Effects of fillers on the properties of thermoplastic elastomers

Veli Deniz, Nursel Karakaya, and Osman G. Ersoy

Silica and calcium carbonate are commercially useful as reinforcing agents for producing soft, elastomeric transparent goods and cost-effective filler, respectively.

Thermoplastic elastomers (TPEs) are rubbery materials with an equivalent elastic performance to that of conventional thermoset rubbers (molded through heat). In addition, they can be processed and recycled like thermoplastic materials.1 Because of environmental considerations and favorable manufacturing methods, replacement of conventional vulcanized rubber by TPE for industrial applications is growing rapidly. Poly(styrene-b-elastomer-b-styrene) (SEBS)/polypropylene (PP) blends constitute the best-performing elastomers.2 Fillers can enhance their processability and mechanical compound properties, as well as reduce material costs. Filler behavior in these compounds is affected by factors like the particle-size distribution, surface area, shape, color, and surface chemistry.3

Reinforcing styrenic (aromatic hydrocarbon)-based TPEs with fibers, such as aramid,4 conductive-polymer-modified carbon black,5 and thermotropic liquid-crystalline polymer (exhibiting phase transitions with changing temperature),6-11 results in better mechanical properties. Clay-based nanofillers have also been considered as reinforcement fillers.12-14 However, the effects of silica loading on major SEBS/PP/oil-blend system properties have not yet been investigated in detail. We therefore investigated the consequences of different levels of silica loading for the physical, mechanical, thermal, and optical properties of such blends. We compared our results with those of blend systems including calcium carbonate (or calcite: CaCO₃) fillers with different average particle sizes, from fine to coarse.

We prepared poly[styrene-b-(ethylene-co-butylene)-b-styrene] block-copolymer-based thermoplastic elastomer composites in a co-rotating intermeshing twin-screw extruder. SEBS (supplied as Kraton G1657), PP (Borealis HE125MO), and oil (Petroyag WOP68) loads in composites were fixed at 100, 20, and 35phr (parts per hundred rubber), respectively. The composites were loaded with 10, 20, and 30phr of calcite (from Omya Madencilik) and silica fillers (supplied by Ege Kimya). We used calcite with three different average particle sizes (as

Figure 1. (a) Perpendicular and (b) parallel tensile (stress/strain) strength versus filler concentration (parts per hundred rubber: phr) in our composites (see Table 1). 1KA, 3 Extra KA, 40KP: Calcite compounds supplied by Omya Madencilik (Turkey). BM30: Precipitated amorphous silica from Ege Kimya (Turkey).
a function of increasing average particle size, 1KA, 3 Extra KA, and 40KP as well as silica (BM30) to prepare 12 composites (see Table 1). We then injection molded 2 and 6mm sheet samples (using an injection machine with 50t maximum clamping capacity), with which we conducted hardness, density, tensile- and tear-strength, compression-set, wear-resistance, transmittance, and haze measurements. We investigated the composites’ thermal properties using a differential scanning calorimeter, and used a scanning-electron microscope (SEM) to examine their composite morphologies.

To investigate the effect of orientation within the mold, we performed both tensile and tear tests with the specimens cut parallel and perpendicular to the flow direction of the injection-molded sheets (see Figures 1 and 2). The orientation tendency of SEBS and PP chains while filling the mold under injection pressure results in higher mechanical properties parallel to the flow.

Regardless of the average particle size, increasing the calcite amount in the composites lowers their tensile and tear strengths—both perpendicular and parallel to the flow direction for all calcite types that we investigated (see Figures 1 and 2). Calcite particles function as a foreign noninteracting material, whose inclusion as a filler leads to weak regions in the composites.

With silica loading, the filler surface is wetted by the polymeric blend, leading to improvements in mechanical properties such as tear strength (see Figure 2). Perpendicular to the flow direction, the tensile strength does not change (see Figure 1). We observe a smaller reduction in tensile strength parallel to the flow direction with silica compared to calcite loading at 30phr. This indicates that the flow-induced chain orientation is suppressed as the silica amount increases.

Continued on next page
Table 1. Composite recipes

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Figure 4. Haze versus filler concentration in our composites.

Figures 3 and 4 show the composites’ transmittance and haze values. All calcite fillers clearly worsen the optical properties of the SEBS/PP/oil blend. However, silica-loaded composites retain transparency, while their haze values are very close to those of the unfilled blend at low loading levels.

Figure 5. Scanning-electron-microscope images of 30phr-filled composites (broken with liquid nitrogen). (a) C3 (30phr calcite: 1KA), (b) C6 (30phr calcite: 3 Extra KA), (c) C9 (30phr calcite: 40KP), and (d) C12 (30phr silica: BM 30).

We examined the composites’ morphologies with an SEM. Injection-molded test bars of 2mm thickness were immersed into liquid nitrogen for 2hr and broken with a sudden impact. Figures 5(a)–(d) show that the observed filler particles are homogeneously dispersed. Calcite surfaces are not fully wetted by the polymer. In addition, cavities exist between the surfaces of the calcite particles and the polymer. This clearly indicates that there is no calcite-polymer interaction. On the other hand, Continued on next page
silica particles that are deeply embedded in the polymeric matrix can be seen in Figure 5(d), which implies a strong interaction between filler surface and polymeric matrices. The silica surface is wetted by the polymer and we do not observe any large cavities between polymer and filler.

Our results have thus shown that calcite can be used in composites as a filler to decrease the production costs of nontechnical goods. On the other hand, silica can be used as reinforcing agent in SEBS/PP/oil polymeric blends, especially for production of transparent and soft technical parts. Future work will concentrate on examining the impact of various additives and antioxidants, among others, on the properties of the composites.

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References