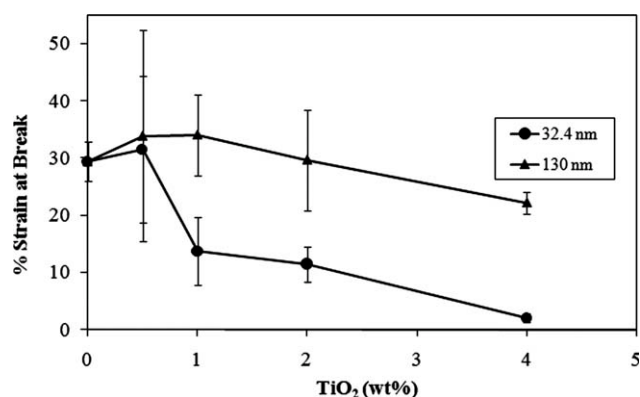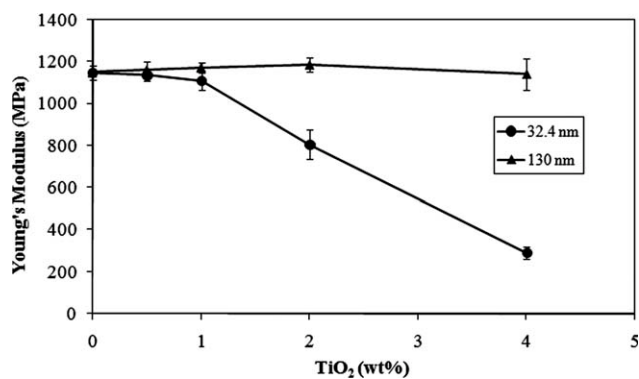

Figure 3 Young's modulus of pure POM and POM/TiO$_2$ nanocomposites at various particle sizes of TiO$_2$.

decrease in percent crystallinity taking place with increased content of TiO$_2$, as shown in the following section. However, the abrupt decrease in tensile strength of TD32.4 may be a result of the specific agglomeration of TiO$_2$ size 32.4 nm, which cannot be diminished by the method of blending, contrary to the case of TiO$_2$ size 130 nm or ZnO.[24] The percent strain at break, illustrated in Figure 2, has a similar trend as the tensile strength. However, the percent stain at break of TD130 in the low concentration range was slightly better than nascent POM. At a concentration higher than 1% of TD32.4, the percent stain at break dropped down significantly. This confirmed the agglomeration effects present in TD32.4, and absent in all ZnO nanocomposites or TD130, regardless of the same sample preparation method.

The Young's modulus and stress at break of TD32.4 and TD130 are shown in Figures 3 and 4, respectively. The Young's modulus and stress at break of POM/TD130 nanocomposites did not change significantly after adding TD130, opposite to the Young's modulus from the less aggomerated ZnO nanocomposites (both prepared from ZnO size 71 and 250 nm), which showed a substantial increase. The Young's modulus and stress at break
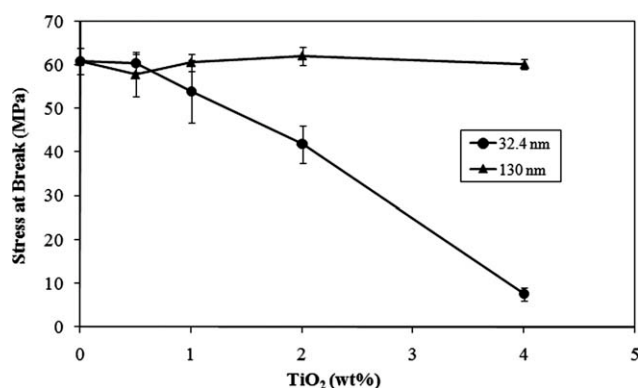

Figure 2 Percent strain at break of pure POM and POM/TiO$_2$ nanocomposites at various particle sizes of TiO$_2$.

