Effect of a Coupling Agent on the Electromagnetic and Mechanical Properties of Carbon Black/Acrylonitrile–Butadiene–Styrene Composites

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ABSTRACT: Titanate coupling agent (TCA) is widely used as a plasticizer in filled polymer processes. In this study, the effect of TCA with different contents (2 and 10 wt %) on the electrical conductivity, wave absorption, and mechanical properties of carbon black (CB)/acrylonitrile–butadiene–styrene (ABS) composites were investigated. The results indicate that with the addition of 2 wt % TCA to the filled CB, the electrical conductivity of CB/ABS composites improved greatly, but its wave absorption performance was weakened. In contrast, the addition of 10 wt % TCA to the filled CB improved the microwave absorption performance of the CB/ABS composites but led to poor electrical conductivity. However, TCA, regardless of the contents of 2 or 10 wt %, greatly improved the mechanical properties of the composites. The probable reasons for this are discussed on the basis of the fracture morphology of the sample, a chemical band between the filling and resin, and the physical coating between the filling and TCA. J Appl Polym Sci 102: 1839–1843, 2006

Key words: additives; composites; conducting polymers; mechanical properties; particle size distribution

INTRODUCTION

Carbon black (CB) is widely used as the main reinforcement filler for high-performance composite materials. These materials have various useful properties, including corrosion resistance, low density, thermal expansion, electrical conductivity, and wave absorption.[1,2] So they are attractive substitutes for various metal, alloys, and other materials. They offer versatile applications in the fields of aerospace, batteries, solar cells, resistors, semiconductor elements, antistatics and electromagnetic shielding, and absorption materials.[3–6]

The properties of a composite, such as the strength and modulus, are important factors in the production of high-quality composites. The properties of the filler and matrix make a critical contribution to the quality of a polymer composite. In addition, the physicochemical interaction at the filler–matrix interface plays an important role in improving the mechanical properties of a polymer composite. Many researchers have tried to improve the adhesion between fillers (e.g., CB, carbon fiber, metal powder) and matrix resins by chemical reactions with a coupling agent.[3,7]

An additional coupling agent in a polymer composite may not only improve its mechanical properties but may also improve its electrical conductivity and electromagnetic characteristics.[8] In this article, we report the influence of a titanate coupling agent (TCA) on the mechanical properties, electrical conductivity, and microwave properties of CB-filled acrylonitrile–butadiene–styrene (ABS); the probable reasons for the results are discussed on the basis of the fracture morphology of the sample, a chemical band between the filling and resin, and the physical coating between the filling and TCA.

EXPERIMENTAL

The basic components in the objects investigated were composed of ABS CH510 (Panjin Ethylene Industry Co., China), acetylene CB N234 (FuShun DongXin Chemical Co., Ltd., China), and TCA NDZ-105 (WuHan HuaChang Application Technology Institute, China)

To get rid of the oxygenous group and to activate CB, CB was heat-treated at 700°C for 30 min in flowing argon. At the same time, TCA was diluted with isopropyl alcohol (35 wt % of the TCA), and the treated CB was immersed in its solution subsequently; we stirred the intermixture adequately. At last, the CB treated with the TCA was dried at 100°C. The contents of the TCA in CB was 2 and 10 wt %, respectively. ABS was heat-treated at 100°C for 120 min in air; the water

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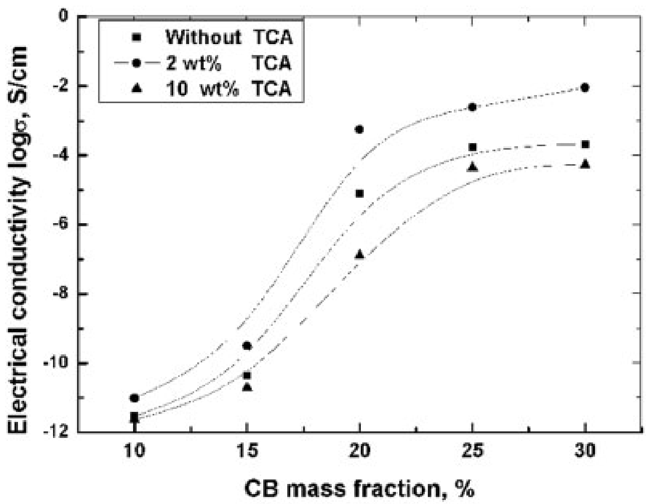

Figure 1 Effect of TCA on the electrical conductivity of CB/ABS composite. The curves are only to guide the eye.

content in ABS was less than 0.1% (mass fraction). Subsequently, we stirred the treated CB into ABS with a blender, and the CB content in the mixture was varied from 5 to 30% (mass fraction). After this, the mixture was processed by extrusion in a plastic extruder (SJ25-25) at a temperature of 175°C. Finally, this mixture processed by the extruder was used to prepare the compact slab sample. The compact slab was prepared by compression at a pressure of 10 MPa and a temperature of 180°C.

