

Water Treeing, AC Breakdown, and Dielectric Loss Characteristics of EVA-OH as a Function of Conversion Rate

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Received 26 August 2003; accepted 23 May 2005

DOI 10.1002/app.22840

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Four kinds of ethylene–vinyl acetate–vinyl alcohol (EVA–OH) terpolymers containing different contents of hydroxyl groups were prepared using the transesterification reaction between a ethylene–vinyl acetate (EVA) copolymer and alcohol. Structural and thermal analyses of the EVA–OH produced were performed with Fourier transform infrared spectroscopy and differential scanning calorimetry. Electrical properties such as water treeing, AC breakdown, and dielectric loss characteristics were investigated. It was found that both water tree length and the probability of water tree generation decreased as a function of hydroxyl group content. AC breakdown characteristics

such as average breakdown strength and characteristic breakdown strength (breakdown probability = 63.2%) of EVA improved as a function of the conversion rate of EVA–OH from acetate to hydroxyl groups. Dielectric loss increased with hydroxyl group content in the low-frequency range. In contrast, it was observed that dielectric loss decreased with hydroxyl group content in the high-frequency range. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 420–424, 2006

Key words: graft copolymer; dielectric properties; FTIR; differential scanning calorimetry; melting point

INTRODUCTION

In recent years most power cables have been insulated with polymeric materials. Among those materials, polyethylene has been extensively adopted as a major insulating material of power cables because of its great electrical and mechanical strength in electrical insulation. However, long-term operation using this type of insulation results in degradation problems such as water treeing and leads to electrical breakdown. Therefore, the development of polyethylene with better resistance to water treeing has been one of the major subjects of investigation of most materials scientists working in the field of electrical insulation. Efforts to achieve this improved resistance began with the use of additives such as voltage stabilizers or other chemicals, which was followed by the use of polymer blends. Recent studies have focused on developing new insulating materials by copolymerization or grafting.^{1–5}

Ethylene–vinyl acetate (EVA) is a polymeric material that has good toughness and high impact strength. Therefore, it is known that EVA retards water treeing when this material is blended with polyethylene.^{2,6}

However, because it has a bulky acetate group, EVA has a melting temperature that is so low that it has poor thermal resistance. In addition, the applications of EVA to blending are limited because EVA increases $\tan \delta$, representing dielectric loss. The melting temperature of EVA can be elevated through the transesterification reaction between EVA and alcohol.⁷ The ethylene–vinyl alcohol (EVOH) copolymer resulting from the full hydrolysis of EVA is an excellent barrier to gases and hydrocarbons and has outstanding chemical resistance. However, it is believed that this material is not appropriate for use as a component of blending with polyethylene for insulating materials of power cables because it has too high a melting temperature and is too brittle. Moreover, EVOH containing only hydroxyl groups could be affected by moisture because hydrogen bonds by hydroxyl groups between molecules would be intercepted by water.⁸

In light of this background, in the current study four kinds of ethylene–vinyl acetate–vinyl alcohol (EVA–OH) terpolymers with varying hydroxide contents were prepared through partial conversion of the acetate group in EVA into a hydroxyl group. Electrical properties of these four types of EVA–OH, such as water treeing, AC breakdown, and dielectric loss characteristics, were investigated in order to examine the possibility of their application to insulating materials.

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EXPERIMENTAL PROCEDURES

Preparation of samples

The EVA-OH used in this study was prepared using the transesterification reaction between EVA and alcohol. This EVA, a Dupont product, has a VA content of 28%. 1-Octanol (reagent grade, Junsei Chemical) was used, and sodium methoxide (Aldrich) was added as a catalyst. First, sodium methoxide/1-octanol solutions in ratios of 1 : 6 and 1 : 9 were prepared. These solutions were mixed with EVA at 130°C for 15 min using a batch-type kneader. The amount of solution added was 10, 20, or 30 g for the 1 : 6 sodium methoxide/1-octanol and 40 g for the 1 : 9 sodium methoxide/1-octanol. Residual alcohol and catalyst were extracted in 40°C ethanol for 48 h, and the washed EVA-OH was dried at 50°C for 48 h in a vacuum oven.

Characterization of samples

Structural and thermal analyses of the EVA-OH were accomplished with Fourier transform infrared spectroscopy (FTIR) and differential scanning calorimetry (DSC), respectively.

