

Electrical Properties of Organic/Inorganic Hybrid Composites for Insulation Materials

Sangcheol Kim*, Jeong Bin Ok, Myeong Jin Ahn, Do Hyun Park, and Gun Joo Lee
Polymer Research Group, LG Cable Ltd. R&D Lab., Gyeonggi 431-080, Korea

E-mail : robo99@empal.com

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In this work, the surface of inorganic fillers were modified with some functional groups such as stearic acid, aliphatic long chain, vinylsilane and aminosilane to control the interaction between inorganic fillers and polymer matrix. Ethylene-vinyl acetate copolymers (EVA) with various amount of vinyl-acetate and copolyether-ester elastomer were used as polymer matrix. The addition of inorganic fillers increases flame retardancy, but results in steep drop of electrical and mechanical properties, which may be caused by the defects in the interface between organic/inorganic hybrid composites. The hybrid composites are found to show better mechanical properties and higher volume resistivities as inorganic fillers are well dispersed and have good adhesion with polymer matrix. Also, the most effective type of functional group coated on fillers depends on the chemical structure of polymer.

Keywords : Magnesium hydroxide, Ethylene-vinyl acetate, Insulation, Volume resistivity

1. INTRODUCTION

Ethylene vinyl acetate (EVA) copolymers are used extensively in the wire and cable industry for making heat shrinkable insulation, semi-conductive insulation jackets and flame retardant insulation[1-4]. For this purpose, high insulation resistance, good mechanical properties and flame retardancy are required. These polymers are, however, easily flammable and so flame retardancy becomes an important requirement due to their chemical constitution. This property can be achieved in several ways, especially by incorporation of additives such as aluminum or magnesium hydroxides [5-8]. The inorganic flame-retardants decompose endothermally with the release of water around the temperature at which polymers themselves decompose and do not induce the smoke and corrosive gas problems. Nevertheless, they must be used in large amounts (usually up to 60 wt%) to achieve the desired flame retardancy, which results in the loss of mechanical properties and electrical properties. Through the chemical modification of filler surface, the dispersion of inorganic fillers can be improved and the water absorption due to polar surface can be reduced. As a result, the deterioration caused by the incorporation of fillers can be overcome[9-13].

In this study, organic/inorganic hybrid composites are prepared by blending rubbery polymer and magnesium hydroxides for the application of wire and cable insulation. Ethylene-vinyl acetate copolymer (EVA) with various amount of vinyl-acetate and copolyether-ester elastomer were used as polymer matrix. The surface of inorganic fillers was chemically modified to give specific interactions with polymer matrix and the behavior of electrical and mechanical properties of composites was investigated.

2. EXPERIMENTAL

2.1 Materials

The polymers used in this study are ethylene-vinyl acetate copolymer (19 and 28% vinyl acetate by weight, EVA Dupont Co.) and copolyether-ester elastomer (TPE, keyflex 55D LG Chem.). The chemical structures are shown in Fig. 1. Magnesium hydroxides ($Mg(OH)_2$, MDH, Martinswerk Co.) are used as the additives to increase the flame retardancy and reduce the evolution of smoke during the combustion of materials. The surface of MDH was modified to have chemically-different characteristics as follows: 1) unmodified, 2) stearic acid ($CH_3(CH_2)_{16}COOH$), 3) aliphatic long chain, 4) vinyl

silane ($-\text{SiCH}=\text{CH}_2$), and 5) amino silane ($-\text{SiNH}_2$). The total content of inorganic fillers were 55 wt% for ethylene-vinyl acetate copolymer and 10 wt% for copolyether-ester elastomer.

The composites of ethylene-vinyl acetate copolymer and inorganic fillers were processed in a double roll plasticator at $50 \sim 80^\circ\text{C}$ for 30 minutes. To get the sheets ($200 \times 200 \times 1 \text{ mm}^3$) for electrical and mechanical tests, the mixtures were pressed at 170°C for 10 minutes. Copolyether-ester elastomer was mixed with inorganic fillers by twin-screw extruder (Dr Collin Co.) at 240°C and the specimens were injection-molded.

