FEG–ESEM Investigation of Micromechanical Deformation Processes in Ultrafine Monospherical SiO$_2$ Particle-Filled Polymer Composites

G.-M. KIM,[1] D.-H. LEE[2]

[1] Dutch Polymer Institute, Materials Technology, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

[2] Department of Polymer Science, Kyungpook National University, 702-701, Taegu, South Korea

ABSTRACT: Micromechanical deformation processes responsible for toughening mechanisms in ultrafine monospherical inorganic particle-filled polyethylene were investigated *in situ* by a field-emission gun-environmental scanning electron microscope (FEG–ESEM) with low-voltage techniques. In general, the ultimate properties of polymer composites are largely dependent on the degree of dispersion of filler particles into the matrix. Very often, the agglomeration is one of inevitable occurrences in polymer composites, mixed with ultrafine filler particles. In the present work, the effects of agglomerates, consisting of ultrafine monospherical filler particles, were reexamined in polymer composites on the toughening mechanism. The results show that the dominant micromechanical deformation processes are the multiple debonding processes inside agglomerates, in which the ratio of the matrix strand and the size of agglomerate plays a great role of matrix yielding. In the specimen, where the agglomerates are isolated in the matrix, deformation begins at the equatorial region of agglomerates and propagates through them. However, in the case of closely placed agglomerates, deformation occurs homogeneously within the whole area inside the agglomerates. In both cases, in conjunction with the multiple debonding processes, the major part of energy during the deformation dissipates through the shear-flow processes of the matrix material. In particular, the micromechanical deformation processes observed in this work confirm that the agglomerates do not always have negative effects on the mechanical properties—at least, in the shear deformable semicrystalline polymer matrices. The agglomerates may be effectively used for the improvement of toughness. Furthermore, the FEG–ESEM with low-voltage techniques offers an extremely promising and efficient alternative method to study the morphology as well as *in situ* micromechanical deformation processes in nonconducting polymer systems. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 82: 785–789, 2001

Key words: micromechanical deformation process; ultrafine particles; agglomerate

INTRODUCTION

Rigid inorganic filler particles have been widely used to improve the physical properties of poly-

mers for specific applications. In general, the addition of rigid inorganic filler particles into polymers leads to an increase in stiffness and thermal stability, but, unfortunately, it is accompanied by a reduction in the ultimate fracture strain.[1–4] One of the major requirements of particle-filled polymer composites is not simply to enhance the stiffness, but to achieve this without excessive sacrifices in other attractive properties, that is, the balance of properties has to be optimized.[5] Some of the most exciting developments in the

polymer composites are taking place in the research area of submicron-size inorganic filler particle-reinforced thermoplastics.[1] Many experimental and theoretical investigations have been carried out to identify the parameters that govern the mechanical behavior. The findings are as follows:[4–9] For a given filler content, the yield stress of the composites decreases with the filler size. For a given filler size, an increase in filler content leads to an increase of the composite modulus. Good adhesion is generally considered desirable because it can result in higher values of the modulus and strength. However, the influence of interfacial adhesion on the toughness is still in debate. In the present work, this effect is not taken into account.

Because the size of the interface can be increased by using smaller fillers (which possess the larger specific surface areas), in the polymer composites with ultrafine filler particles, the filler particles may intensively interact with each other, indicating an increased probability of aggregation. Aggregation results by interaction of the filler particles in the matrix, which usually leads to the formation of higher-order structures (agglomerates). Agglomerates can be relatively easily broken down under an external load.[10] In our previous work, it was shown that the toughening mechanisms involved in different heterogeneous blend systems are influenced decisively by the morphology of the given system. In particular, the micromechanical deformation processes in particle-filled thermoplastics are very similar to processes in rubber-modified polymers. Many studies indicate that polymer blends containing clustered rubber particles give much better toughness compared to those containing discrete dispersed particles. However, in the particle-filled polymer composites, the agglomerates are simply considered as defects and, consequently, undermine the impact strength; in the other words, the effects of agglomerates always show a negative impact strength.

