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EFFECTS OF pH OF TEOS SOLUTION ON MORPHOLOGY, THERMAL STABILITY AND MECHANICAL PROPERTIES OF EVA/SILICA NANOCOMPOSITES PREPARED BY SOL-GEL METHOD

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ABSTRACT

Ethylene-vinyl acetate copolymer/silica nanocomposites (EVA/silica) were prepared by mixing EVA solutions and tetraethylorthosilicate (TEOS) solutions. Silica particles were formed through sol-gel mechanism with the aid of hydrochloric acid catalyst and dispersed in EVA matrix. The pH of TEOS solutions was controlled from 1 to 6. The influence of pH on formation of silica in EVA matrix, as well as morphology, thermal stability of the nanocomposites were characterized by using Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA) and field emission scanning electron microscopy (FESEM). The FTIR spectra of the nanocomposites clearly indicated the presence of silica in EVA matrix, the shifts of Si-O stretching vibration in the nanocomposites in comparison with pure silica were also observed. This can be explained by hydrogen bonding between SiOH groups of the silica and carbonyl groups of vinyl acetate units in EVA. The TGA results of the nanocomposites showed that silica could improve thermal stability of EVA. Comparing preparation conditions at pH from 1 to 4, it is clear that at the lower pH the higher content of silica was formed in EVA matrix, 3.78; 3.70; 2.50 and 2.09 wt.% respectively. The FESEM images of the nanocomposites showed that nanoscale dispersion of silica was observed obviously at pH of 4 - 6, whereas during their preparation at pH of 1 - 3, the obtained silica particles formed mainly in microscale. The pH also affected on the mechanical properties (tensile strength, elongation at break) of EVA/silica nanocomposites. At pH of 1 - 3, the silica particles formed mainly in larger size, thereby they reduced the mechanical properties of EVA. At pH of 4 - 6, the nanosilica particles had significantly improved mechanical properties of EVA, particularly at pH of 4. The improvement of shear modulus of EVA/silica was also discussed.

Keywords: nanosilica, ethylene-vinyl acetate copolymer, EVA/silica nanocomposites, sol-gel mechanism, pH influence.

1. INTRODUCTION

Polymer nanocomposites have been the subject of growing interest. Polymer nanocomposites are materials in which nanoscopic inorganic particles dispersed in an organic polymer matrix. The presence of inorganic particles especially in nanoscale can improve polymer properties such as mechanical strength, thermal stability, gas permeability barrier properties, etc [1 - 9]. Among various types of inorganic materials used as nanoscale building blocks in polymer matrix, nanosilica is viewed as very important [1, 3]. Silica filled polymer nanocomposites has potential to combine the desired properties of inorganic and organic systems. These nanocomposites can be obtained by adding nanosilica particles into polymer matrix. The polymer/silica nanocomposites can be prepared by melt or solution blending methods [10 - 12], in situ polymerization method [13 - 14], whereas silica precursors are used in the sol-gel process, among which the most widely used ones are silicon alkoxides, such as tetraethylorthosilicate (TEOS) and tetramethoxysilane (TMOS) [6].

Ethylene-vinyl acetate copolymer (EVA) has polar vinyl acetate (VA) units randomly dispersed in the backbone, which give EVA excellent flexibility, fracture toughness, light-transmission properties, and adhesion to inorganic materials. However, EVA has some disadvantages such as low tensile strength, elastic modulus, hardness, thermal stability and flammable retardance, therefore it is necessary to enhance its properties. Several reports had been made to prepare and study on properties of nanosilica filled EVA nanocomposites [7 - 12].

P. Cassangau et al. [11, 12] had made reports in which the silica filled EVA composites were prepared by solution and melt blending methods, non-porous Aerosil 130 silica with a primary particle diameter of 16 nm was used. Their results showed that complex modulus (G' and G") of molten EVA and diluted EVA/xylene increased as a function of silica concentrations. However, it was clearly showed that silica aggregates in clusters, furthermore showed that agglomeration tendency of these clusters at high concentrations leads to the formation of a percolation-like filler network.

M. Sadeghi et al. had prepared the EVA and hybrid EVA–silica membranes via thermal phase inversion method. Silica nanoparticles were prepared by hydrolysis of TEOS, through the sol-gel mechanism [7 - 9]. The results obtained in their studies confirmed the superior properties of the EVA membrane in gas separation as well as its desirable mechanical properties. The effects of membrane preparation conditions, such as thermal and thermal/wet phase inversion, and the type of solvent on the gas separation properties of EVA membranes were investigated [9]. However, effects of inorganic acid concentration were not clear in these studies.

