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ELECTRICAL PROPERTIES AND THERMAL OXIDATIVE AGING STABILITY OF THE EVA/SILICA NANOCOMPOSITES USING EVAgMA COMPATIBILIZER

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ABSTRACT

The ternary nanocomposites based on ethylene-vinyl acetate copolymer (EVA, 18 % vinyl-acetate group) without and with 1wt.% of EVAgMA (EVA - grafted - maleic anhydride) and 2 – 5 wt.% of nanosilica were prepared by melt mixing in a Haake intermixer at 160 °C, roto speed of 50 rpm for 5 minutes. The volume resistivity, dielectric breakdown and dielectric loss of the nanocomposites were measured in according to ASTM D257, D149 and D150, respectively. The nanocomposites were tested in a hot air circulating oven at 70°C for 168 hours to investigate thermal oxidation aging stability. The obtained results showed that nanosilica decreased volume resistivity and dielectric loss of the nanocomposites but it increased dielectric breakdown of EVA. The dielectric constant of the EVA/EVAgMA/silica nanocomposites is lower than that of the EVA/silica nanocomposites. The EVA/silica nanocomposites without and with EVAgMA are good electrical insulation materials (volume resistivity in the range of 10^{13} - 10^{14} Ω.cm, dielectric loss of about 10^{-3} and dielectric breakdown in the range of 22.1 - 26.7 kV/mm). The percentage of retention in mechanical properties of the EVA/EVAgMA/silica nanocomposites is higher than that of EVA. FTIR analyses of the nanocomposites before and after thermal oxidation aging indicated that nanosilica and EVAgMA limited to degradate EVA macromolecules.

Keywords: nanosilica, ethylene-vinyl acetate copolymer, EVAgMA, resistivity, dielectric loss, dielectric breakdown.

1. INTRODUCTION

Recently, polymer/silica nanocomposites have been attracted a great deal of researchers interest [1 - 2]. However, there are relatively a few studies related to ethylene - vinyl acetate copolymer (EVA)/nanosilica nanocomposites in some literatures [3 - 5]. In our previous studies [6 - 9], EVA/silica nanocomposites prepared by melt mixing in Haake intermixer were investigated and their morphology and some properties were characterized. The obtained results showed that nanosilica can improve the mechanical properties, thermal stability and UV-thermo-humidity complex resistance of EVA [6 - 9]. In addition, emphatic enhancement in some properties of EVA/silica nanocomposites could be achieved when using 1 - 1.5 wt.% (compared with EVA weight) of EVAgMA [7 - 9].

In order to apply the EVA/silica nanocomposites for insulation materials, the electrical properties and thermo-oxidation degradation stability of the nanocomposites were thoroughly examined. The effect of nanosilica and EVAgMA on these properties of the nanocomposites were also investigated and discussed.

2. EXPERIMENTAL

2.1. Materials

Ethylene - vinyl acetate copolymer (EVA) containing 18 wt.% vinyl acetate, with brand name Taisox 7350M, density of 0.983 g/cm^3 at 23 °C and melt flow index of 2.5 g/10 min (at 190 °C / 2.16 kg) was purchased from Taiwan. EVA-grafted-maleic anhydride (EVAgMA) with MA content of 0.5 wt.% was suplied by Hanwha Company (South Korea). Nanosilica powder, with a content of 99.8 % SiO_2, the average particle diameter of 12 nm and specific surface area of 175 - 225 m^2/g was supplied by Sigma-Aldrich Co.

2.2. Preparation of EVA/silica nanocomposites in the presence or absence of EVAgMA

EVA/silica nanocomposites containing 2, 3, 4 and 5 wt.% of nanosilica, in the presence or absence of EVAgMA (0, 0.5, 1, 1.5 and 2 wt.%) (both in comparison with EVA weight) were prepared by melt mixing in a Haake internal mixer at 160 °C for 5 minutes [5]. Immediately after melt mixing, the nanocomposites were hot-pressed by a compressor in melting state at 160 °C with the pressure of about 12 - 15 MPa into about 1 - 1.2 mm-thickness sheets. The plate samples were kept at least 24 hours in standard conditions before characterizations. The samples of EVA/silica nanocomposites without and with EVAgMA were denoted as: EVAsilX and EVAsilXg, respectively, where X is nanosilica content. The EVA sample containing 1 wt.% EVAgMA was denoted as EVAg.