Up to now, an understanding of how changing the structure of an agglomerate under a load may affect the subsequent deformation mechanism and its effect on the fracture toughness has been somewhat rudimentary. The object of this work was, therefore, to elucidate further the role of agglomerates on the micromechanical deformation processes responsible for improved toughness in polymer composites with ultrafine monospherical inorganic filler particles in the order of 250 nm. Special attention was paid in this study to the micromechanical deformation processes depending on the dispersion of filler particles using an environmental scanning electron microscopy with a field-emission gun (ESEM–FEG) with a low-voltage technique.

EXPERIMENTAL

Low-voltage (LV) ESEM is a promising new technique for polymer morphological characterization.[11,12] Operating at low voltage has particular advantages: (1) high resolution, (2) negligible beam damage of samples, and (3) absence of the need for coating with conducting films to eliminate sample charging under a beam. Moreover, an LV–ESEM equipped with a field-emission gun (FEG) source, which provides high brightness, small spot size, and low-energy spread in comparison to the conventional beam, can produce images of polymers at a substantially higher magnification with a better resolution than can a conventional SEM, comparable to those of TEM. From the advantages mentioned above, ESEM–FEG with a low-voltage technique offers the capability of being able to perform the *in situ* deformation experiments, which can provide complementary information on the deformation events.

Polyethylene (PE) was used as the matrix polymer in the experiments. The SiO_2 inorganic filler particles were monospherical in the order of 250 nm in diameter and had an extremely narrow size distribution. The composites were polymerized using a Ziegler–Natta catalyst in the presence of SiO_2 inorganic filler particles. Composites with two different weight percentages (7 and 18 wt %) of filler particles were studied.

The specimens for FEG–ESEM investigations were microtomed from the bulk at −80°C containing a thickness of about 1 μm using a Leica Ultra E cryoultramicrotome. These sections were stacked fast in between two adhesive metallic films and mounted in a home-made special tensile device. To characterize the micromechanical deformation processes, the specimens were uniaxially deformed at room temperature and investigated *in situ* by FEG–ESEM (using an accelerating voltage of 1 keV).

RESULTS AND DISCUSSION

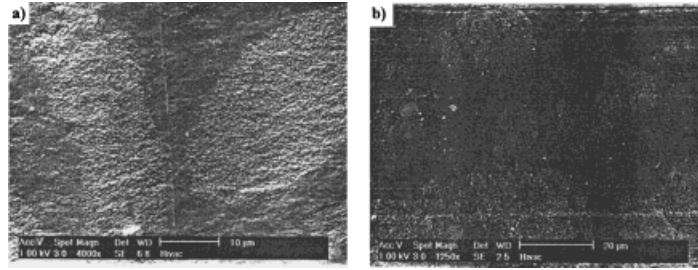Figure 1 shows typical morphologies from low-voltage FEG–ESEM studies as a function of the

Figure 1 SiO_2 agglomerates in PE composites: (a) 7 wt % SiO_2; (b) 18 wt % SiO_2.

SiO2 content. In both PE composites with 7 and 18 wt % SiO_2, the filler particles are not finely dispersed in the PE matrix but locally form agglomerates of the order of 10–50 μm in size. In the case of the PE composite with 7 wt % SiO_2, the agglomerates are separately dispersed in the matrix, whereas in the case of the PE composite with 18 wt %, they are closely dispersed. Although the diameter of the agglomerates is relatively of the same order in both cases, the ratio of the distance between the agglomerates and the diameter of the agglomerates in the PE composite with 7 wt % SiO_2 is comparably larger than that in the case of the PE composite with 18 wt %. In turn, this great difference in the ratio plays a decisive role during deformation under uniaxial tensile.

