EPDM/Clay 컴파운드의 절연특성

Dielectric Properties of EPDM/Clay Compounds

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Abstract

In EPDM/ATH/clay compounds, clay rich compounds show lower tensile strength due to lower cure state derived from acidic nature of clay filler. As the ATH is replaced by clay, dielectric properties such as tan δ, dielectric constant and volume resistivity improve, Polar nature of ATH is responsible for the higher hot water ingress. The amount of charge in the EPDM/clay compounds increases with an increase of clay concentration.

1. Introduction

Clays are important in EPDMs and they are currently used in the production of insulating compounds for low, medium, high voltage cables and cable splices because of their excellent electrical properties. Surface modified calcined kaolins have been used to reinforce EPDM formulations for over 30 years. These specialty kaolins provide excellent electrical stability for critical requirements [1-2]. Clays are hydrated aluminium silicates from the group of natural kaolinitic clays derived from the mineral, with chemical composition $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$. For use in cable insulation based on EPDM rubbers, usually hard clay is calcined to remove bound water (of which it contains up to 14%). Calcined clay is semi-reinforcing filler and it gives rubbers a higher hardness and tensile strength and it increases electric resistance in comparison with hard clays [3].

In recent years, a considerable research effort has been directed towards the filler-EPDM elastomer using ATH or clay alone [4-7]. However, studies of the dependence of mechanical and electrical properties on both ATH and clay filled EPDM have not been reported earlier. In this study, effects of filler ratio (ATH/clay) on mechanical and electrical properties such as dielectric losses and 90℃ moisture absorption are presented. Changes of space charge depending on clay concentration are also investigated.

2. Experiment

A commercially available medium viscosity, general purpose elastomer (DuPont's Nordel 1040) was used as a base polymer. Fine particle size ATH (Sumitomo Chemical) of 1.0 ㎛ and medium particle size calcined clay (Translink 37 of Engelhard) of 1.4 ㎛ were used as main fillers. Fillers were incorporated into EPDM rubber in a continuous kneader at 80℃ for 10 min with the other additives such as paraffinic oil and wax, followed by roll-milling for another 10 min. DCP was added during the roll-mill process in order to prevent premature decomposition during the kneading process. Crosslinked samples of desired thickness were prepared by compression molding at 170℃ for 10 min using a hot press. Typical thickness of samples were 2.0 mm for mechanical tests, 1.0 mm for dielectric properties and 0.7 mm for space charge, respectively.

Two series of EPDM/clay compounding studies were conducted. For the first study, EPDM/ATH/clay compounds were formulated by gradual replacement of ATH by clay as shown in Table 1, and total amount of fillers was fixed to be 200 phr. The second study, for the purpose of the effects of a clay filler concentration in EPDM compounds on the space charge, EPDM with clay varying 0 to 200 phr were prepared.

Table 1. Main formulations of EPDM/ATH /clay compounds (particle size: ATH; 1 ㎛, clay; 1.4 ㎛)

Identification	200/0	150/50	100/100	50/150	0/200
EPDM	100				
ATH	200	150	100	50	0
Clay	0	50	100	150	200
DCP	4				

3. Results and Discussion

3.1 EPDM/ATH/Clay Compounds

Fig. 1 shows the tensile properties of EPDM filled with ATH and clay fillers. As the concentration of ATH increases and clay decreases, tensile strength increases whereas elongation at break decreases, in spite of good adhesion between polymer and clay in EPDM/clay compound. This could be explained by two cases.

One possibility is the difference of crosslinking density between ATH rich and clay rich compounds. In the peroxide curing system, acidic ingredients promote ionic breakdown of peroxide rather than free radical initiation [8], i.e. peroxide cure is inhibited by acidic components in the mixture. The acidity of clay (pH 4-6) is much greater than ATH (pH ≈10) [9]. Due to the acidic nature of clay filler, the cure state of clay filled EPDM becomes less than ATH filled EPDM. This is confirmed with the result of Oscillating Disk Rheometer (ODR) tests (Fig. 2).

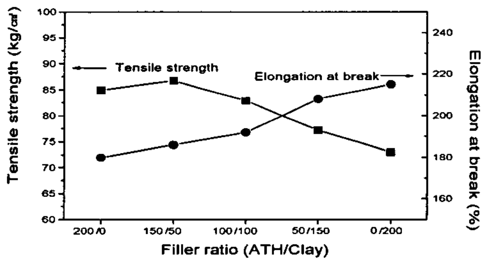

Fig. 1 Effects of filler ratio (ATH/clay) on mechanical properties of EPDM compounds

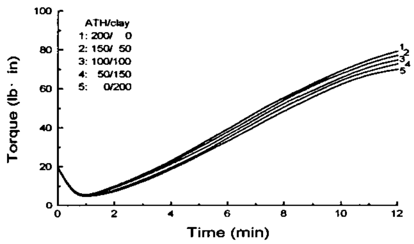

Fig. 2 ODR graphs of EPDM compounds having ATH and clay fillers (Set temperature: 175℃, arc: 3°)

As the clay filler is replaced by ATH, a maximum torque becomes higher, thus the cure state becomes higher. Therefore, as the amount of ATH filler increases, tensile strength increases and elongation at break decreases in EPDM/ATH/clay compounds. The other possibility is the difference of particle size between clay and ATH filler. Larger particle size for the clay could produce less uniform distribution in cross section, leading to smaller tensile strength.

Table 2 shows the change of hardness and specific gravity in EPDM/ATH/clay compounds as a function of filler ratio. Due to the difference of the filler hardness (Mohs, ATH; 2.5~3.5, clay; 6~8) [9], clay filled compounds become harder. Specific gravity also increases as a result of difference of the gravity of the fillers (ATH; 2.42, clay; 2.63

[9]).