2.3. Characterizations and methods

Dielectric constant and dielectric loss of the nanocomposites were determined by a type TR-10C set (ANDO, Japan), according to ASTM D150 at frequencies of 1 kHz. Volume resistivity of the nanocomposites was measured by I-V method, according to ASTM D257 using vibrating reed electrometer TR-8401 (Takeda, Japan), DC applied voltage of 100V. Dielectric breakdown of the nanocomposites was measured in accordance with ASTM D149 at 25 °C, 60 % relative humidity, using AC 50 Hz voltage by the increment of 1 kV/second.

Thermo-oxidation aging experiment was tested for EVA and the EVA/silica nanocomposites in a hot air circulating oven at 70 °C for 168 hours according to TCVN 6614-1-2:2008. Then, the samples were kept in standard conditions for at least 16 hours before carrying out mechanical property and FTIR characterization. The thermo-oxidation aging stability of the samples was evaluated by the percentage retentions of tensile strength and elongation at break of the samples after aging in comparison with the initial samples.

The nanocomposites films were analyzed by Fourier Transform Infrared (FTIR) using a spectrometer (Nicolet/Nexus 670, USA) in the range of 4000 - 400 cm^{-1} with resolution of 4 cm^{-1} and 16 scans.

The mechanical properties (tensile strength and elongation at break) of the EVA/silica nanocomposites before and after thermo-oxidation aging were determined by using a Zwick-I tensile tester at room temperature with a crosshead speed of 100 mm/min, according to ASTM D638.

3. RESULTS AND DISCUSSION

3.1. Electrical properties

3.1.1. Dielectric constant and dielectric loss

The variation of dielectric constant of EVAsilX and EVAsilXg nanocomposites as function of nanosilica content is represented in Figure 1. It can be seen that nanosilica increases the dielectric constant of EVAsilX and EVAsilXg nanocomposites. This is simply recognized that dielectric constant of nanosilica (3.9 - 4.5) is larger than that of EVA (2.305) or EVAg (2.310) [10]. Remarkably, all dielectric constant values of EVAsilXg nanocomposites are smaller than those of EVAsilX at the same nanosilica content (X in wt.%). This is caused by the presence of EVAgMA facilitated the formations of hydrogen bonds and bipolar interactions between siloxane groups (Si–O–Si) at the surface of nanosilica particles and C=O, C–O groups of EVAgMA [7]. Therefore, in some polymer segments where hydrogen bonds and bipolar interactions took place, the free movements of these segments have been restricted despite the presence of alternative electrical field. This phenomenon reduces the dielectrical permeability of EVAsilXg nanocomposites [1, 2, 10].