We obtained FTIR spectra with a resolution of 2 cm^{-1} using an Avatar 320 instrument (Nicolet Co.). Thirty-two scans were averaged in each measurement. Specimens were prepared in the form of thin films about $100\text{ }\mu\text{m}$ thick using a hot press.

Thermal analysis of EVA-OH was carried out using DSC with a TA 2910. The heating rate was $10^\circ\text{C}/\text{min}$, and the value of a second scan was calculated in order to eliminate thermal history. Measurements were performed in a nitrogen environment.

Water-treeing test

The water-treeing test was performed under specific conditions—ac voltage of 4 kV, 1 kHz, for 162 h at room temperature. The electrolyte was 0.2M AgNO_3 (silver nitrate) aqueous solution. The AgNO_3 solution was used as a liquid electrode to accelerate the growth of water trees in polymer specimens. The water trees grown in the AgNO_3 solution could be colored spontaneously during their formation, their areas were brownish-yellow, and they grew fast. A water tree grown in AgNO_3 solution was conveniently called a "silver tree."⁹ A schematic diagram of the water-treeing test is shown in Figure 1. Specimens that had eight cone-shaped indentations were prepared by compression molding at 130°C for 10 min using a hot press.

The samples having water trees were observed using an optical microscope. The averaged value of eight indentation measurements was taken as the water tree length.

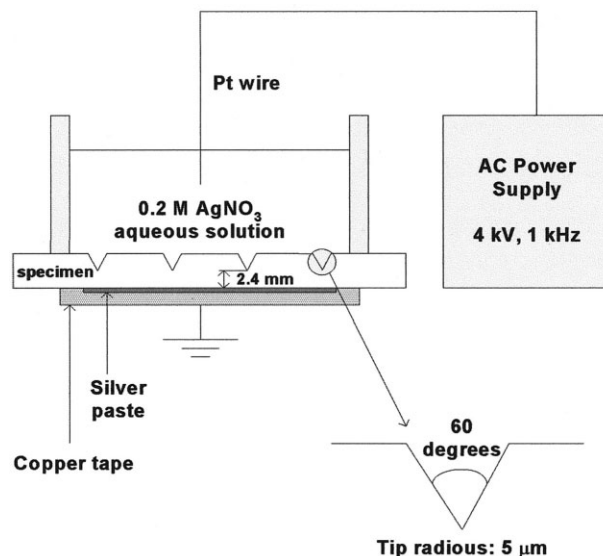


Figure 1 Schematic representation of test cell for water-treeing test.

AC breakdown test

EVA and the four kinds of EVA-OH were made into thin films about $200\text{ }\mu\text{m}$ thick for the ac breakdown test using a hot press at 130°C for 10 min. The electrode was spherical, and breakdown happened at the center of the sample. All tests were carried out at 1 kV/s in an insulating oil bath.

Measurement of dielectric loss

To examine the dielectric loss characteristics of EVA and the four kinds of EVA-OH, we measured the $\tan\delta$ of each sample. The film specimen was about $200\text{ }\mu\text{m}$ thick and prepared using a hot press at 130°C. DETA (broadband dielectric thermal analyzer; Novocontrol GmbH) was used for measuring $\tan\delta$. Measurements were made in the range of 1–1E7 Hz at room temperature.

RESULTS AND DISCUSSIONS

FTIR and DSC

Figure 2 shows the FTIR spectra of EVA and EVA-OH. The different intensity of the broad peak in the region between 3100 and 3600 cm^{-1} , which was attributed to hydrogen-bonded OH stretching vibrations, resulted from the different hydroxyl group contents of the samples. Ester carbonyl group of vinyl acetate has its own characteristic peak at around 1740 cm^{-1} and this peak decreased concurrently as the peak in the region between 3100 and 3600 cm^{-1} , which is an indication of the transesterification reaction between EVA and alcohol being successfully accomplished.

