Effects of Silica's Particle Size on the Mechanical/Foaming Properties of Microcellular Injection Molded PP/silica Composites

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In this study, organically modified silica of different particle sizes (micro and nano) and polypropylene (PP) composites were prepared. The PP micro/nano composites were then molded by conventional and microcellular injection molding process. The effects of silica particle sizes on the mechanical and rheological properties were investigated. The results showed that PP/silica nanocomposites have better tensile strength than that of foamed nanocomposites. The addition of nanosilica also increased the tensile strength of the PP/silica nanocomposites, but decreased the tensile strength of PP/silica microcomposites. The silica particles helped the nanocomposites to develop small cells on the foaming process. Rheological results showed an increase in the viscosity with the addition of nanosilica and microsilica to PP. The viscosity increase for the silica nanocomposites was greater than that of microcomposites.

Key words : Maleic anhydride/Nanocomposites/Silica/Microcellular injection molding/Rheology/TEM/XRD/Foam/Composite/PP

1 . Introduction

Polypropylene (PP) is one of the most widely used polyolefins, because of having balanced physical and mechanical properties, and recyclability and low cost. There are several types of fillers, like clay and silica, which can be used to enhance foaming process.

The shape of clay particles is a multi-layers type, but silica particles are spherical. Several researchers^{1), 2)} have studied the influence of micro-sized filler particles as nucleating agent of foaming process. PP is a non-polar polymer, and organoclay is a polar material ; thus, PP needs polar compatibilizers, like maleic anhydride grafted PP (PPgMA)³⁾, to improve the compatibility of PP with clay. Silica is usually found in nature as sand or quartz. Silica is manufactured in several forms ; including fused quartz, crystal, fumed silica, colloidal silica, silica gel, and aerogel. Fumed silica are non-porous particles and silica can be mesoporous⁴⁾ if made by sol-gel method. Silica based particles are often introduced into various polymers using a variety of approaches to enhance the thermal and mechanical stability of the neat polymer^{5), 6)}. Recently, mesoporous silica has been attracted by the researchers which can be used as molecular sieve and in drug delivery systems, like MCM-41⁷⁾. It was obtained from the

surfactant-templating route exhibiting regular hexagonal shape. Silica has been incorporated to a variety of polymers to form a series of organic-inorganic mesocomposite materials providing novel physical properties.

In 2006, Park *et al.* reported a study of the epoxy/silica mesocomposites with enhanced tensile properties and oxygen permeability.⁸⁾ Lai *et al.*⁹⁾ studied the properties of polyether ether ketone (PEEK)/silica nanocomposites, the results showed the maximum tensile strength at 5 wt% of the filler content for both modified and unmodified silica. The modified silica was surface treated with stearic acid. Wu *et al.*¹⁰⁾ studied the effects of silica on the viscosity of polycarbonate (PC)/silica and PC/thermotropic liquid-crystalline polymer (TLCP)/silica nanocomposites. The viscosity of the PC/silica nanocomposites increased 50% with silica contents up to 9 wt%, while the viscosity of PC/TLCP/silica nanocomposites decreased with the addition of TLCP into PC/silica nanocomposites.

In addition, polymer nanocomposites are used in the foaming process where the clay or other nanofiller serves as the foam nucleation agent, leading to smaller cells¹⁰⁾. These foams are useful in acoustic and thermal insulator applications¹¹⁾. In microcellular foaming process, a polymer is blended with a supercritical fluid. As a result of pressure release and evaporation of the fluid, a large number of microcells with a cell size of smaller than 10 μm are created¹²⁾.

There are considerable numbers of literature associ-

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ated with the polymer nanocomposites foaming. However, polymer/silica nanocomposites foaming have seldom been reported. Most of the polymer-nanocomposites foaming processes reported in the literature are conducted in batch processes, which have insignificant commercial and mass production value.