Through tubing die extrusion, the wire using conductor of 1.38 mm diameter was prepared by single-screw extruder. The insulation composites were extruded and drawn down onto the wire at the line speed of 58 m/min. The outer diameter of obtained wire was 1.98 mm when the inner diameter of the die was 2.08 mm.

2.2 Characterization

Thermal analysis

The thermal properties of composites were measured at a heating rate of $10^\circ\text{C}/\text{min}$ by using differential scanning calorimeter (DSC2910, DupontTA instruments Co.).

Morphology

The shapes of inorganic fillers were observed by using a scanning electron microscopy (S-2500C, Hitachi Co.). The samples were coated with gold-palladium and the accelerating voltage was 25kV.

Electrical properties

The 1mm-thick sheets of composites were prepared and

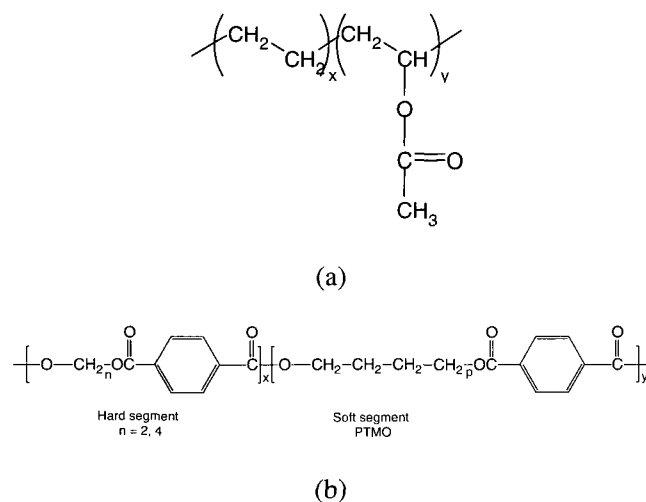


Fig. 1. The chemical structures of (a) ethylene-vinyl acetate copolymer and (b) copolyether-ester elastomer.

DC-volume resistivity ($\Omega \cdot \text{cm}$) was measured using Hewlett Packard High Resistance Meter according to ASTM D257-78. Insulation resistance is the resistance to the passage of direct current through the dielectric between two electrodes. In the case of an electric cable, insulation resistance ($\text{M}\Omega \cdot \text{km}$) is the value of resistance between the conductor and the earthed core screen, i.e. insulation materials per 1 km cable. The end of a wire specimen is connected electrically to a DC terminal and the specimen is immersed in a water bath. After 4 hr of immersion, the specimen is subjected to a potential of 500 V applied between the conductor and the water bath, which serves as the second electrode.

Mechanical properties

A dumbbell type specimen with the width of 5 mm and the gauge length of 20 mm was tested at 500 mm/min for ethylene-vinyl acetate copolymer and 50 mm for copolyether-ester elastomer by using Instron 6022. The number of specimens was at least 5.

3. RESULTS AND DISCUSSION

Figure 2 shows the scanning electron micrographs of various magnesium hydroxide (MDH) ($\times 10,000$). The unmodified MDH (Fig. 2 (a)) is very rough platelet and has large size distribution from submicron to $3 \mu\text{m}$. As shown in Fig. 2 (b) and 2 (c), when the surface of MDH is chemically modified with aliphatic long chain and amino silane, MDH becomes smooth and regular. It is more remarkable especially for aliphatic long chain-modified MDH.