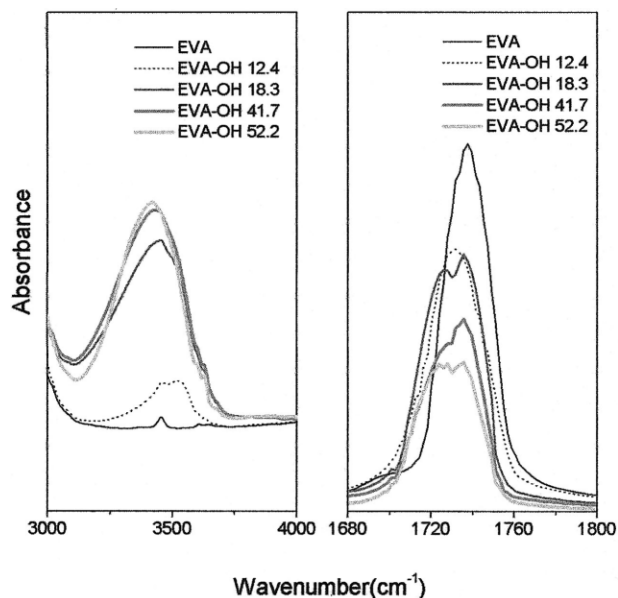


Figure 2 FTIR spectra of EVA and the four kinds of EVA-OH.

Using the area of this peak centered at around 1740 cm^{-1} as a measure of vinyl acetate content, we were able to calculate the conversion rate of EVA-OH from acetate to hydroxyl groups as follows¹⁰:

$$\text{Conversion rate (\%)} = 100 \times \frac{\text{corrected peak area of EVA-OH}}{\text{corrected peak area of EVA}} \times 100$$

The results of thermal analysis using DSC showed that the melting temperature of EVA-OH was elevated as a function of the amount of the sodium methoxide/octanol solution.

Table I shows the conversion rate of EVA-OH from acetate to hydroxyl groups and the melting temperature as a function of the amount of the added sodium methoxide/octanol solution.

Water tree characteristics

Figure 3 shows the water tree lengths of EVA and the four kinds of EVA-OH. As shown in Figure 3, it was

TABLE I
Conversion Rate and Melting Temperature of EVA and EVA-OH as a Function of Amount of Added Sodium Methoxide/Octanol Solution

Amount of sodium methoxide/octanol solution (g)	0	10	20	30	40
Conversion rate (%)	0	12.4	18.3	41.7	52.2
Melting point (°C)	71.7	75.3	80.1	86.6	91.9

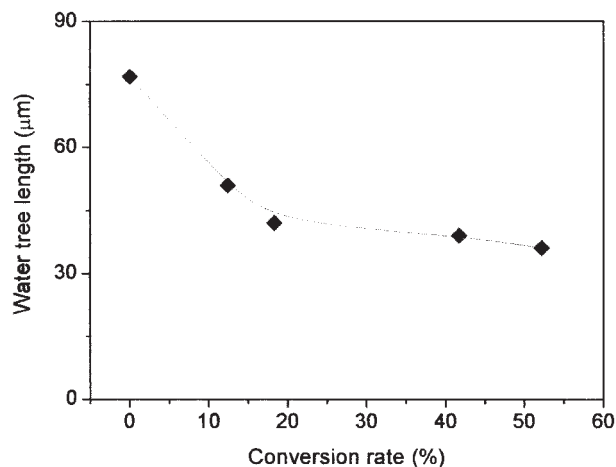


Figure 3 Water tree lengths of EVA and the four kinds of EVA-OH as a function of conversion rate.

found that the resistance to water trees of EVA and EVA-OH was much higher than that of conventional polyethylene, in which water trees should grow up to nearly $1000\text{ }\mu\text{m}$ under the same conditions. With EVA, the length of the average water tree was $76.9\text{ }\mu\text{m}$. With EVA-OH, the water tree length decreased as a function of the conversion rate of EVA-OH from acetate to hydroxyl groups and was $36\text{ }\mu\text{m}$ in EVA-OH 52.2. Moreover, water trees appeared at all eight cone-shaped indentations in EVA, but water trees were generated at only 2–3 cone-shaped indentations in EVA-OH. So we were able to confirm that the probability of water tree generation also decreased. Therefore, it was believed that the conversion of acetate into hydroxyl groups using the transesterification reaction had an effect on the increase in resistance to water treeing. The improved water tree characteristics of EVA-OH could be attributed to the increase in hydrophilicity by the introduction of hydroxyl groups.¹¹ It is known that polymeric material that has reduced hydrophobicity, which reduces the tendency of water to condense from the bulk dielectric into electro-oxidized regions, restraining the initiation and growth of water trees.¹² Another reason could be that EVA-OH contains hydroxyl groups provided by the vinyl alcohol segments and thought to generate inter- and intramolecular bonding via hydrogen bonds. These hydrogen bonds block the amorphous fraction of the material by decreasing the fractional free volume available for diffusion, and therefore impede the permeation process of gases and hydrocarbons.⁸ Although the hydrogen bonds between polymer molecules can be weakened by water molecules,¹³ it is thought that the extra force from hydrogen bonds plays a role in the retardation of water treeing. Figure 4 shows the images of water trees generated in EVA and the four kinds of EVA-OH.