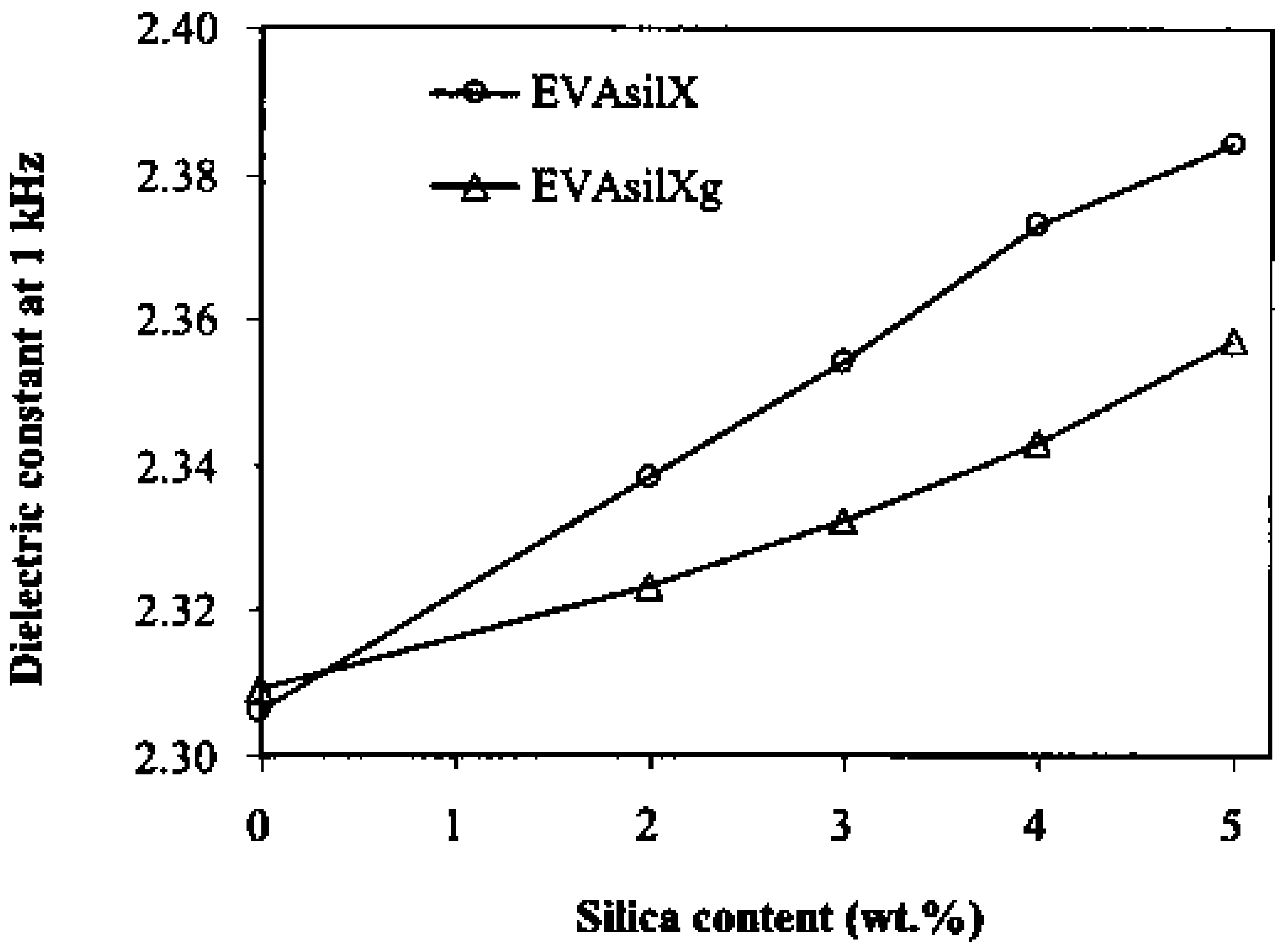

Figure 1. Dielectric constant of EVAsilX and EVAsilXg nanocomposites.

Table 1 shows that the dielectric loss of EVAsilX nanocomposites are increased with increasing nanosilica content. The above properties of EVAsilX are also increased in presence of EVAgMA (EVAsilXg samples). Thanks to numerous silanol groups on the surface of silica nanoparticles can reduce the electrical resistance of EVA matrix leading to increase in the dielectric loss of EVA. Nevertheless, with very small values of dielectric loss, the nanocomposites are good electrical insulation materials. Table 1 also indicates that EVAgMA plays a role in decrease of the dielectric loss for EVAsilX nanocomposites. This relates to the formation of the hydrogen bonds and bipolar interaction which decrease the mobility of dipole moments and charge carriers in the nanocomposites as aforementioned.

Table 1. Dielectric loss of EVAsilX and EVAsilXg nanocomposites.