Many factors influence the kinetics of the hydrolysis and condensation reactions in the sol-gel method, which include the pH of base or acid catalyst medium, temperature, stirring speed, water/silane ratio, nature of solvent, and so forth. By this method, the morphology or surface characteristics of the growing silica phase in the polymer matrix can be controlled by these reaction parameters [3, 6]. Therefore, in this work, we firstly prepared the nanocomposites based on EVA and silica precusor of TEOS by sol-gel method with different hydrochoric acid concentration (the pH). The results of characterization analyses by FTIR, TGA, FESEM and mechanical properties of the obtained nanocomposites were also investigated and thoroughly discussed.

2. EXPERIMENTAL

2.1. Materials

Ethylene vinyl acetate copolymer (EVA) containing 18 wt.% vinyl acetate with the density of 0.938 g/cm^3 and melt flow index of 2.5 g/10 min (at 190 ^{o}C/2.16 kg) was purchased Taiwan (China). Tetraethylorthosilicate (TEOS) was purchased from Merck Co (Germany). Xylene (99.0 %), ethanol (99.7 %) and hydrochloric acid were obtained from Guangdong Jinhuada Chemical Reagent Co., Ltd. (China).

2.2. Sample preparation

The EVA/silica nanocomposites were prepared by sol-gel method. To perform this process, 2 mL TEOS and distilled water (molar proportion of 1 : 2) were dissolved in 40 mL absolute ethanol, dilute hydrochloric acid was drop wise for adjusting pH of each solution to values of 1, 2, 3, 4, 5, 6. After 1 hour of magnetical stirring, clear silica sols were formed. In order to verify formation of silica, a sample of silica powder was prepared by evaporation of one clear sol (with pH of 3) at room temperature for 72 hours. Separately, 12 g EVA was completely dissolved in 200 mL xylene solvent at 70 ^{o}C for 30 minutes. The EVA-xylene solution was mixed with every silica sol at 70 ^{o}C for 1 hour under magnetical stirring, then, the mixture was casted on a wide glass surface, the evaporation was done at room temperature for 72 hours to obtain the nanocomposite films. For mechanical tests, the obtained EVA/silica nanocomposites were heat up to 120 ^{o}C and pressed into about 1 mm-thickness sheets. By this way, neat EVA sheet was also prepared.

2.3. Characterizations and methods

Silica particles (prepared by sol-gel method), EVA and hybrid EVA/silica films were analyzed by Fourier Transform Infrared (FTIR) using a spectrometer (Nicolet/Nexus 670, USA) in the range of 4000 - 400 cm^{-1}. The surface morphology of the EVA/silica nanocomposites was observed by a Field Emission Scanning Electron Microscopy S-4800 (FESEM, Hitachi, Japan). Mechanical properties of EVA and EVA/silica nanocomposites were determined according to ASTM D638 on a tensile tester (WMP, Germany) with crosshead speed of 100 mm/min at room temperature.

Shear modulus of samples with dimensions of 50 × 12 × 1 mm were carried out at temperature of 30 ^{o}C by a rotational rheometer (CVOR-150, Bohlin Company, England). In yield test mode, shear modulus can be determined from shear stress-strain curve slope.

3. RESULTS AND DISCUSSIONS

3.1. FTIR characterizations

Figure 1 shows FTIR spectra of EVA, silica and EVA/silica nanocomposites prepared at pH 1 and 6 by sol-gel method. In FTIR spectrum of silica, the Si-O-Si asymmetric and symmetric stretching peaks appear at 1082 cm^{-1} and 795 cm^{-1}, respectively [7]. In FTIR spectrum of EVA, the peak at 1022 cm^{-1} are attributed to C-O stretching. These peaks also can be observed in the all spectra of EVA/silica nanocomposites, in which the Si-O-Si asymmetric and symmetric stretching peaks appear at 1093 - 1094 cm^{-1} and 800 cm^{-1}, respectively. The presence of above Si-O peaks originally confirms that silica are formed through sol–gel reaction successfully. Moreover, the significant shift of Si-O-Si asymmetric stretching peaks in the EVA/silica nanocomposites (about 12 cm^{-1}) can be explained by hydrogen bonding between carbonyl groups of vinyl acetate units in EVA and OH groups of the silica particles.