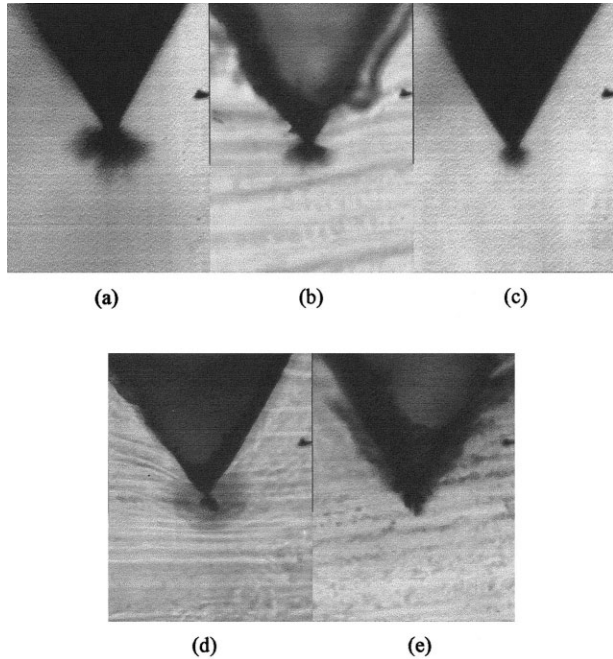


Figure 4 Images of water trees generated in EVA and the four kinds of EVA-OH: (a) EVA, (b) EVA-OH 12.4, (c) EVA-OH 18.3, (d) EVA-OH 41.7, and (e) EVA-OH 52.2

AC breakdown characteristics

AC breakdown strength of EVA and the four kinds of EVA-OH together with the Weibull statistical analysis results are summarized in Table II. As shown, only with minimum breakdown strength (breakdown probability = 1%) did EVA and the four kinds of EVA-OH show similar values; on the other hand, when the breakdown strength and characteristic breakdown strength was average (breakdown probability = 63.2%), the four kinds of EVA-OH had higher values than EVA. It also was found that average breakdown strength and characteristic breakdown strength of the four kinds of EVA-OH increased as a function of the conversion rate, as with resistance to water treeing. The minimum breakdown strength, average breakdown strength, and characteristic breakdown strength of EVA and the four kinds of EVA-OH are shown in Figure 5. Even though many factors

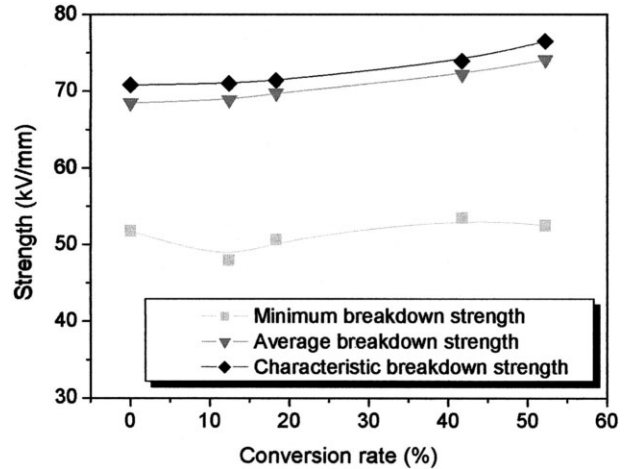


Figure 5 Minimum breakdown strength, average breakdown strength, and characteristic breakdown strength of EVA and the four kinds of EVA-OH as a function of conversion rate.

influenced breakdown strength, it seems certain that modification of material through the introduction of hydroxyl group improves the AC breakdown characteristics of EVA.

Dielectric loss characteristics

Figure 6 displays the $\tan \delta$ curves of EVA and the four kinds of EVA-OH as a function of frequency of 1–1E7 Hz at room temperature. As shown in the result, $\tan \delta$ curves of the four kinds of EVA-OH were similar to that of EVA, and the position of curve was elevated as the hydroxyl group content introduced increased in the range of 1–3E5 Hz. In contrast, the order of $\tan \delta$ values was reversed in the range of 3E5–1E7 Hz. In a previous work, it was found that the conductivity of EVA-OH increased with the introduction of hydroxyl groups.¹⁴ In a low-frequency range (1–3E5 Hz), the dielectric loss from conduction could be the main factor that determined the position of the $\tan \delta$ curve. On the other hand, it seems that the dielectric loss by the acetate group dominated in the high-frequency range (3E5–1E7 Hz). In Figure 7, the $\tan \delta$ values of materials at 60 Hz and 1E6 Hz are compared.

