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Effect of Carbon Black and/or Elastomer on Thermoplastic Elastomer-based Blends and Composites

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Abstract. It was aimed to investigate the effect of carbon black and/or elastomer on the electrical conductivity and mechanical properties of thermoplastic elastomer (TPE). Carbon black (CB) and ethylene-glycidyl methacrylate (E-GMA) were used as additives in the main matrix. The blends and composites were characterized in terms of their electrical conductivity and mechanical properties. CB concentration was varied as 0.5, 1, 3 and 5 wt.%. In order to modify the surface of CB, paraffinic oil and silane coupling agents were used. E-GMA was added to the matrix at 5, 10, 20, and 30 wt.% concentration. In order to prepare ternary composites, 5 wt.% of modified or unmodified carbon black and 10 wt.% of E-GMA were mixed with the TPE matrix. The tensile strength, impact strength and elongation at break values of TPE/CB composites decreased while elastic moduli and electrical conductivities increased with increasing CB concentration. It was observed that the surface modification of CB did not alter the tensile properties significantly. However, impact strength of the composites improved upon modification. For TPE/E-GMA blends, E-GMA addition enhanced the tensile strength and impact strength values of neat TPE. Nevertheless, elongation at break values began to decrease at 10 wt% and higher concentrations of E-GMA. It was observed that CB was more effective than the E-GMA on the mechanical properties of the ternary composites. The addition of 10 wt.% E-GMA increased the electrical resistivity and impact strength values of the ternary composites, as expected.

Keywords: Thermoplastic elastomers; Carbon black; Elastomer; Modification; Silane treatment; Processing

PACS: 81.05.Qk

INTRODUCTION

Thermoplastic elastomers (TPEs) are copolymers that combine the properties of both elastomeric and thermoplastic materials within a certain temperature range. All thermoplastic elastomers include two or more distinct polymer phases which are the combination of crystalline hard and amorphous soft phases. Because of molecular motion in a rubbery state, the soft segment is a reversible phase and elastomeric behavior is gained by flexible soft segment which has amorphous regions at high temperatures. The hard segments form physical crosslinks arising from polar interactions, hydrogen bonding and crystallization in the hard domain that liquefied at high temperatures [1].

Since TPE shows thermoplastic behavior, its mechanical properties are similar to vulcanized rubber. However, TPE's many advantages make them superior to rubbers. TPE can be softened and melted so that they can be reprocessed in order to make completely reversible polymers. Their fast processability and elasticity properties allow design and process that cannot be provided by thermoset materials [1]. Their unique structure offers good mechanical properties suitable for many applications such as automobiles, electronics, medicine, etc. [2].

Thermoplastic elastomers are elastic, flexible and low modulus polymers. Their processing is relatively easy, they have superior oil and heat resistance, good chemical resistance, light weight and fatigue-resistant properties. TPEs can be processed in shorter cycle time than conventional rubbers [3]. All these properties of thermoplastics are basically relevant to the connection of crosslinked macromolecule series in an infinite network structure [1].

One class of TPE is poly(ether ester), which was used as the main matrix of this study. The reason is that poly(ether)ester block copolymers are high performance engineering materials and bridge the gap between rigid thermoplastics and crosslinked elastomers [2].

There were two steps followed through this study. In the first step, carbon black surface modification was applied by using four different silane coupling agents and paraffinic oil. In the second step, composites/blends were produced and their properties were investigated. In order to decide the best composition ratios, binary composites were prepared first. The carbon black at 0.5, 1, 3, 5 wt.% and the elastomer at 5, 10, 20, 30 wt.% concentrations were mixed with TPE by using a co-rotating twin screw extruder. After selecting the best ratios among all binary compositions, ternary composites of TPE, CB and elastomer were prepared.

EXPERIMENTAL

Materials

In this study, poly(ether ester) with trade name of Hytrel 7248 was supplied by DuPont Türkiye Kimyasal Ürünler San. ve Tic. A.Ş. (Turkey). Carbon black (CB) was delivered by Orion Engineered Carbons (USA). Elastomer (E-GMA) was obtained from Atofina Chemicals Inc., (France). Paraffinic oil (RX430) from Shell Oil Company, γ -Glycidoxypropyltrimethoxysilane (γ -GPS), 3-Methacryloxypropyltrimethoxysilane (3-MPTS), N-(β -aminoethyl- γ -aminopropyl-trimethoxysilane (AEAP) from Cam Elyaf Sanayii A.Ş. (Turkey) were used as surface treatment agents of carbon black.