Figure 4 Stress at break of pure POM and POM/TiO$_2$ nanocomposites at various particle sizes of TiO$_2$.
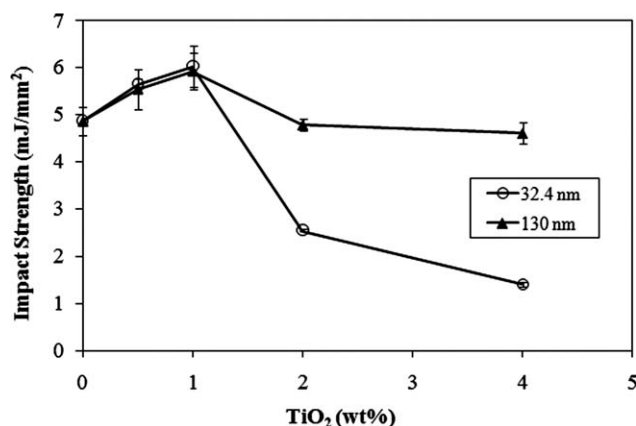
Figure 5 Impact strength of pure POM and POM/TiO$_2$ nanocomposites at various particle sizes of TiO$_2$.

of POM/TD130 nanocomposites were higher than those of POM/TD32.4 nanocomposites in the range of 2–4% and equal in the range below 1%. No significant improvement in the Young's modulus and stress at break was observed in nanocomposites containing TiO$_2$ due to the weak interfacial bonding among filler and matrix when increasing TiO$_2$ content,[34] contrary to the case of ZnO nanocomposites. The abrupt changes in Young's modulus and stress at break of TD32.4 at 2–4% composition are probably caused the specific agglomeration of TiO$_2$ particles in POM matrix. Although the TD130 nanocomposite showed less agglomeration, the TiO$_2$ nanocomposite showed no improvement in mechanical properties, as found with the ZnO nanocomposite.

The Charpy impact strengths of the nanocomposites of POM/TiO$_2$ are shown in Figure 5. The impact strength increased slightly with an increase in the TiO$_2$ content and reached a maximum when the TiO$_2$ concentration was 1%, although the agglomerates of TiO$_2$ in the matrix can become sites of stress concentration and lead to a decrease in the impact strength. Thus, the mechanical properties of the nanocomposites were strongly dependent on the dispersion morphology of the TiO$_2$ nanoparticles.[35] The TD32.4 showed better impact strength in the range below 1% than the nascent POM, when the mixing method was able to disperse the small amount of TiO$_2$. However, at higher concentration of TiO$_2$ (2–4%), the impact strength of TD32.4 decreased abruptly when compared with that of the TD130, because of a more significant agglomeration of TiO$_2$ 32.4 nm at higher concentrations.

The mechanical properties are very sensitive to agglomeration of nanoparticles. The same mixing method, that can produce the homogenous composite of the ZnO, cannot produce homogenous nanocomposite in the case of TiO$_2$. The mechanical properties of TD130 still showed some agglomeration (the Young's modulus and the stress at break),

which were not found in the ZnO even for smaller particle sizes (71 nm, ZnO71). This result clearly shows the differences in properties and agglomeration caused by the particle type. However, the smaller particle sizes in both TiO$_2$ and ZnO seemed to produce a similar trend, and were more difficult to produce homogeneous mixing. Therefore, more agglomerations were observed in SEM pictures.

Effect of particle type on the percent crystallinity

The percent of crystallinity calculated from the heat of crystallization melting divided by heat of crystalline melting of 100% crystal of POM, reported in the experiment section. The percent crystallinity of POM/TiO$_2$ nanocomposites is shown in Figure 6. It can be seen that addition of TD32.4 and TD130 resulted in a small decrease of the percent crystallinity of POM, regardless of the agglomeration of the nanoparticle. Unfortunately the percent crystallinity of the ZnO nanocomposite was not reported.[24] However, it showed that the percent crystallinity was not very sensitive with the degree of agglomeration.