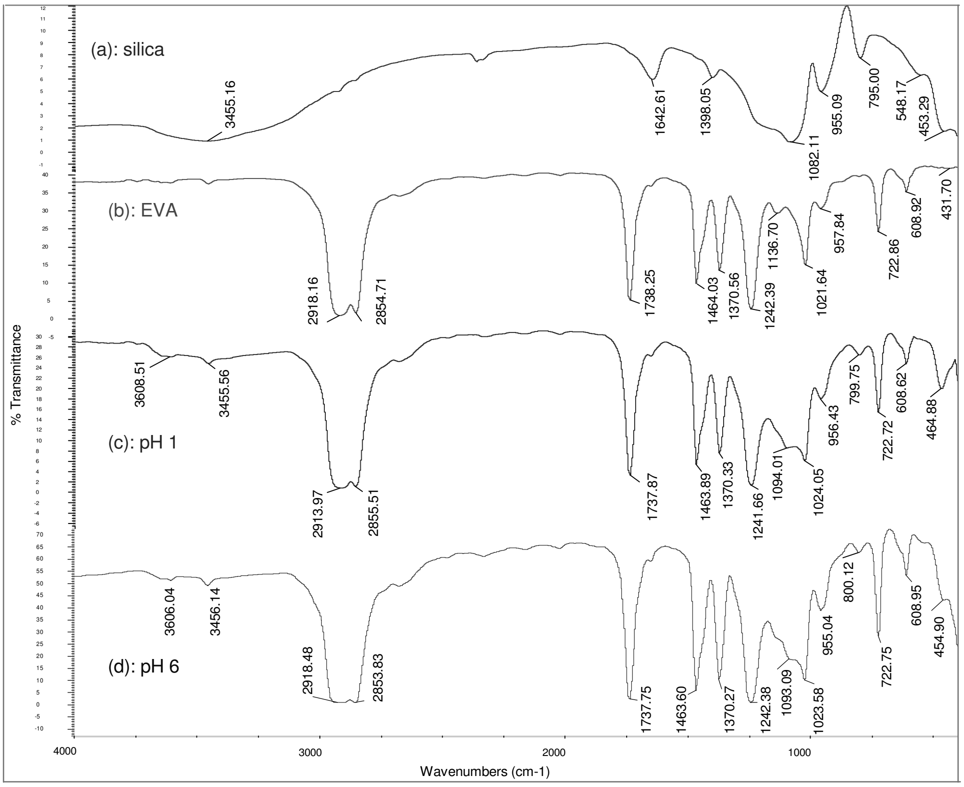

Figure 1. FTIR spectra of silica, EVA and EVA/silica nanocomposites.

3.2. Morphology of EVA/silica nanocomposites

Figure 2a shows the FESEM image of silica particles prepared by sol-gel method from a silica sol. It can be seen that silica particles are formed in large sizes of about 0.3 - 5 μm because of the self agglomeration of SiO_2. Figures 2 (b, c, d, e, f), show FESEM images of EVA/silica nanocomposites prepared at pH of 1; 2; 3; 4; 6, respectively. In figure 2.b, silica particles aggregate with diameter of about 400 nm or less than 100 nm, and in figures 2 (c, d), their diameter of about 50 - 250 nm. Meanwhile, at pH 4 or 6, smaller aggregates with diameter of about 100 nm or less are visible in figures 2.e or 2.f. It is expected that silica sol in ethanol solvent can be separated into micelles by precence of EVA macro-molecules, xylene solvent and stirring, which gives rise to reduce the cluster-cluster growth of silica. Whereby, the sizes of silica particles in the EVA/silica composites are much smaller than those of silica particles obtained from a silica sol. Otherwise, in preparation of EVA/silica composites, the pH of TEOS solution also acts as a main role. It is known that under higher acid concentrations (corresponding to low pH of 1 and 2), the hydrolysis will become faster [1]. This leads to increased condensation rate and more silica is produced and then aggregated in clusters. Therefore, at investigated processing conditions, the nanocomposites of EVA/silica only can be completely obtained at pH from 4 to 6, whereas, some parts of the composites still perform in microscale at pH from 1 to 3.