Vinyl acetate content has two fundamental effects that influence the properties of EVA copolymers. The first effect is to disrupt the crystalline regions formed by the polyethylene segments of the copolymer. Low and medium density polyethylene, produced by the high pressure bulk process typically exhibit degrees of crystallinity in the range of $40 \sim 65\%$ as measured by X-ray diffraction and confirmed by differential scanning calorimetry. This crystallinity is progressively reduced by increasing VA content until, at some point between 40 and 50wt% VA, the material becomes completely amorphous. The second overriding effect of vinyl acetate content results from the polar nature of the acetoxy side chain. Thus, as the vinyl acetate content increases, so does the polarity of the copolymer. This allows better incorporation of inorganic fillers, gives greater tackiness and adhesion to most substrates, and reduces resistance to chemicals.

EVA copolymers with 19 and 28 wt% vinyl acetate have 88 and 70°C melting temperature, respectively, by DSC measurements. Figure 3 shows the DSC



Fig. 2. Scanning electron micrographs of various MDH: (a) unmodified, (b) aliphatic long chain-modified, and (c) amino silane-modified.

thermograms of EVA (28 wt%)/MDH. By addition of MDH, three peaks are observed. The higher melting peak of EVA observed at 70°C diminishes, the second sharp peak develops around 60°C and the lower peak at 48°C moves to about 40°C. Because the crystallization of EVA is prohibited by the presence of MDH, the peak temperature decreases and the shape becomes broad. As the interaction between EVA and MDH becomes stronger, this change becomes more remarkable. When the surface of MDH is modified with aliphatic long chain, the crystallization is less affected and two melting peaks are still observed.

Figure 4 shows the behavior of mechanical properties for EVA (28 wt%)/MDH. The unmodified MDH gives the lowest tensile strength and elongation, but these mechanical properties are improved as the surface of MDH is chemically modified to have functional groups such as stearic acid, aliphatic long chain, and vinyl silane. The surface of MDH is very polar and reactive due to $-OH$ group and thus the interactions between EVA and MDH are so strong as to prevent the dispersion of fillers in polymer matrix. It may cause the failure at the interface between EVA and MDH, or through MDH agglomerations. When MDH is modified with amino silane, the surface is still so polar and reactive with EVA that the dispersion cannot be improved. However, the additions of functional groups such as stearic acid, aliphatic long chain, and vinyl silane form the non-polar layer on MDH and thus, in addition to making entanglements with polymer, reduce the polarity. Consequently, these functional groups can play the role as lubricants. It results in the enhancement of the dispersion of MDH and thus improves the mechanical properties. For EVA (19 wt%)/MDH, the mechanical properties show the similar behavior in Fig. 5. But, the

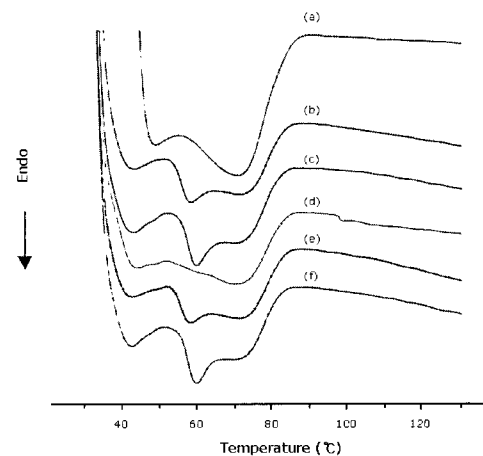


Fig. 3. DSC thermograms of (a) EVA (28wt% VA) and of hybrid composites of EVA and MDH modified with: (b) unmodified, (c) stearic acid, (d) aliphatic long chain, (e) vinyl silane, and (f) amino silane.

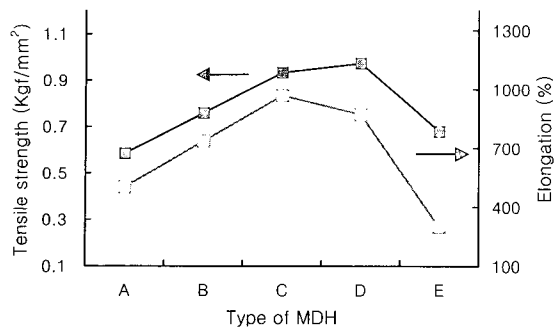


Fig. 4. Mechanical properties of hybrid composites of EVA (28wt% VA) and MDH modified with: A; unmodified, B; stearic acid, C; aliphatic long chain, D; vinyl silane, and E; amino silane.