Composite Preparation

The carbon black particles were treated with 1 wt.% silane coupling agents and 1 wt.% paraffinic oil in a dilute solution. The 150 g treating solution (90% methanol + 10% water) was prepared with silane coupling agents. The pH of the solution was adjusted to 4.5-5 by using acetic acid. The hydrolysis time was 15 minutes and the mixing time with unmodified carbon black (UMCB) was 10 minutes at room temperature. The methanol-water solution was evaporated at 80°C. In the oil treatment stage, the required amount of paraffinic oil was taken into 150 g acetone and necessary amount of CB was added into the solution. They were agitated slowly for 10 minutes to get them properly mixed. The acetone was evaporated at 40°C. At the end of both silane and oil treatments, modified carbon black (mCB) particles were oven dried under vacuum at 110°C for 24 hours.

Prior to extrusion process, TPE and E-GMA pellets were dried in an oven for overnight at 110°C and 80°C, respectively. Co-rotating twin screw extruder (Thermo PRISM TSE-16-TC) was used to prepare the blends and the composites. The extrusion process was performed using the temperature profile of 230-240-240-240-240°C and a screw speed of 80 rpm. Specimens for tensile test and impact test measurements were prepared by using an injection molding device (DSM Micro 10 cc Injection Molding Machine) at 13 bars while the temperature of the sample holder and mold was 240 and 30°C, respectively. Specimens for electrical conductivity measurements were prepared by using a compression molding device at 240°C. A square shaped mold (15x15cm) that has 1 mm thickness was used to prepare the samples. During compression molding, pressure was applied at 50 bar for 2 minutes and then at 200 bar for 3 minutes. Binary and ternary systems were prepared by adding mCB/UMCB and/or E-GMA to TPE matrix.

Composite Characterization Techniques

Electrical properties of the samples were measured by using a two point probe Keithley 2400 resistivity tester. Compression molded samples were cut to get “n” shaped specimens whose dimensions are 1 mm in thickness, 5 mm in width of both ends, 30 mm in length of both parallel arms and 15 mm in total width. A constant voltage (20 V) was applied to the samples and the current was recorded from the instrument. The volume resistivity was calculated by:

$$\rho = R \frac{A}{L} \quad (1)$$

where R is the resistance (Ω), L is the length of sample, 4.5 cm, A is the cross sectional area of composite (0.5 cm width x 0.1 cm thickness) and ρ is the volume resistivity (Ω .cm).

Mechanical properties of the materials were tested with a Shimadzu Autograph AG-IS 100 KN universal tensile testing instrument, according to ISO 527-2 5A standards. Tensile specimens had 2 mm thickness, 4 mm width and 20 mm gauge length. Crosshead speed of testing instrument was 50 mm/min.

Impact strength of the samples were determined applying Charpy impact test with a Ceast Resil Impactor 6967 according to ASTM D 5947 Standards, instrumented with a 7.5 J hammer. In Charpy test, the notch was cut by means of a notch-cutting machine. Specimens for impact tests had 2 mm thickness, 10 mm width and 7.5 cm length.

RESULTS AND DISCUSSION

Electrical Properties

The volume resistivity of neat TPE was $10^{15}\Omega\cdot\text{cm}$ according to IEC 60093, which was in insulator range [4]. Introducing CB addition into polymer matrix decreased electrical resistivity since conductive filler concentration was increased (Fig. 1). TPEs with 0.5% and 1% CB addition were in semi-insulator range; whereas, TPEs with 3% and 5% CB were in semi-conductor range. The sharp decrease between 1% and 3% CB concentrated TPE was because of the increase of conducting paths. This means that the number of agglomerates increased and hence the conductivity was higher [5]. As surface modification provided better distribution of CB particles, conductive CB chains decreased and resistivity of the composite increased especially at 5 wt.% CB loading. In ternary composites, resistivity increased because of a breakdown of existing conductive networks and formation of new conductive networks by rearrangements and orientation of CB particle aggregates [6].