Effect of particle type on thermal properties

Figures 7 and 8 show the melting temperatures of pure POM, POM/TD32.4, and POM/TD130 nanocomposites at various filler contents. The results show that the melting temperatures were not significantly changed when TD32.4 or TD130 was incorporated in the polymer matrix, the same as in the case of ZnO in the same matrix.[24]

The effects of TD32.4 and TD130 on the degradation temperature of all nanocomposites are shown in Figure 9. The degradation temperature was measured by TGA and was calculated at 10% weight loss of the nanocomposites. It can be seen that the degradation temperatures of POM/TiO$_2$ nanocomposites increased with increasing filler content and were
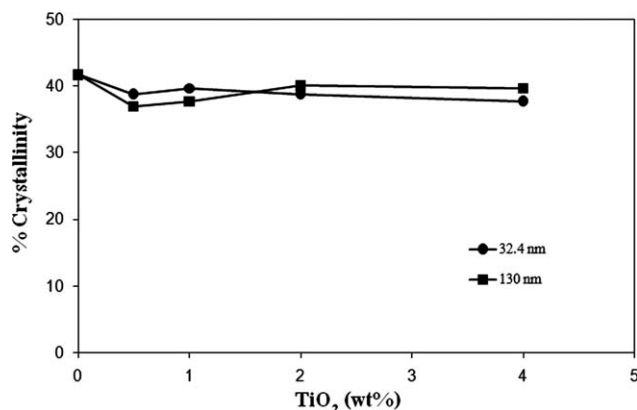

Figure 6 % Crystallinity of pure POM and POM/TiO$_2$ nanocomposites at various particle sizes of TiO$_2$.
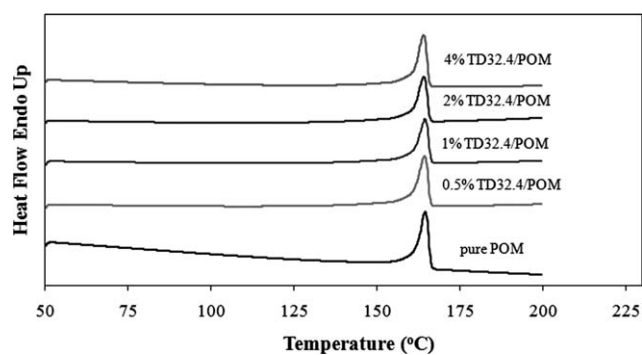
Figure 7 Melting temperatures of pure POM and POM/TD32.4 nanocomposites.

higher than the degradation temperature of pure POM. Thus, pure POM showed lower thermal stability than POM/TiO$_2$ nanocomposites, similar to the case of ZnO nanocomposites. The degradation temperatures of POM/TD32.4 and POM/TD130 were very similar, regardless of the TiO$_2$ particle size. The thermal stability of the nanocomposite represented by the decomposition temperature, that depended on amount of TiO2 cooperated regardless to the agglomeration and size of nanoparticles.

Effect of particle type on morphology

The morphology of fracture surfaces of impact specimens of the nanocomposites was examined by SEM. Figure 10(a) shows the micrographs of the impact fracture surface of pure POM while Figure 10(b–e) show the micrographs of the impact fracture surfaces of POM nanocomposites, filled with 0.5, 1, 2, and 4 wt % of TD32.4, respectively. The results indicate that the dispersion of the TD32.4 on the polymer surface was not uniform especially in the range above 2%. This nonuniform dispersion led to local agglomeration of TD32.4 within the polymer. Fracture surfaces and the surface roughness of POM/TD32.4 nanocomposites and pure POM were similar.
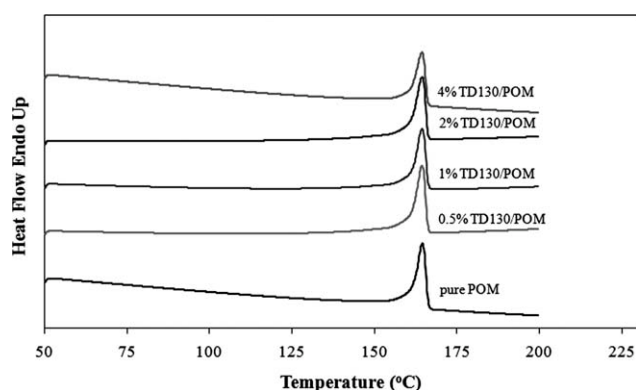
Moreover, the agglomeration of TD32.4 particles in the polymer matrix increased with increasing TD32.4 content especially in the range above 2% addition, and influenced the mechanical properties of POM nanocomposites.