Figure 2 shows the deformation structures and the schematic micromechanical deformation processes of the PE composite with 7 wt % filler, in which the agglomerates are separately dispersed. The pictures show fibrils inside the agglomerates
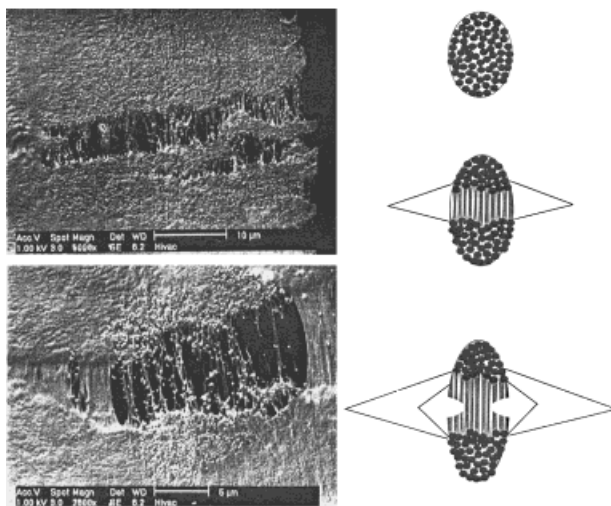

Figure 2   Deformation structures and schematic micromechanical deformation processes in PE composites with 7 wt % SiO_2.

at their equator regions as well as the strongly plastically deformed matrix material in the neighborhood of fibrillized agglomerates. Because of the relatively weak adhesion between the matrix and filler particles inside the agglomerates, the phase separation (debonding) at the interface between the matrix and the filler particles easily takes place, which leads to the forming of microvoids. Moreover, the interparticle distance in the agglomerate is too small, so that the matrix strands in between the filler particles are fibrillized during the stretching of the microvoids. Upon elongation of the specimen, the matrix material of the neighborhood agglomerates is strongly plastically stretched at their equator in the direction of the applied stress. With further increasing of the strain, the fibrils built up inside the agglomerates break down; in other words, all the agglomerates are torn at their equator. Surprising, the crack does not initiate in the matrix.

By common sense, at such a high level of strain, the crack should initiate in and propagate through the matrix, leading to catastrophic failure of the specimen. The reason for that could be the morphology of the filler particles used here. Each particle uniformly initiates microvoids at the polar region of the particle. Due to the rigidity of inorganic filler particles, the maximum stress concentration lies at the both sides of the particles perpendicular to the applied uniaxial tensile stress. As the strain of the specimen increases, the microvoid caused by debonding will be elongated by the several orders of magnitude in the length/width ratio. However, the SiO_2 filler particles are too small in dimension; such a small scale of elongation of the microvoids is insufficient to initiate crack in the matrix. Moreover, the strain of matrix material in the neighborhood of the agglomerates at their equator will be accumulated by uniform elongation of successive microvoids, so that the matrix material at the equatorial regions of the agglomerates can deform plas-

tically by shear yielding without initiating a crack.

It also should be emphasized here that although each particle inside the agglomerates consists of rigid inorganic filler particles such agglomerates act on the whole similarly to rubber-modified particles during the deformation processes, comparable with the salami particles in HIPS, which initiate multiple crazing.[13,14] For this reason, at the beginning of deformation, the stress concentration takes place at the equatorial region of the agglomerates, so that here the plastic deformation is initiated in the form of fibrillization. Thus, the crazelike deformation structure inside the deformed agglomerates is exhibited. With increasing strain in the direction of the applied stress, the fibrils break down in the equatorial region of the agglomerates (transparticular fracture), and then the crack initiates in the matrix material in these regions. The large extent of plastic deformation shown by the matrix polymer may lead to enhanced energy absorption and impact resistance. In the previous work, this kind of micromechanical deformation process was defined as a multiple debonding process.[15,16]