Nanosilica content X (wt.%)	Dielectric loss	
	EVAsilX	EVAsilXg
0	0.0037	0.0024
2	0.0038	0.0032
3	0.0039	0.0034
4	0.0039	0.0037
5	0.0040	0.0038

3.1.2. Dielectric breakdown

As seen in Table 2, the dielectric breakdown (E_b) of EVAsilX and EVAsilXg nanocomposites is higher than that of neat EVA and reaches to maximum values at nanosilica contents of 2 and 3 wt.%, respectively (with the enhancement of 9.5 % and 20.8 % in comparison with E_b of EVA). This is a remarkable difference between the polymer nanocomposites and the conventional polymer composites containing micro-size fillers. Roy M., et al. [10] have explained that nanosilica can reduce defects in polymer matrix and increase the electron scattering at interfacial sites of the nanocomposites. In this study, nanosilica can disperse regularly in the EVA matrix at the content smaller than 3 wt.%. For this reason, EVA/silica nanocomposites exhibit dielectric breakdown higher than neat EVA. However, when nanosilica content is over than 3wt.%, the dielectric breakdown of EVAsilX, EVAsilXg nanocomposites tends to decrease because of the agglomeration of silica nanoparticles. Therefore, bigger - size silica particles disperse not regularly in EVA matrix and are easy to form defects in the nanocomposites.

Table 2. Dielectric breakdown of EVAsilX and EVAsilXg nanocomposites.

Nanosilica content X (wt.%)	Dielectric breakdown (KV/mm)	
	EVAsilX	EVAsilXg
0	22.1	22.1
2	24.4	24.5
3	23.7	26.7
4	23.5	24.2
5	22.2	22.5

3.1.3. Volume resistivity

It is can be seen from Table 3 that volume resistivity of EVAsilX and EVAsilXg nanocomposites is gradually decreased with rising nanosilica content up to 5wt.%. This is due to the hydrophilic surfacial silanol groups of nanosilica can absorb the moist directly from natural air. The phenomenon is hardly avoided in keeping and preparation of the nanocomposites. Moreover, the increase of nanosilica content can lead to the closer connection between silica nanoparticles whose conductivity is higher than that of insulating polymer [2, 11]. As a result, the electrical resistivity of EVAsilX and EVAsilXg nanocomposites decreases as a function of nanosilica content. However, the volume resistivity values of these nanocompostes are relatively high enough (10^{13} - 10^{14} Ω.cm) for electrical insulation materials.

Table 3. Volume resistivity of EVAsilX and EVAsilXg nanocomposites.

Nanosilica content X (wt.%)	Volume resistivity (Ω.cm)	
	EVAsilX	EVAsilXg
0	7.62×10^{14}	-
2	2.85×10^{14}	4.10×10^{14}
3	2.17×10^{14}	3.34×10^{14}
4	6.80×10^{13}	2.39×10^{14}
5	5.30×10^{13}	1.93×10^{14}