The impact-fractured surfaces of pure POM and the POM/TD130 nanocomposites at various filler contents as captured by SEM are shown in Figure 11. The SEM results showed the good dispersion of the TD130 particles, only few agglomerations were seen to be present in the pictures, as shown in Figure 11(b–e), and indicates the good adhesion between nanoparticles and matrix of POM/TD130 nanocomposites. These observations supported the results of the tensile tests because the POM/TD130 nanocomposites displayed better mechanical properties than the POM/TD32.4 in the concentration range of 2–4%. However, some agglomeration can still be observed in the TD130 nanocomposites.

A comparison of the micrographs of the impact-fractured surfaces of POM/TD32.4 and POM/TD130 nanocomposites at various filler contents, showed that the POM/TD32.4 nanocomposites had more agglomeration than POM/TD130 nanocomposites in the range above 2%. However, in the range below 1%, there was less difference in agglomeration between the two systems.

The SEM pictures of ZnO and TiO$_2$ showed some small scale agglomeration, which affected other properties as described before. However, differences in the type of particles also influenced the properties of the nanocomposite, especially the agglomeration condition. The amount of agglomeration cannot be distinguished by thermal degradation properties, but can be easily distinguished by mechanical properties or SEM pictures. The sizes of nanoparticles strongly affected the agglomeration in both systems (TiO$_2$ and ZnO), as shown in the SEM pictures. However, different types of nanoparticles in the same matrix showed different SEM morphology, pointing to the
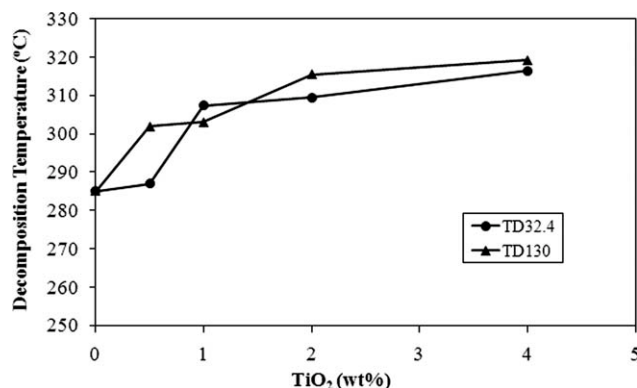

Figure 8 Melting temperatures of pure POM and POM/TD130 nanocomposites.