The test specimens were obtained in different sizes: 115 × 1.5 mm for electrical conductivity and 200 × 200 × 6 mm for microwave absorption property measurements. A three-electrode method was used to measure the volume resistivity. An HP8720B vector network analyzer and standard horn antennas were used to measure the reflection loss (microwave absorption) in an anechoic chamber, and the testing frequency bands ranged from 8 to 18 GHz. Dumbbell-like specimens (GB/T 1040-92) were punched out of the sheets and submitted to tensile strength measurements.

RESULTS AND DISCUSSION

Effect of the coupling agent on the electrical conductivity

Figure 1 shows electronic conductivity plots of various composites for different TCA contents as a function of CB mass fraction, wherein the points represent the measured values and lines are only to guide the eye. As indicated, the electrical conductivity increased with the CB mass fraction, but it showed interesting variation with TCA incorporation. With the addition of 2 wt % TCA to the filled CB, the electrical conductivity of the CB/ABS composites improved greatly in comparison to that with no TCA, and the improved tendency by TCA was more and more obvious with the content of CB filler. However, with the incorporation of 10 wt % TCA, the composites were poor in electrical conductivity compared to that with no TCA, as illustrated in Figure 1.

It has been postulated that TCA will improve the compatibility of a CB filler with a ABS polymer by the enhancement of their interfacial adhesion.[7] The mechanism of the TCA reaction on the inorganic CB filler surface is represented in Figure 2. TCA reacts with the hydroxyl groups at the inorganic CB filler surface, which results in the formation of a monomolecular layer on the inorganic surface to increase the compatibility of the filler–matrix interface. When the content of TCA was 2 wt % to the filled CB, the dispersion of CB particles in the ABS phase was enhanced by the replacement of the water of hydration at the inorganic surface of the CB, with organofunctional titanate making the CB/ABS interface compatible[7,9,10] and thereby eliminating air voids in the system. Consequently, this resulted in deagglomeration and more uniform dispersion in melt blending, which contributed to a decrease in the net resistance [$R_C + R_A$ (see Fig. 3,[11]), where R_A is the resistance within the conducting particles aggregate (Ω) and R_C is the contact resistance between the conducting particles aggregate (Ω)]. The gaps between the conducting particles agglomerate at high filler loadings became very small or negligible, and the net resistance became practically equal to R_A. So the conducting channel and the electrical conductivity of the filled composites improved greatly.

However, when the content of TCA reached 10 wt % to the filled CB, the filled CB particles had not only a chemical reaction with TCA (as mentioned previously) but also with the physical coating by TCA (as shown in Fig. 4), which had an adverse influence on the formation of conducting chains among the CB particles, although TCA also improved the compatibility of the CB filler with the ABS polymer and uniform dispersion in the ABS matrix. This was because there were barriers to the flow of electrons through the TCA coating. So R_C between the CB particle agglomerate was enhanced; this resulted in an increase in the net resistance ($R_C + R_A$). Moreover, the interface of the TCA coating or ABS matrix between the CB particle

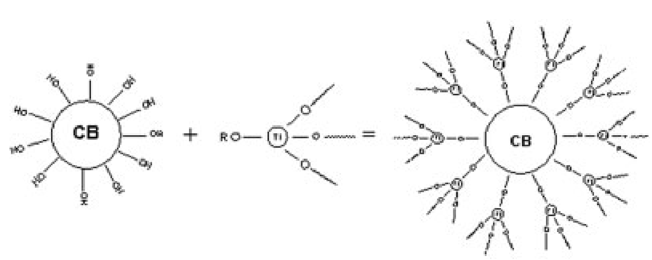

Figure 2 Mechanism of the titanate reaction on the CB filler surface.[7]