3.2. Thermal oxidative aging stability

3.2.1. FTIR spectra of the nanocomposies before and after thermal oxidative aging

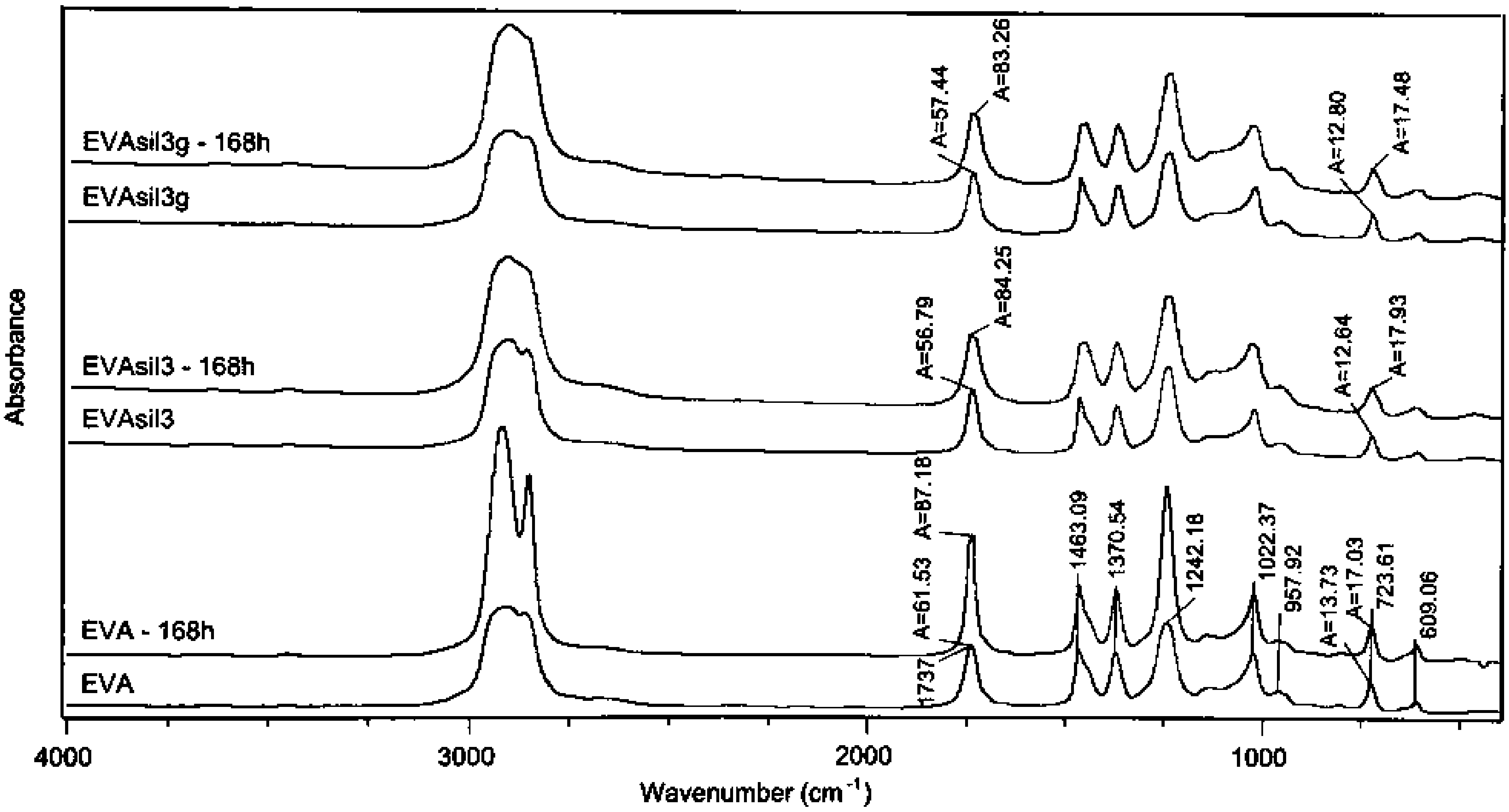

Figure 2. FTIR spectra of EVA and EVAsil3, EVAsil3g before and affter thermal oxidative aging.

Figure 2 displays the FTIR of EVA and EVAsil3, EVAsil3g nanocomposites before and after thermal oxidative aging at 70 °C for 168 hours. For assessment of the thermal oxidative aging stability, the carbonyl index (CI) is evaluated by the ratio between the absortion peak area of C=O groups around 1737 cm^{-1} (A_{1737}) and that of CH_2 groups around 723 cm^{-1} (A_{723}) in each FTIR spectrum. The obtained results are listed in Table 4. It is clear that CI values of unaged EVA and unaged nanocomposites are relatively equal to each other. After thermal oxidative aging, the CI index of EVA and the nanocomposites increases in comparison with initial values because of the generation of new C=O groups such as ketone, lactone and acetaldehyde under thermal oxidation [12]. However, the CI value of EVA is larger than that of the EVAsil3 and the smallest CI value is gained for EVAsil3g nanocomposites. This means that the amount of C=O groups formed in aged EVA is higher than that of aged EVAsil3 or aged EVAsil3g nanocomposites. It can be explained that silica nanoparticles have acted as barriers which limit the permeability of oxygen into the EVA matrix, while EVAgMA improves the interfacial interaction between nanosilica and EVA matrix leading to reduce degradation of EVA.

Table 4. Carbonyl index (CI) of EVA and EVAsil3, EVAsil3g nanocomposites before and after thermal oxidative aging.