TABLE II
Strength of AC Breakdown of EVA and EVA-OH with Results of Weibull Statistical Analysis

Sample	Average strength (kV/mm)	Weibull characteristic strength (kV/mm)	Weibull minimum strength (kV/mm)	Weibull shape parameter
EVA	68.7	70.8	51.8	2.63
EVA-OH 12.4	68.9	71.0	48.0	1.65
EVA-OH 18.3	69.8	71.4	50.7	2.29
EVA-OH 41.7	72.2	73.9	53.5	3.02
EVA-OH 52.2	74.1	76.5	52.5	3.37

CONCLUSIONS

The four kinds of EVA-OH were prepared through the partial conversion of the acetate group in EVA into a hydroxyl group. The electrical properties of these materials such as water treeing, AC breakdown, and dielectric loss characteristics were investigated, and the following conclusions were drawn from the experimental results:

1. By FTIR analysis, we were able to confirm that the partial substitution of the acetate group in EVA to a hydroxyl group occurred and to calculate the conversion rate. From the DSC results, we found that the melting temperature of EVA-OH was increased as a function of the amount of the sodium methoxide/octanol solution.
2. It was verified that the resistance of EVA to water treeing was improved by the introduction of the hydroxyl group. It was found that both water tree length and the probability of water tree generation decreased as a function of the content of the hydroxyl groups introduced. These improved characteristics could be attributed to the increase in hydrophilicity and hydrogen bonding.
3. It seems certain that the modification of material through the introduction of hydroxyl groups improved the AC breakdown characteristics such as average breakdown strength and characteristic

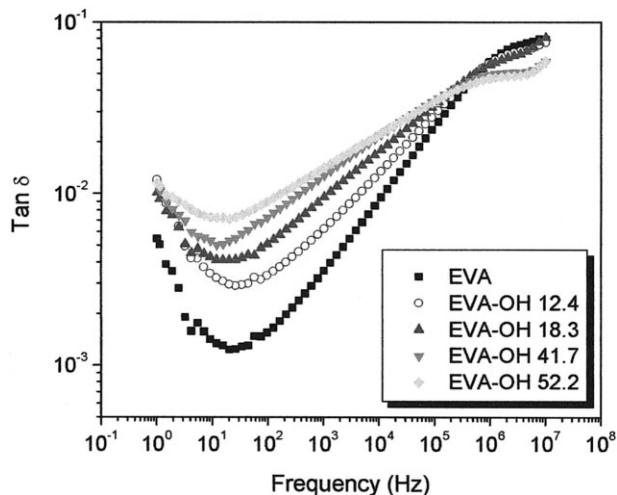


Figure 6 Frequency dependence of dielectric loss tangent of EVA and the four kinds of EVA-OH.

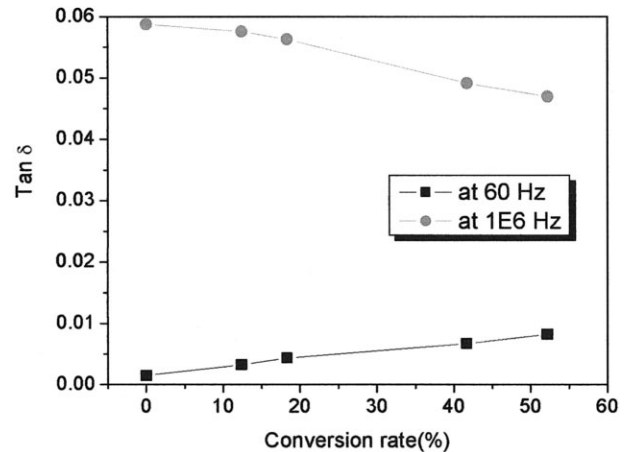


Figure 7 Comparison of dielectric loss tangent at 60 and 1E6 Hz as a function of conversion rate.

breakdown strength (breakdown probability = 63.2%) of EVA.

4. Dielectric loss increased with hydroxyl group content in the low-frequency range. In contrast, it was observed that dielectric loss decreased with hydroxyl group content in the high-frequency range.

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