Typical deformation processes in the PE composite with 18 wt % SiO_2 performed in FEG–ESEM using an *in situ* tensile device are shown in Figure 3. The pictures show a strongly plastically stretched matrix between the agglomerates, in which the SiO_2 filler particles as well as totally torn agglomerates can also be seen in the plastically deformed matrix. The dominating micromechanical deformation process is also the multiple debonding process as in the PE composite with 7 wt % SiO_2, but the progress of this process is completely different. The multiple debonding process in this case progresses homogeneously within the whole area in agglomerates during the deformation, in contrast to the isolated agglomerates such as in the PE composite with 7 wt % SiO_2, in which multiple debonding occurs predominantly at the equatorial region inside the agglomerates. In this specimen, the agglomerates are dispersed in the matrix relatively near to each other. The dimension of the matrix strands between the agglomerates is up to about one-third of the diameter of the agglomerates.

Because of the narrow distances between the agglomerates in contrast to their sizes, the shear-flow process easily takes place in the matrix material between the agglomerates. This shear-flow process is combined with simultaneous stretching and tilting of the agglomerates in the direction of
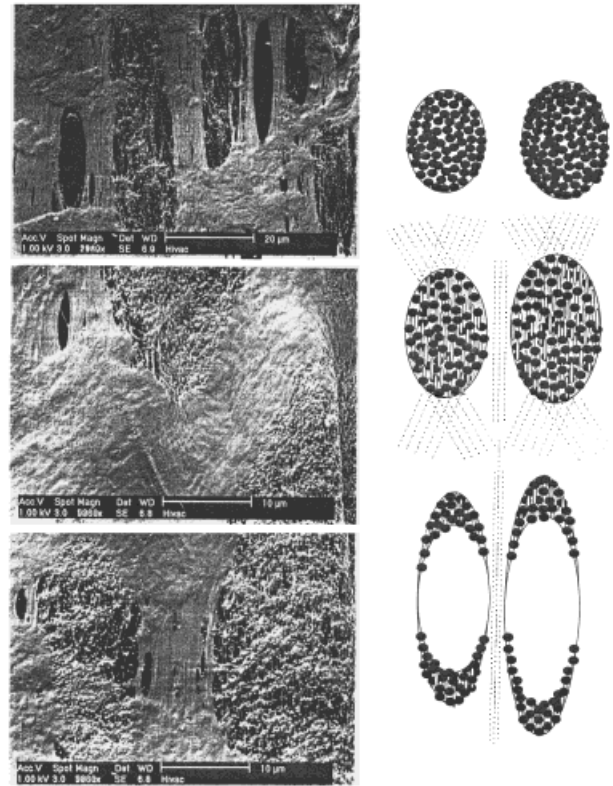

Figure 3 Deformation structures and schematic micromechanical deformation processes in PE composites with 18 wt % SiO_2.

the external stress, caused by intensive overlapping of stress fields around the agglomerates with the strain. It is also interesting to note that the shear bands do not appear in the equatorial region of the agglomerates, but only form at the polar regions of highly elongated agglomerates with about 45° in the tensile direction. The size of the shear-flow zone depends clearly upon the number of adjacent agglomerates. From this result, it may be concluded that the plastic deformation of the matrix material between the agglomerates begins prior to the microvoid formation inside the agglomerates. If the microvoid formation takes place prior to the shear yielding of the matrix, then the plastic deformation should be localized only at the equatorial region of the agglomerates. When the specimen will be further strained, the fibrils break down in relatively smaller agglomerates, and large holes appear in the deformation structures. Despite these appearances, most agglomerates will be highly elongated in the tensile direction. The fibrils caused by multiple debonding remain without breaking down in the agglomerates. As a consequence, the

transparticular fracture of the agglomerates does not appear in the deformation structures, and the shear yielding is significantly enhanced in the matrix. This kind of micromechanical deformation process will be defined in this work as a homogeneous multiple debonding process.