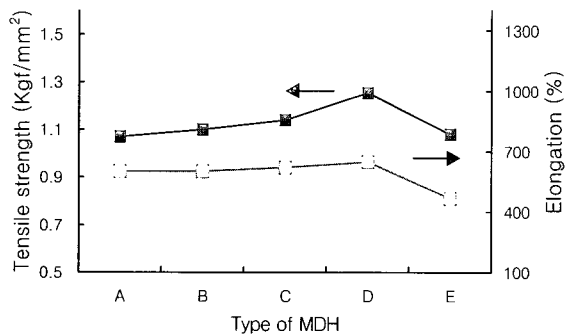


Fig. 5. Mechanical properties of hybrid composites of EVA (19wt% VA) and MDH modified with: A; unmodified, B; stearic acid, C; aliphatic long chain, D; vinyl silane, and E; amino silane.

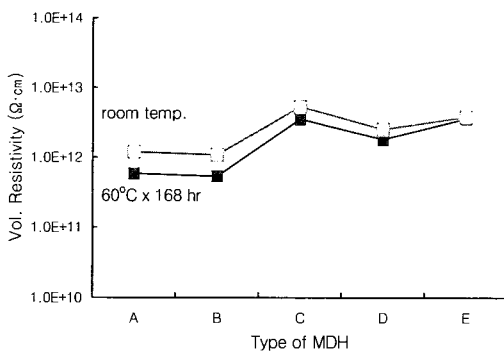


Fig. 6. Volume resistivity of hybrid composites of EVA (28wt% VA) and MDH modified with: A; unmodified, B; stearic acid, C; aliphatic long chain, D; vinyl silane, and E; amino silane.

properties are less dependent on the surface of MDH because EVA is less polar due to the small amount of VA. The adhesion between EVA and MDH becomes more important than the dispersion. As a result, to overcome the steep drop of mechanical properties by the addition

of fillers, both the dispersion and the adhesion of inorganic fillers in polymer matrix should be optimized.

The volume resistivities for 1-mm thick sheet are reported to be 2.5×10^{16} and $3 \times 10^{14} \Omega \cdot \text{cm}$ for 19% and 28% VA content, respectively. These values are reduced by the addition of MDH. Figure 6 shows the volume resistivity for MDH with the different surface characteristics. While the unmodified MDH has the lowest value, the increase of volume resistivity is brought on by the surface modification, especially by aliphatic long chain. As discussed in the above, it is speculated that the variation of volume resistivity is dependent on the surface characteristics of MDH. If the insulation organic/inorganic hybrid composites are homogenous, the volume resistivity should be determined by only volume fraction of added MDH. But, this variation means that the interface between EVA and MDH may cause the inhomogeneity in insulation composites. For EVA (28 wt%)/MDH, the polarity of MDH surface prevents the dispersion of MDH in EVA matrix and promotes local agglomeration, which results in the inhomogeneity of insulation composites. The other reason is that the polar surface of unmodified MDH gives the affinity to water. When the amino silane functional group is introduced onto MDH, the hydrophilicity is reduced and higher volume resistivity is obtained. After immersed in the water at 60°C and for 168 hr, the volume resistivity decreases and exhibits larger drop for unmodified MDH. The unmodified MDH has the surface covered with only polar -OH group and thus is very susceptible to water absorption. On the other hand, there is little change in the insulation composites of EVA and MDH modified with vinyl silane or amino silane. Figure 7 shows the similar behavior of volume resistivity for EVA (19 wt%)/MDH. Due to the low VA content, the interfacial interaction between EVA (19 wt%) and MDH is lower and the insulation composites are more affected by water absorption. Thus, compared to EVA (28 wt%), the volume resistivity is more reduced after immersed in the water. In case of vinyl silane and amino silane, it is observed that the volume resistivity is less affected by the water immersion.