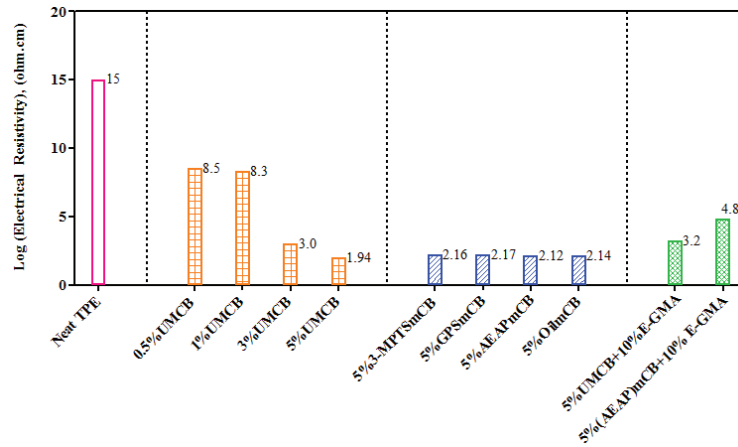


FIGURE 1. Electrical resistivity values of neat TPE, TPE/CB, TPE/E-GMA and TPE/CB/E-GMA composites

Mechanical Properties

The mechanical test results are shown in Figures 2-5. As the CB filler concentration increased, CB tended to aggregate and tensile strength decreased [2] (Fig. 2). 5wt.% UMCB was selected for surface modification because of its best electrical conductivity among the other composites (Fig.1). However, surface modification did not change tensile strength significantly. As AEAP gave the best results in tensile strength and elongation at break, AEAP surface modification was applied to UMCB while preparing ternary composites. For TPE/E-GMA blends, as the E-GMA concentration increased, tensile strength values decreased slightly. In ternary composites, it is clear that CB effect on tensile strength was more effective than E-GMA addition.

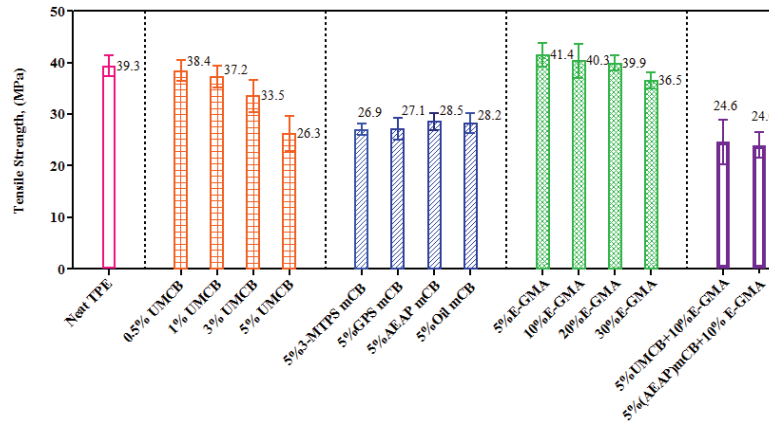


FIGURE 2. Tensile strength values of neat TPE, TPE/CB, TPE/E-GMA and TPE/CB/E-GMA composites

As seen in Figure 3, elongation at break properties decreased with the addition of filler indicating interference by the filler in the mobility or deformability of the matrix. This interference is created through the physical interaction and immobilization of the polymer matrix by the presence of mechanical restraints. The materials became more brittle, as the filler concentration increased [2, 7]. According to TPE/E-GMA blends, as the E-GMA concentration increased, elongation at break values decreased. Especially, there was a sharp decrease beyond 10wt.% E-GMA concentration.

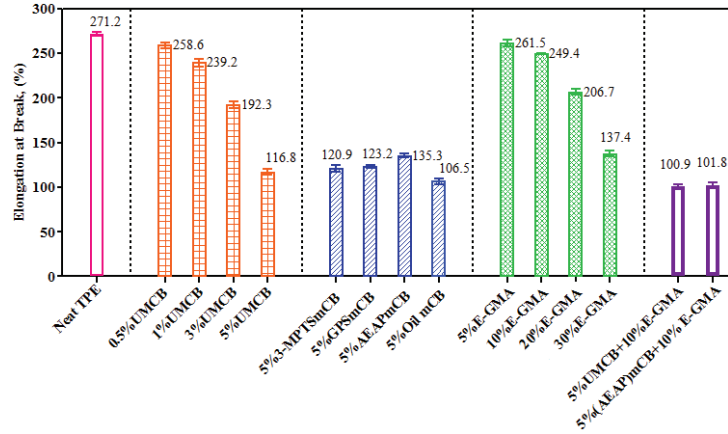


FIGURE 3. Elongation at break values of neat TPE, TPE/CB, TPE/E-GMA and TPE/CB/E-GMA composites

In Figure 4, the elastic modulus clearly increased after CB addition because of the rigidity of CB particles. The presence of filler agglomerates also led to increase in modulus. This was attributed to the lower mobility of the matrix with the presence of the agglomerates [7, 8]. When surface modification was applied, agglomerates decreased, and modulus also slightly decreased except for the oil treated CB for which a small increase in modulus was obtained due to better dispersion possibility of the particles in the TPE matrix. With the addition of E-GMA, tensile modulus decreased as E-GMA was a low modulus material.