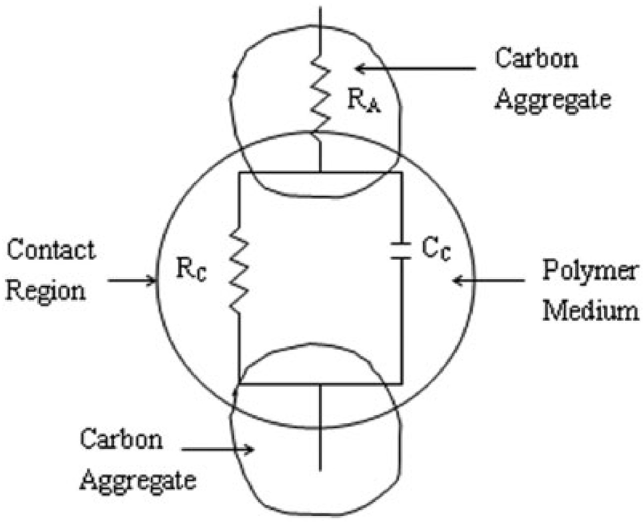

Figure 3 Equivalent resistor–capacitor circuit in the contact region of the CB filler aggregates in a polymer compound.

aggregate brought on the presence of the capacitance (C_C in Fig. 3). R_C and C_C played a important role in the electrical conductivity of low CB loading ($\leq$ 15 wt %) or coated CB loading (by 10% TCA) composites, which is generally called hopping or tunneling conduction.[11]

To investigate this effect and to relate the TCA mechanism to the morphology, the fracture surfaces of the composites were examined with a scanning electronic microscope, as illustrated in Figure 5(a–c).

Fracture morphology of the CB/ABS composite

Figure 5(a–c) shows the fracture morphology of 20 wt % CB-filled ABS composite specimens containing no

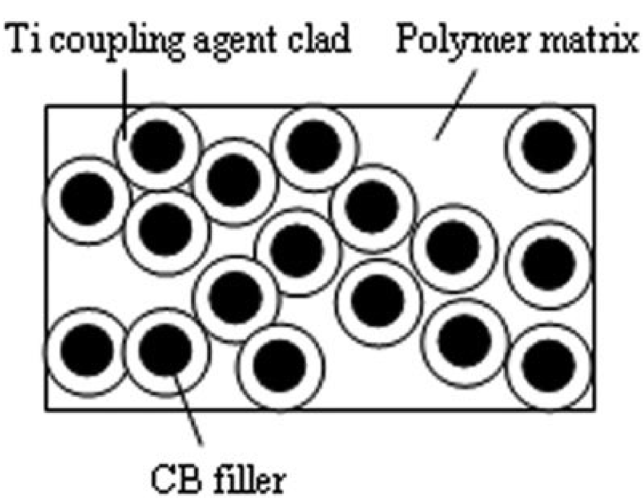

Figure 4 Coated CB particles by TCA. When the content of TCA reached 10 wt %, the CB particles were coated by TCA, in which the conduction channel was blocked.