Materials	$CI = A_{1737}/A_{723}$
Unaged EVA	4.481
Aged EVA	5.119
Unaged EVAsil3	4.493
Aged EVAsil3	4.698
Unaged EVAsil3g	4.488
Aged EVAsil3g	4.657

Table 5. The thermal oxidative aging coefficients Hσ và Hε of EVAsilX and EVAsilXg nanocomposites.

Nanosilica content X (wt.%)	Hσ (%)		Hε (%)	
	EVAsilX	EVAsilXg	EVAsilX	EVAsilXg
0	92.5	-	89.7	-
2	94.5	97.0	90.8	91.3
3	96.4	97.7	91.5	91.7
4	95.7	97.2	93.4	93.9
5	94.6	97.2	94.4	95.7

3.2.2. Mechanical properties of the nanocomposites before and after thermal oxidative aging

The thermal oxidative aging stabilty of the nanocomposites is assessed in terms of the variation coefficients of tensile strength (Hσ) as well as elongation at break (Hε) of the aged nanocomposites to the unaged nanocomposites. The results are represented in Table 5. It can be seen that the retentions of Hσ and Hε of the nanocomposites containing nanosilica and/or EVAgMA are higher than those of neat EVA due to the presence of nanosilica and EVAgMA.

Table 5 also demonstrates that the Hσ coefficients of the EVA/silica nanocomposites without or with EVAgMA reach to highest values at 3 wt.% nanosilica content.

4. CONCLUSIONS

The nanocomposites without and with EVAgMA have been prepared by melt mixing with 2 – 5 wt.% nanosilica. Dielectric constant and dielectric loss of the nanocomposites increase with increasing nanosilica content. EVAgMA can be used as compatibilizer for the EVA/silica nanocomposites because of the formation of hydrogen bonds and dipole-dipole interactions between EVAgMA and nanosilica. With very low dielectric loss (around 10^{-3}), relatively high volume resistivity (5.3×10^{13} - 4.1×10^{14} Ω.cm), high electric breakdown (22.2 - 26.7 kV/mm), the EVA/silica nanocomposites without or with EVAgMA are good electrical insulation materials. Moreover, the EVA/ EVAgMA/silica nanocomposites have better thermal oxidative stability than EVA and EVA/silica nanocomposites.

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TÓM TẮT

NGHIÊN CỨU TÍNH CHẤT ĐIỆN VÀ ĐỘ BỀN LÃO HÓA OXI HÓA NHIỆT CỦA VẬT LIỆU NANOCOMPOZIT EVA/SILICA CÓ SỬ DỤNG CHẤT TƯƠNG HỢP EVAgAM

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Vật liệu nanocompozit trên cơ sở etylen vinyl axetat (EVA) không có và có 1 % EVA ghép anhydrit maleic (EVAgAM) và nanosilica (với hàm lượng 2 - 5 %, so với khối lượng EVA) được chế tạo bằng phương pháp trộn nóng chảy trên thiết bị trộn nội Haake ở 160 °C trong 5 phút với tốc độ trộn 50 vòng/phút. Điện trở suất khối, điện áp đánh thủng và tổn hao điện môi của vật liệu nanocompozit được xác định theo các tiêu chuẩn ASTM D257, D149 và D150 tương ứng. Kết quả cho thấy vật liệu thu được có khả năng cách điện tốt (điện trở suất khối trong khoảng 10^{13} - 10^{14} Ω.cm, tổn hao điện môi vào cỡ 10^{-3} và điện áp đánh thủng trong khoảng 22,1 - 26,7 kV/mm). Nanosilica làm giảm điện trở suất khối nhưng làm tăng điện áp đánh thủng và tổn hao điện môi của EVA. Độ bền lão hóa oxi hóa nhiệt của vật liệu nanocompozit EVA/EVAgAM/silica lớn hơn so với EVA. Phổ hồng ngoại (chỉ số cacbonyl) của vật liệu nanocompozit trước và sau khi thử nghiệm lão hóa oxi hóa nhiệt cho thấy nanosilica và EVAgAM hạn chế khả năng phân hủy đứt mạch của các đại phân tử EVA.

Từ khóa: nanosilica, copolyme etylen vinyl acetat, EVAgAM, điện trở suất, tổn hao điện môi, điện áp đánh thủng.