CONCLUSIONS

Micromechanical deformation processes in a polymer composite of PE with two different contents of SiO_2 ultrafine monospherical inorganic filler particles were investigated using tensile tests carried out *in situ* in the FEG–ESEM with a low-voltage technique. The morphologies of both polymer composites indicate evidence of the agglomerate formation of high-order structures. Deformation mechanisms are strongly affected by the dispersion of agglomerates in the matrix. Because the agglomerates are held together by a weak adhesive interaction, the nucleation of the microvoids, caused by multiple debonding processes, thus occurs at the initial stage of the loading. Although the dominant main toughening mechanism is the multiple debonding processes inside the agglomerates, which is independent of the content of the filler particles, the successive events of deformation are clearly accompanied by the content as well as by the dispersion of the filler particles. Based on the micromechanical deformation processes observed in our studies, the following conclusions can be drawn:

1. During deformation, the function of the agglomerates is very similar to large rubbery modifier particles with several inclusions surrounded by a rubbery shell.
2. In a polymer composite revealing isolated agglomerates, the yielding of the agglomerate occurs prior to that of the matrix; the multiple debonding process is strongly localized at the equatorial region of the agglomerates and propagates through the agglomerates perpendicular to the external stress (trans-agglomerate fracture).
3. In the polymer composite revealing closely interconnected agglomerates, the matrix yields prior to the agglomerates; the multiple debonding process progresses homogeneously on the whole area inside the agglomerates.

Our present work, therefore, well supports the toughening mechanism discussed by the quantitative results of Bartczak et al. based on the high-density polyethylene toughened with calcium carbonate filler particles.[5] Indeed, the ability of the agglomerates to be load-bearing as well as stress concentrators is one reason why agglomerates may be particularly effective for toughening the semicrystalline polymer composites.

REFERENCES

1. Sumita, M.; Tsukumo, Y.; Miyasaka, K.; Ishikawa, K. J Mater Sci 1983, 18, 1758.
2. Maiti, S. N.; Sharma, K. K. J Mater Sci 1992, 27, 4605.
3. Pukánszky, B.; Turcsányi, B.; Tüdos, F. In Interfaces in Polymer, Ceramic and Metal Matrix Composites; Ishida, H., Ed.; Elsevier: New York, 1988; p 467.
4. Pukanszky, B.; Vörös, G. Compos Interf 1993, 1, 411.
5. Bartczak, Z.; Argogon, A. S.; Cohen, R. E.; Weinberg, M. Polymer 1999, 40, 2347.
6. Bazhenov, S.; Li, J. X.; Hiltner, A.; Baer, E. J Appl Polym Sci 1994, 52, 243.
7. Dubnikova, I. L.; Oshmyan, V. G.; Gorenberg, A. Ya. J Mater Sci 1997, 32, 1613.
8. Jancar, J.; Kucera, J Polym Eng Sci 1990, 30, 707.
9. Jancar, J.; Dibenedetto, A. T. J Mater Sci 1994, 29, 4651.
10. Fekete, E.; Molnar, Sz.; Kim, G.-M.; Michler, G. H.; Pukanszky, B. J Macromol Sci Phys B 1999, 38(5,6), 885.
11. Butler, J. H.; Joy, D. C.; Bradley, G. F.; Krause, S. J Polymer 1995, 36, 1781.
12. Vezie, D. L.; Thomas, E. L.; Adams, W. W. Polymer 1995, 36, 1761.
13. Flexman, E. A.; Huang, D. D.; Synder, H. L. Polymer Preprints, No. 29; Riew, C. K.; Kinloch, A. J., Eds.; American Chemical Society, Washington, DC, 1988; p 189.
14. Kim, G.-M.; Michler, G. H.; Rösch, J.; Mülhaupt, R. Acta Polym 1998, 49, 88.
15. Kim, G.-M.; Michler, G. H. Polymer 1998, 39, 5689.
16. Kim, G.-M.; Michler, G. H. Polymer 1998, 39, 5699.