Table 2 Changes of hardness and specific gravity as a function of filler ratio (ATH/clay)

Sample	200/0	150/50	100/100	50/150	0/200
Hardness (Shore A)	75	77	77	78	79
Specific gravity	1.491	1.504	1.510	1.519	1.547

Changes of dielectric losses and volume resistivity before and after hot water immersion are shown in Fig. 3 to 5. In the case of non-immersed samples, as the amount of ATH increases and the amount of clay decreases, tan δ and dielectric constant increase, whereas volume resistivity decreases. This could be explained by the polar nature of ATH derived from the hydroxyl group in ATH. In the case of only clay filled EPDM compounds, it has been reported that the clay filler affects electrical conductivity of filled EPDM [4, 6, 7]. They observed that the clay filler caused mainly interfacial polarization resulting in increase of conductivity in EPDM compounds. Therefore, it cannot be said that clay filler does not affect the electrical properties of EPDM compounds. Thus, it can be said that ATH provides the polarity in EPDM compounds leading to marked decrease of dielectric properties, which overwhelms the interfacial polarization to encourage the decrease of dielectric properties in EPDM/clay compounds.

Dielectric properties drastically reduced as a result of 90℃ hot water immersion for 200 h, this tendency accentuates in EPDM compounds having larger concentration of ATH. It can be explained by that the polarity of ATH tends to increase water absorption of filled EPDM, leading to reduce their dielectric properties.

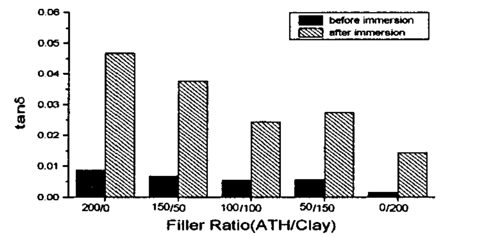

Fig. 3 Change of tan δ before and after immersion in 90℃ hot water

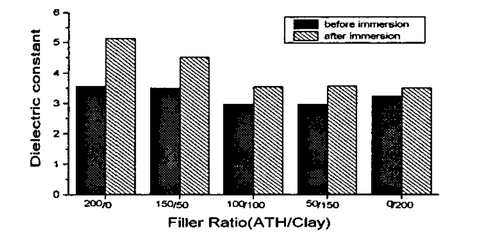

Fig. 4 Change of dielectric constant before and after immersion in 90℃ hot water

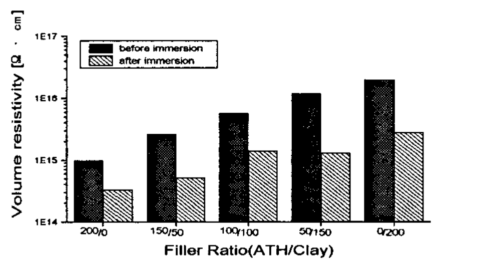

Fig. 5 Change of volume resistivity before and after immersion in 90℃ hot water

3.2 Charge Formation in EPDM/Clay Compounds

The presence of space charges in the insulation bulk and/or at insulation-electrode interfaces can affect considerably the electric field distribution, and, in turn, a field concentration can locally induce accelerated damage able to trigger early insulation breakdown [10-12]. Of course, in addition to space-charge accumulation, the cause of breakdown is mainly assigned to manufacturing features, such as the presence of contaminants, voids, protrusions and defects able to trigger localized degradation process such as PD (partial discharge) and electrical treeing [13, 14]. Recently works looking more carefully at the contribution of space charges to insulation damage have acquired more interest, because extra-clean, dry-cured materials are now being used in insulation systems [15].

As shown in Fig. 6, the amount of charge in the EPDM containing clay increases with the increase of clay concentration, which agrees well with the previous observation. Yin et al. [16, 17] have reported that charge increases when fillers such as kaolin and clay are added to LDPE (low density polyethylene). A similar result was observed by Jeffery and Damon [7] for a mixture composed of clay and EPDM.

For this reason, the increase of space charge due to clay could be explained by the enhancement of interfacial polarization, i.e. enhanced trapping of injected charge at the interface between EPDM and clay. As illustrated in Fig. 7 [6], an increase of the filler concentration brings about an increase of trap density at the interface.

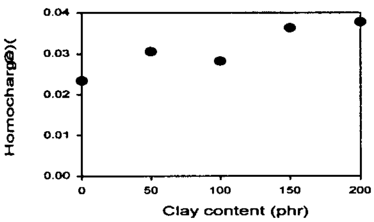

Fig. 6 Charge in EPDM/clay compounds as a function of clay concentration

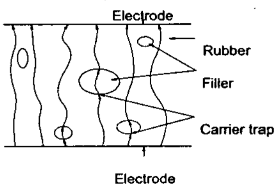

Fig. 7 The simple model for the charge trapping in polymer/filler interfaces [6]

4. Conclusions

For the EPDM/ATH/clay compounds, mechanical reinforcing effect is prominent at a lower clay level, i.e. higher ATH level. This is explained by retardation of vulcanization in EPDM compounds due to inherent acidic nature of clay filler. Tracking resistance improves, whereas dielectric properties decrease with increasing ATH levels. For the EPDM with a higher ATH filler level, it is also obtained that dielectric properties markedly decrease when immersed in 90℃ hot water. This is attributed to the increase of water absorption derived from the polar hydroxyl group (-OH) in ATH. In only clay filled EPDM compounds, the amount of charge increases with an increase of clay concentration.

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