In this paper, we investigated microcellular injection molding process, as a commercially useful process. We studied the effects of the particle size of silica on the mechanical and rheological properties of microcellular injection molded PP/silica micro and nanocomposites. The primary purpose of the research was to investigate the processing benefits and properties improvements as a result of combining nanocomposites with the microcellular injecting molding process.

2. Experimental

Materials

Micro-sized (OMicron® NP 3) and nano-sized silicas (Aerosil R 974) were supplied by Sovitec, France and Degussa, Germany with average particle sizes of 3 μm and 12 nm, respectively. Aerosil R 974 is a hydrophobic fumed silica treated with dimethyldichlorosilane.

Compounding and foaming process

The microcomposites and nanocomposites were prepared through the blending of the micro and nano silica with PP using a kneader. The loadings of silica were 0, 2, 4, 6, 8, and 10 wt%. Then, the microcomposites and nanocomposites were molded by conventional and mucell® injection molding processes separately. The mucell® injection molding process was performed on a 100 ton AR-BURG-420 C injection molding machine, equipped with a microcellular foaming system. N₂ was used as a physical blowing agent for foaming.

The rotor speeds of the kneader were 30 and 24 rpm while compounding temperature and time were 160°C and 30 min, respectively. Then the micro and nano composites were molded by conventional and mucell® injection molding processes. The injection molding setup is shown in Figure 1. The process parameters both for conventional and mucell® moldings are shown in Table 1.

Instrumentations

The cellular structures of the foamed samples of composites were examined using a JEOL JSM 6360 scanning electron microscope (SEM) system. Specimens were cut into small pieces and sputter coated with gold, before examining by SEM.

The dispersion of the silica in the composites was evaluated using transmission electron microscopy (TEM) technique. The samples for TEM study were prepared by placing the bulk of the polymer silica nanocomposites (PSN) materials into epoxy resin capsules, followed by

Fig. 1 Wide angle XRD patterns of solid PP/silica micro and nano composites

Table 1 Process parameters both for conventional and mucell® moldings

Process parameters	Solid	mucell®
Shot size (cm³)	26	20
Melt temperature (°C)	200	200
Mold temperature (°C)	60	60
Injection speed (cm³/s)	100	100
Injection pressure (bar)	1000	1000
Packing pressure (bar)	600	200
Back pressure (bar)	50	187
Screw speed (m/min)	20	20
Cooling time (s)	40	30
SCF content (%)	—	0.4
SCF flow rate (kg/h)	—	0.24

curing the epoxy resin at 100°C for 24 h in a vacuum oven. The cured epoxy resin containing PSN materials was microtomed with a Reichert-Jung Ultracut-E into slices of 60~90 nm thickness. Subsequently, one layer of carbon, with a thickness of 10 nm, was deposited on these slices on 300-mesh copper nets for TEM observations on a JEOL JEM-2010 with an acceleration voltage of 200 kV.

The diffraction pattern of the PP/silica composites after molding was examined by x-ray diffraction (XRD). Wide-angle X-ray diffraction study of the samples was performed on a Panalytical X'Pert Pro X-ray diffractometer with copper target and Ni filter at a scanning rate of 2°/min. The decomposition temperatures of the nanocomposites were determined using differential scanning calorimetry (DSC) technique, along with thermogravimetric analysis (TGA) technique. A DuPont thermal analysis system equipped with model TA DSC-Q 10 and TA TGA-Q 50 was used for the thermal analyses under N₂ and air flow.

The molded samples were subjected to tensile testing

(ASTM-D-638-02) and impact testing (ASTM-D-256-02). The mechanical properties data reported were the average of five successful tests. The tensile tests of the ASTM standard samples were carried out using a tensile test analyzer, and an HT-9102 M system, manufactured by Hong-Da Company. A capillary rheometer, smart RHEO (CEAST), was used to measure the viscosity of the PP/silica micro and nano composites. The L/D of the capillary die was 20.