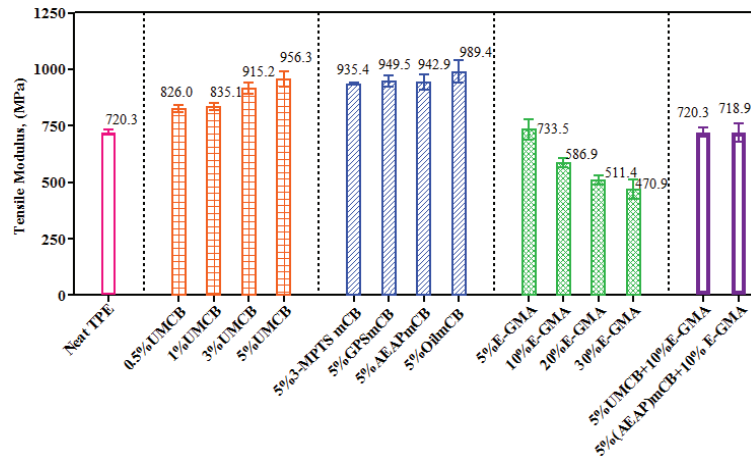


FIGURE 4. Tensile modulus values of neat TPE, TPE/CB, TPE/E-GMA and TPE/CB/E-GMA composites

Figure 5 illustrates the variation of impact strength with CB concentrations. The impact strength decreased with filler addition because of the reduction of elasticity of material. Filler addition reduced the deformability of matrix because rigid particles might create stress concentrated points [2]. So agglomerates should act as stress concentrated areas and decreased the impact strength of the material [9]. Impact strength of the TPE/E-GMA blends increased dramatically with increasing amount of the elastomer since elasticity of the material increased. However, in ternary composites, the results were not different than the binary composites of TPE/CB. This is because the effect of CB was more dominant on toughness than that of the elastomer.

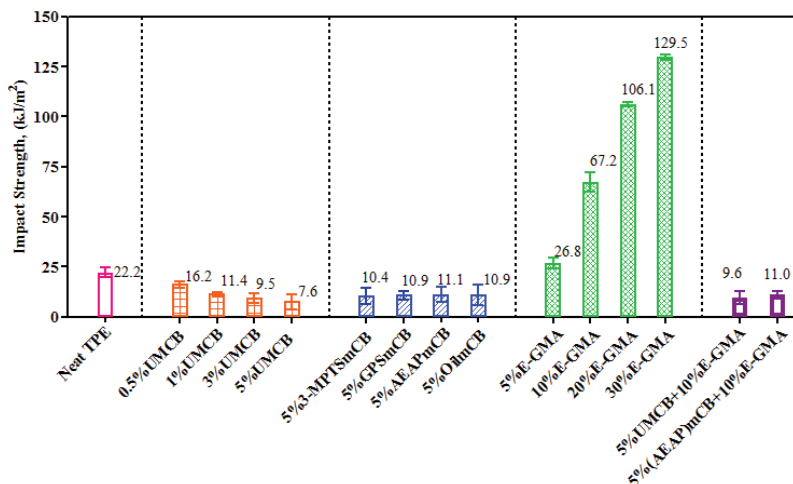


FIGURE 5. Impact strength values of neat TPE, TPE/CB, TPE/E-GMA and TPE/CB/E-GMA composites

CONCLUSIONS

Addition of carbon black and elastomer into TPE matrix affected the electrical conductivity, tensile properties and impact strength of TPE. TPE with 5 wt.% CB loading reached up to the semi-conductor range. As carbon black concentration increased, tensile strength decreased because of the agglomeration in the polymer matrix; elongation at break decreased because of immobilization of the polymer matrix. Tensile modulus of neat TPE improved because the agglomeration lowered mobility of the polymer chains but impact strength decreased due to the stress concentrated regions from the agglomerates. For the composites containing 5wt.% mCB, impact strength values increased possibly due to surface modification providing decrease in agglomeration of CB particles. For TPE/E-GMA blends, tensile and impact strengths dramatically improved with the addition of E-GMA. According to the ternary composite containing 5wt.% of UMCB and 10wt.% of E-GMA, CB was more effective than the E-GMA on the mechanical properties. This was also valid for the ternary composite with modified CB.

ACKNOWLEDGMENTS

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