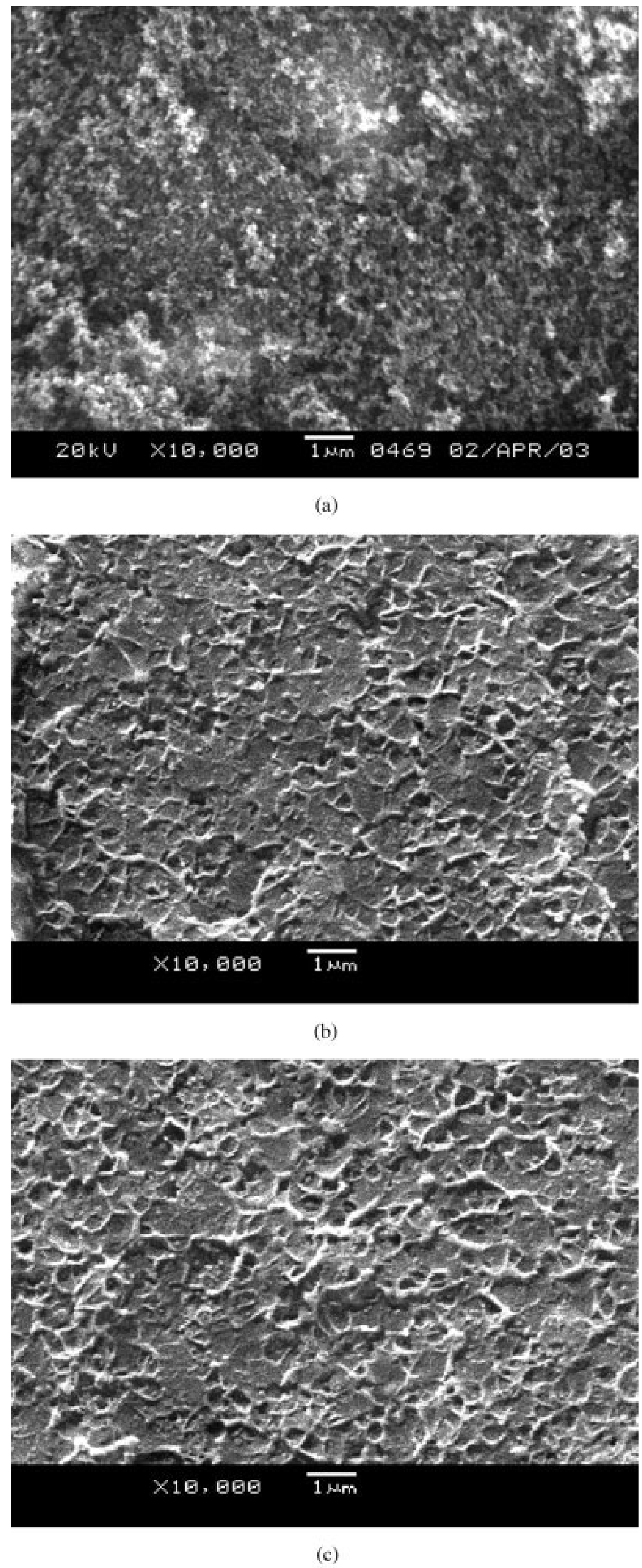

Figure 5 Scanning electron micrographs of the fractured surfaces of the CB/ABS resin composites containing 20 wt % CB filler: (a) without TCA, (b) with 2 wt % TCA, and (c) with 10 wt % TCA.

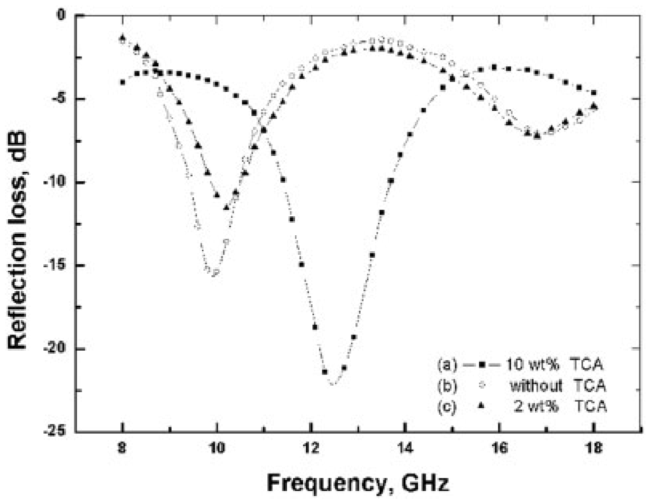

Figure 6 Reflection loss of 20 wt % CB/ABS composites for different TCA contents versus frequency. Added amount of TCA in filled CB: (a) 10, (b) 0, and (c) 2 wt %. The thickness of all of the samples was 6 mm. The curves are only to guide the eye.

TCA and containing 2 and 10 wt % TCA to the filled CB. Figure 5(a) shows poor CB particle dispersion in the ABS matrix and poor adhesion between the CB particles and the ABS resin when no TCA was added to the system. CB particles agglomerated as large white spots under microscopic examination. A significant improvement in CB particle dispersion in the matrix and improved adhesion between CB and the ABS resin are shown in Figure 5(b,c), where 2 and 10 wt % of TCA were added to filled CB, respectively. From Figure 5(c), although CB particle dispersion and adhesion between CB and the ABS resin were improved greatly compared to that of no TCA, some CB particle aggregation was still observed in the micrograph. This was because some CB particles were embraced by TCA and were bound each other, and embraced CB particles did not dispersed well in the matrix and formed isolated conducting island. Other good dispersal CB particles in the matrix were also coated by the TCA and were isolated to each other [Fig. 5(c)].