Figure 9 Decomposition temperatures of pure POM and POM/TiO$_2$ nanocomposites at various particle sizes of TiO$_2$.
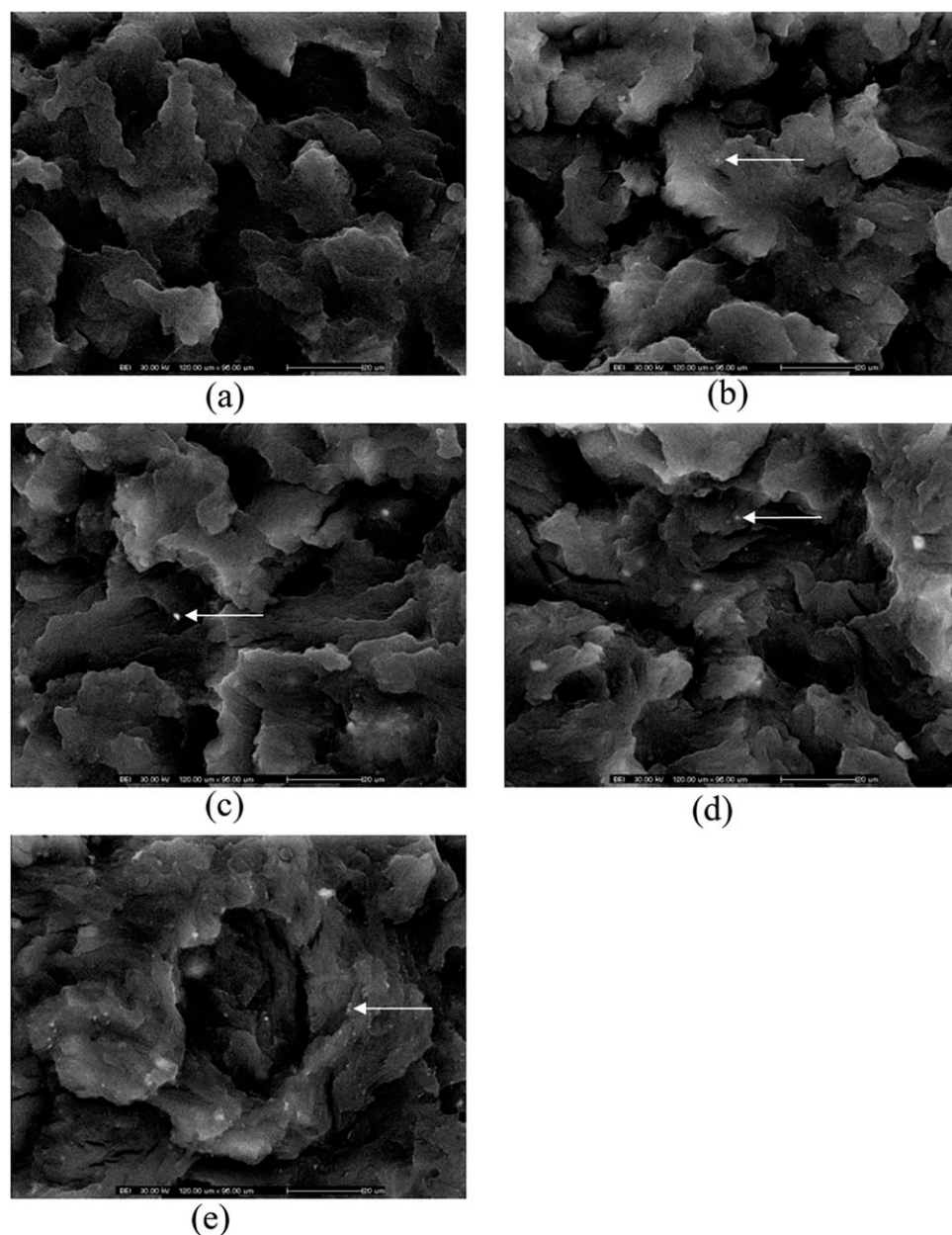
Figure 10 SEM micrographs (a) pure POM, (b) POM after adding 0.5 wt % of TD32.4, (c) POM after adding 1.0 wt % of TD32.4, (d) POM after adding/2.0 wt % of TD32.4, and (e) POM after adding 4.0 wt % of TD32.4.

importance of the type of the nanoparticles in determining the properties of nanocomposites.