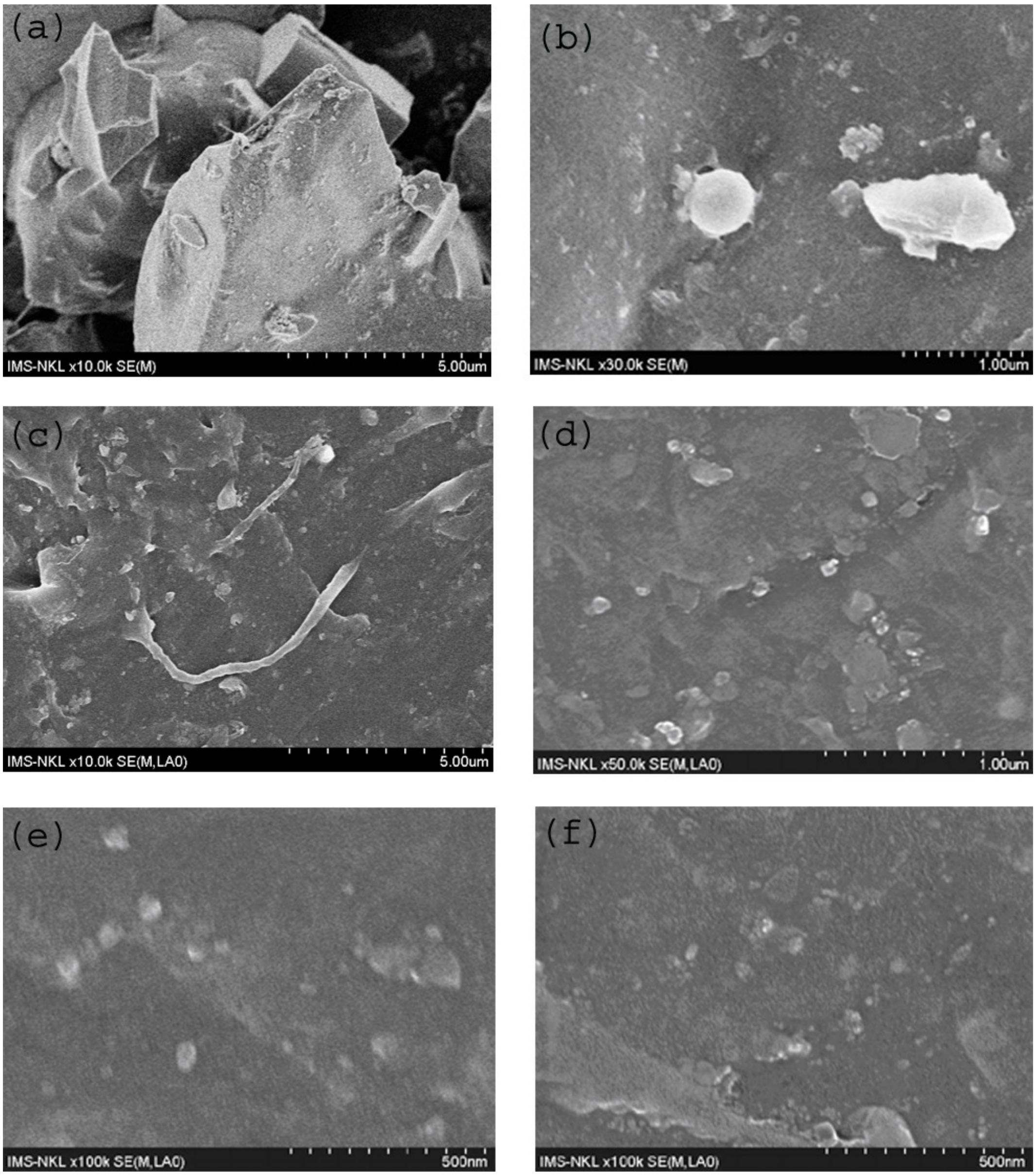

Figure 2. FESEM images of silica particles prepared by sol-gel method (a) and EVA/silica nanocomposites prepared at pH of 1 (b); 2 (c);3 (d);4 (e); 6 (f).