Effect of the coupling agent on microwave absorption

Figure 6 shows the reflection loss for 20 wt % CB/ABS composites of different TCA contents as a function of frequency, which represents the wave absorption performance of the composites versus frequency. As demonstrated, the reflection loss of the CB/ABS composites depended on their electric conductivity and filler particle dispersion in the matrix. With the addition of 2 wt % TCA to the filled CB, the electrical conductivity of the CB/ABS composites was greatly improved compared to that with no TCA, so incident electromagnetic waves were mostly reflected on the sample surface on account of continuous conductive network in the sample, and then, the reflection loss was poor. However, with the incorporation of 10 wt % TCA to the filled CB particles, the reflection loss of the sample was improved dramatically, as shown in Figure 6. The characteristic absorption peak was −21.4 dB at 12.3 GHz, and the effective frequency bandwidth of wave absorption surpassing −10 dB reached 2.3 GHz. Correspondingly, the characteristic absorption peak of the sample without TCA was −15.38dB at 10 GHz, and its effective frequency bandwidth was under 1 GHz. This was because the dispersed CB particles in the matrix were coated by the TCA and were isolated from each other. Furthermore, some CB particles were embraced by TCA and formed isolated conducting aggregates. The contactless (isolated) distribution of the CB aggregates in the ABS matrix led to the improvement of the absorbing and reflection activities. The probable reason for the improved wave absorption was that the plan wave could transmit into the sample containing contactless CB particles and was mostly decayed because of the resistance and interfacial polarization attenuation of the isolated CB particles (aggregates) and multiple scattering losses of different discrete CB particles (aggregates).[12,13]

Effect of the coupling agent on the mechanical properties

Figure 7 shows the tensile strength of the CB/ABS composites for different TCA contents versus CB mass fraction. The tensile strength of the composites with TCA was greatly improved compared with that of the

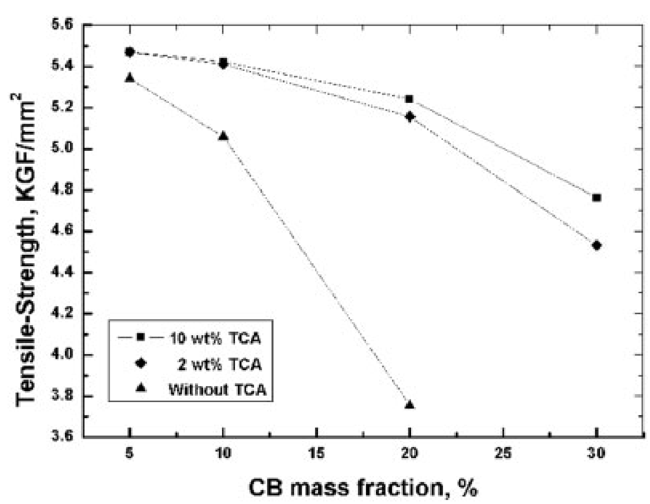

Figure 7 Tensile strength of the CB/ABS composites for different TCA contents versus CB mass fraction. The points represent the measured values, and the lines are only to guide the eye.

composites without TCA. With increasing CB content, the improvement of the tensile strength by TCA was more and more dramatic regardless of the content (2 or 10 wt %). Furthermore, at a fixed CB content, the CB/ABS composites with 10 wt % TCA had higher tensile strengths than that with 2 wt %.

As can be deduced from our earlier findings, TCA did play a role as plasticizer. In this case, the plasticizing effect of titanate was operating possibly in conjunction with interfacial adhesion to yield an increase in toughness. Toughness, however, is the major factor that controls the tensile strength. During tensile strength testing, a crack traveled although the ABS and interfacial region. Generally, a high filler–matrix interfacial adhesion provides effective resistance to crack propagation during impact testing.[7]

CONCLUSIONS

The addition of TCA to filled ABS had a notable influence on the electrical conductivity, electromagnetic wave absorption, and mechanical properties of CB/ABS composites. With the addition of 2 wt % TCA to the filled CB, the electrical conductivity of the CB/ABS composites was greatly improved, but its wave absorption performance was reduced. In contrast, the addition of 10 wt % TCA to the filled CB improved the wave absorption performance of the CB/ABS composites but led to poor electrical conductivity. However, regardless of the content of TCA (2 or 10 wt %), its addition greatly improved the mechanical properties of the composites. The reasons for this are that the TCA improved adhesion between the CB and the ABS resin through the formation of a chemical band between the filling and resin and the dispersion of CB in ABS resin during compression molding.

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