3. Results And Discussion

The study aims to investigate the relationships between processing, structure and properties of PP nanocomposites and microcomposites and their foamed samples produced in a microcellular injection molding process. The microcellular foaming of PP has been studied in solid state and batch process¹³⁾ and molten PP in continuous process¹⁴⁾. This work opens a new window to the development of microcellular composites of PP.

3.1 Microstructures of composites

XRD method has been applied to identify the microstructure, interfacial interaction, and degree of crystallization of the polymer nanocomposites. In this study, XRD was also used to estimate the interfacial interaction between the silica micro and nano fillers and the PP macromolecules.

PP has three types of crystal structures: α , β and γ .¹⁵⁾ The most common crystal form of PP is the α phase, which is thermodynamically the most stable phase having a monoclinic crystal structure and is the primary form under normal processing conditions. The β phase is usually observed in the presence of nucleating sites or under a strong imposed orientation. PP with the β crystals exhibits better impact strength and toughness than α crystals. The γ crystals can be formed during crystallization under high pressure conditions (above 200 MPa). The XRD results of PP/silica with microcomposites and nanocomposites are shown in Figure 2. They have α type crystal on micro and nano composites.

Since the XRD results do not give any insight into silica dispersion, TEM examinations of PP/silica micro and nano composites were conducted. Figures 3 and 4 show the micrographs of PP/silica micro and nano composites (silica 10 wt.%), respectively, where the spherical dark areas represent the silica particles and gray areas represent the continuous PP matrix. A chain-like branched structure of the silica particles¹⁶⁾ can be observed in the PP matrix. The dispersion of filler particles in the polymer matrix can have a major effects on the mechanical properties of the composites. The dispersion of an inorganic filler in a thermoplastic matrix is determined by the shear force during mechanical compounding. When using nanoparticles as filler, the nanofillers have a tendency to agglomerate¹⁷⁾. It can be seen that the micro sil-

Fig. 2 TEM image (magnification = 50 K) of solid 2 wt% PP/silica nanocomposites

ica particles with a size of 3 μm , were uniformly dispersed in the PP matrix. However, MA can improve the interfacial bonding¹⁸⁾ between PP and silica, thus, PPgMA matrix has better bonding with silica than that of PP matrix in the same area. Then, the spherical micro silica particles can be detected in PP matrix by FE-SEM (Fig. 5) and no silica particles were found in the PPgMA matrix.

3.2 Mechanical properties

The most interesting and attractive point for polymer nanocomposites is the improvement of their tensile strength. Figure 6 shows the tensile strength of PP/silica nanocomposites molded in a conventional injection molding process. The tensile strength of the nanocomposites increased when the silica content increased. This reveals that the interfacial bonding between nanosilica and PP is good.¹⁹⁾ It reached the maximum tensile strength at the 2 wt% silica content and then leveled off. Addition of nanosilica into PP can improve the tensile strength of the PP, but the nanoparticles aggregation can decrease tensile strength. However, the elongation-to-break (impact strength) decreased. Wu *et al.*²⁰⁾ reported improvement of the tensile strength and toughening effects at a lower filler content of PP composites. They used pre-grafted nanoparticles by some polymers using irradiation approach. PP/silica microcomposites, presented in Figure 7 showed different trend of decreasing the tensile strength of PP. It is well known that the tensile strength of a particulate composite is usually reduced with increasing the filler content when the bonding between filler and matrix is poor²¹⁾. Elongation-to-breaks of microsilica composites were better than those of nanosilica composites. The reduction in elongation-to-break of the composite filled with nanosilica suggested that the fillers cause a reduction in matrix deformation because of an introduction of

Fig. 3 TEM image (magnification = 10^4) of solid 10 wt% PP/silica microcomposites

Fig. 4 FE-SEM micrograph of 10 wt% PP/silica microcomposites

Fig. 5 Load-displacement curves of solid PP/silica nanocomposites.