CONCLUSIONS

POM/TiO$_2$ nanocomposites were prepared by melt compounding in a twin screw extruder, as same as ZnO nanocomposites.[24] The POM/TD32.4 and POM/TD130 nanocomposites showed similar mechanical properties in the composition range below 1% and the TD32.4 composite showed abruptly inferior mechanical properties than the TD130 one in the range above 2%. The impact strength of POM/TiO$_2$ nanocomposites showed a maximum in the range of 1% of TD32.4, which was higher than that of nascent POM. The degradation temperature of POM/TD32.4 and POM/TD130 nanocomposites increased with increasing filler contents. In addition, the degradation temperatures of POM/TD32.4 nanocomposites were slightly higher than that of POM/TD130 nanocomposites. The morphology of the fracture surfaces of impact specimens of the POM/TD32.4 nanocomposites showed more agglomeration than POM/TD130 nanocomposites, particularly in the range of 2–4% addition, which cannot be found in case of various sizes nanoparticle of ZnO in the same matrix prepared with the same mixing method. The
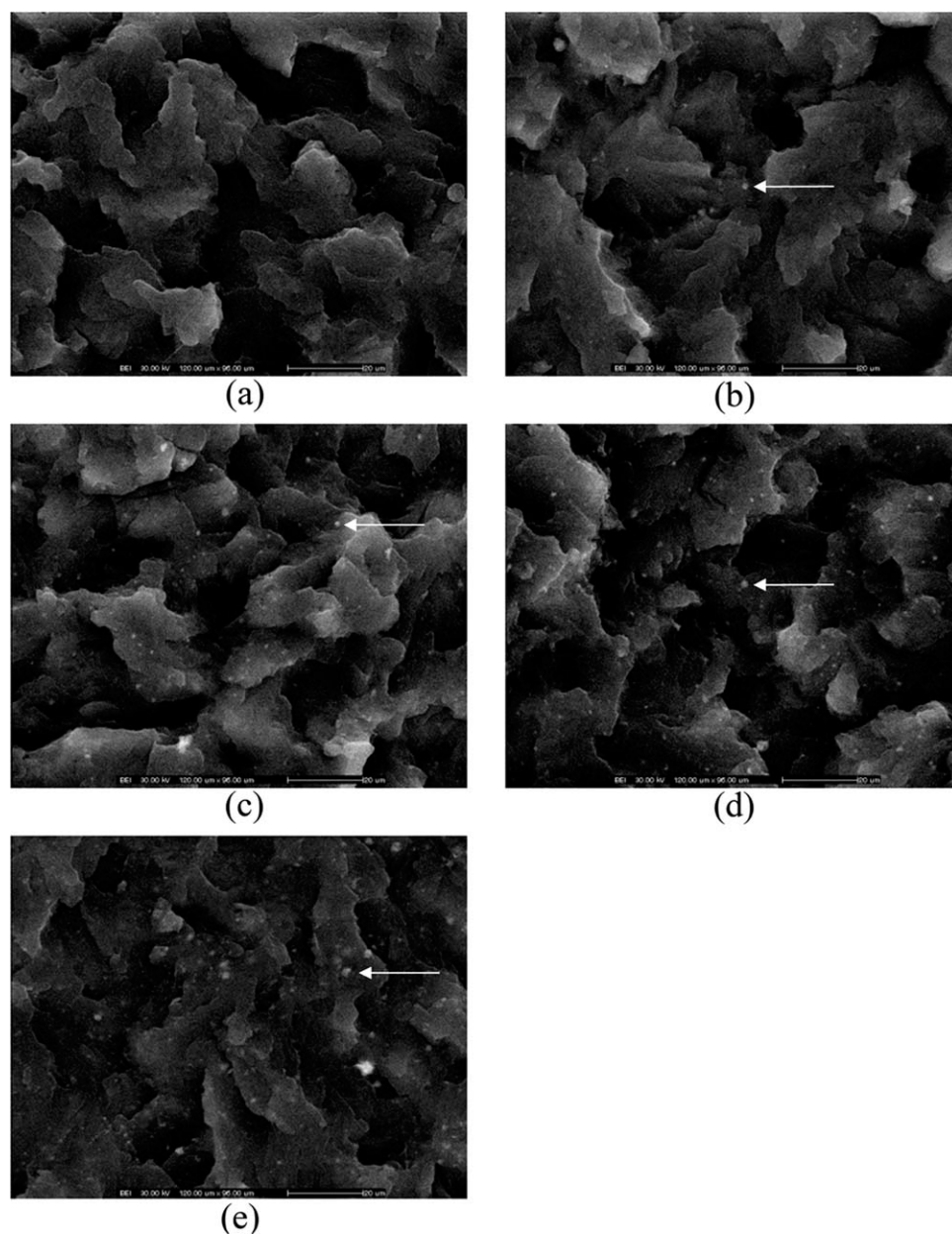
Figure 11 SEM micrographs (a) pure POM, (b) POM after adding 0.5 wt % of TD130, (c) POM after adding 1.0 wt % of TD130, (d) POM after adding 2.0 wt % of TD130, and (e) POM after adding 4.0 wt % of TD130.

nanoparticles of ZnO and TiO_2 in the nanoscale range of the same mixing method and matrix showed a different agglomeration level especially in the lower nanoscale range (32.4 nm).

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