As discussed above, it is very important to optimize the dispersion and the adhesion of inorganic fillers in polymer matrix for good mechanical and electrical properties. To prepare high performance and thin wall insulation, copolyether-ester elastomer (TPE) is mixed with MDH and the mechanical properties are shown in Fig. 8 according to the surface modification. TPE cannot be mixed with as much MDH as EVA and the mechanical properties decrease steeply over 20wt% MDH. In contrast to EVA, MDH modified with stearic acid or aliphatic long chain is not effective. Due to the rigid structure and less polarity of TPE, the adhesion between TPE and MDH is not enough to get high

loading of MDH and prevent the failure at the interface. Therefore, as unmodified and amino silane modified MDH are added, $-OH$ and $-SiNH_2$ group on the surface of MDH interact with ester group of TPE and thus the adhesion at the interface is improved. It results in higher tensile strength and elongation.

For 600-volt insulation cable, the minimum insulation resistance of $500 (M\Omega \cdot km)$ is required. In this case, the volume resistivity of insulation is calculated according to the following equation:

$$R = \frac{3.665}{l} \cdot \rho \cdot \log_{10} \frac{D}{d} \times 10^{-6}$$

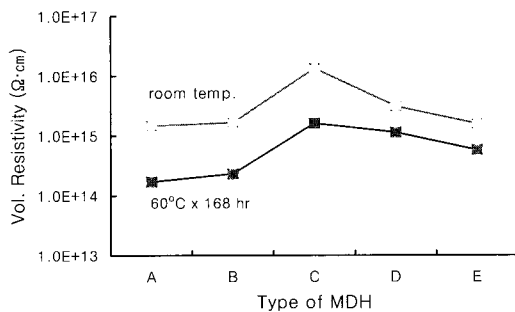


Fig. 7. Volume resistivity of hybrid composites of EVA (19wt% VA) and MDH modified with: A; unmodified, B; stearic acid, C; aliphatic long chain, D; vinyl silane, and E; amino silane.

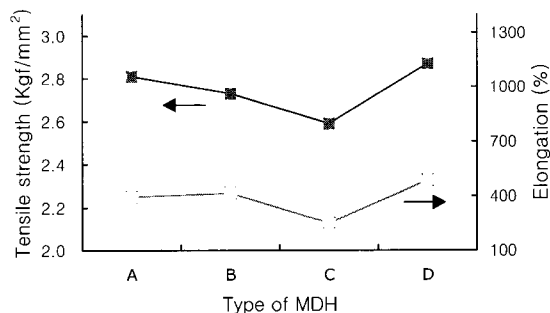


Fig. 8. Mechanical properties of hybrid composites of TPE and MDH modified with: A; unmodified, B; stearic acid, C; aliphatic long chain, and D; amino silane.

where $R (M\Omega \cdot km)$ is the insulation resistance of insulation materials, $\rho (\Omega \cdot cm)$ is the volume resistivity of insulation materials, $l (cm)$ is the length of measured cable, $d (mm)$ is the radius of conductor, and $D (mm)$ is the radius of cable.

From the results in Fig. 8, MDH with amino silane function group is found to be most effective for TPE matrix. Insulation composite of TPE and amino silane MDH (10wt%) is prepared and the cable with D of 1.98 and d of 1.38 is produced. For $R=500$, the volume

resistivity of insulation should be over 8.7×10^{13} . The volume resistivity of this insulation is measured as 6.37×10^{14} . As a result, the cable has tensile strength of 2.69 kgf/mm^2 and elongation of 413% and also satisfies the required insulation resistance as $1,200 (M\Omega \cdot km)$.

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