Fig. 6 Load-displacement curves of solid PP/silica microcomposites

Fig. 7 Tensile strength comparison of solid/foamed PP/silica micro and nano composites

mechanical restraints.

Figure 8 shows the tensile strength comparison of solid and foamed PP/silica micro and nano composites. The tensile strengths of foamed PP/silica micro and nano composites were less than those of their solid counterparts because of the cells inside the nanocomposites. With addition of micro silica to PP, the tensile strength of PP of both solid and foamed samples decreased. The mechanical properties of the composites filled with nanosilica were superior to those with microsilicas filler in both solid and foamed samples. This results is in agreement with the results published by Sumita *et al.*^{22), 23)}

3.3 Microcellular foaming

Figure 9 shows typical SEM micrographs of the fracture surfaces obtained from the foamed specimens of the PP/silica nanocomposites. The images show the effects of silica content on both cell density and cell size of the foamed samples. When the nano silica content increased, cell size decreased and the cell density increased. The dispersion of nano silica in the PP matrix clearly had a significant effects on the cell nucleation⁹⁾.

Fig. 8 Cellular structure of PP/silica nanocomposites foams with varying nano-silica content

Fig. 9 Cell structure of PP/silica microcomposites foams with varying micro-silica content

The decrease of cell size also affected the tensile strength. As the silica content of foamed PP/silica nanocomposites increased, cell size decreased and tensile strength increased (Fig. 8). These results indicate that the nano silica serves as a heterogeneous nucleating agent during the foaming process. In a heterogeneous nucleating system containing filler particles, cells nucleate at the boundary between the polymer matrix and

the dispersed filler particles. The remarkable rise in the cell density in the nanocomposites should be attributed to a dramatic increase in the effectiveness of the nucleating sites.

Figure 10 shows the SEM micrographs of the foamed PP/silica microcomposites. It is seen that the cell size in microcomposites is bigger than that of nanocomposites' larger than 100 μ m. The tensile strength decreased as

Fig. 10 Rheological examinations results of PP/silica nanocomposites at 210°C

the micro silica loading increased (Fig. 8).

3.4 Rheological properties

Figure 11 shows the viscosity measurements of the PP/silica nanocomposites by capillary rheometer. It is apparent from the figure that nanosilicas have a dramatic effects on the rheological behavior. It also reveals that, with addition of nanosilicas into PP, the nanocomposites viscosity increases. And shear thinning effects takes place during high shear rate. However, when the nanosilicas content in the composites increases the nanocomposites viscosities increase as well and the extent of increase was almost the same as that of the shear rate increase.

Figure 12 shows the results of the viscosity measurements of PP/silica microcomposites. These results reveal a similar trend, as shown in Figure 10, that presents shear thinning and viscosity increase. However, the viscosity increase is less obvious as compared to that of nanocomposites when the microsilica content increased. This observation may be caused by the size effects and bonding of spherical silica on the PP matrix. Nanosilica particles have greater surface area and better bonding to PP matrix than those of microsilicas. The effects of the nanofiller is most pronounced at low shear rate and the relative effects diminishes with increasing shear rate because of the shear thinning phenomenon. This observation is in agreement with that of fiber reinforced composites²⁴⁾

4. Conclusions

In this study, effects of silica particle size on the mechanical and rheological properties of the microcellular injection molded PP/silica composites were investigated. PP/silica micro and nanocomposites were fabricated by melt blending of PP and silica. The structures of the samples were characterized by XRD, SEM and TEM. We found that the addition of nanosilicas to the PP resulted in an increase in tensile strength and viscosity.

Fig. 11 Rheological results of PP/silica microcomposites at 210°C

Furthermore, the incorporation of micro and nanosilicas into the PP matrix showed a decrease in the cell size of the resulting injected molded foams. Nanosilicas containing composites resulted in smaller cell size than that of microsilicas composites based on the cell morphology measurements. The rheological results showed an increase of the viscosity when the micro and nano silicas content increased.

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