3.3. Thermal gravimetric analysis of EVA/silica nanocomposites

The thermal stability of neat EVA and EVA/silica nanocomposites prepared at pH 2 and pH 4 are illustrated in figure 3. The thermal degradation (weight loss versus temperature) of EVA and EVA/silica nanocomposites undergo with two steps. The first step is the autocatalytic deacetylation. For neat EVA, this process orcurs at about temperature between 310 and 406 °C. The second step is the degradation of main chain or the rest of polymer [7, 15]. It can be seen the TGA curves of EVA/silica nanocomposites shift to higher temperatures. Table 1 lists results of TGA of EVA and EVA/silica nanocomposites prepared at pH from 1 to 4, including onset degradation temperature - T_{onset} (taken at 3 wt.% weight loss) [15]; $T_{-18\ wt.\%}$ - temperature corresponding to 18 wt.% weight loss; T_{max1} - temperature of the maximal degradation rate of stage 1; T_{max2} - temperature of the maximal degradation rate of stage 2; and residual weight (at 600 °C). The obtained results show that, in the first step, the deacetylation of EVA/silica nanocomposites is slower than that of EVA, the T_{onset} and $T_{-18wt.\%}$ values of the nanocomposites are higher than that of EVA (about 13 - 19 °C, 16 - 29 °C, respectively). These thermal behaviours of the EVA/silica nanocomposites can be explained by high thermal stability of silica and hydrogen bonds between C=O groups of EVA chains and OH groups at surface of silica particles. The hydrogen bond formation has obstructed the thermal deacetylation of EVA and therefore, silica particles can improve thermal stability of EVA. The presented results in table 1 also express that the residual weights of EVA/silica nanocomposites after heating up to 600 °C is consistent with the theoretical silica weight percentages of these nanocomposites [16]. Respectively to our preparation conditions at pH from 1 to 4, the residual weights of these nanocomposites are 3.78; 3.70; 2.50 and 2.09 wt.%. It means with lower pH values and the same time reaction, the higher content of silica was formed in EVA matrix.

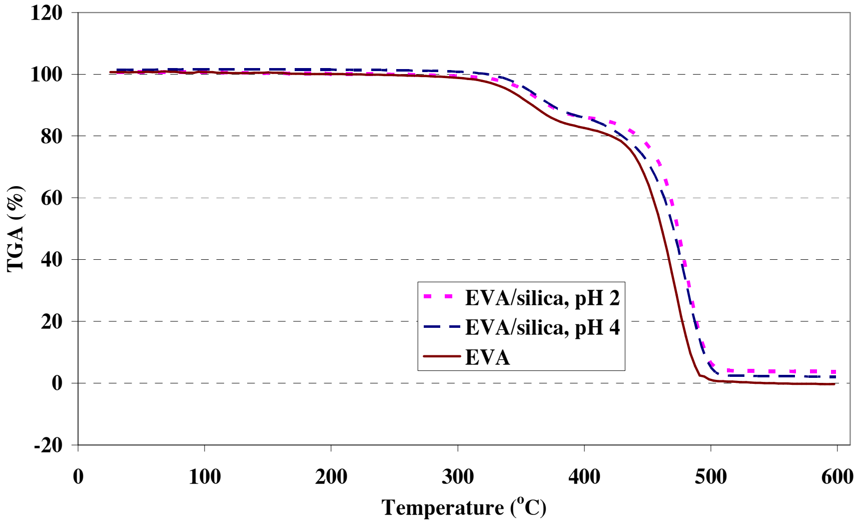

Figure 3. TGA thermograms of EVA and EVA/silica nanocomposites.

Table 1. Thermal characteristics of EVA and EVA/silica nanocomposites.

Samples	**T_{onset} (°C)**	**$T_{-18\ wt.\%}$ (°C)**	**T_{max1} (°C)**	**T_{max2} (°C)**	**Residual weight at 600°C (%)**
EVA	327.6	406.5	351.0	465.1	0
EVA/silica (pH 1)	340.5	332.4	352.0	466.2	3.78
EVA/silica (pH 2)	340.9	435.4	352.3	467.6	3.70
EVA/silica (pH 3)	342.6	432.5	353.3	467.8	2.50
EVA/silica (pH 4)	346.9	422.6	353.9	468.9	2.09

3.4. Mechanical properties of EVA/silica nanocomposites

Table 2 represents the tensile strength (σ) and elongation at break (ε) of neat EVA, EVA/silica nanocomposites prepared at different pH values of TEOS solutions, and shows that the pH affects to σ and ε of EVA/silica nanocomposites. Tensile strength and elongation at break of the EVA/silica nanocomposites prepared at pH from 1 to 3 are smaller than those of neat EVA (σ and ε of EVA are 16.91 MPa and 767 %, respectively). Whereas, σ and ε of the EVA/silica nanocomposites prepared at pH 4 to 6 are higher than those of neat EVA, and at pH of 4, these values are highest (σ = 17.96 MPa and ε = 780 %). These mechanical behaviours of EVA/silica nanocomposites can be explained by considering the microstructure of EVA/silica nanocomposites as showed in figure 2. At pH from 1 to 3, the silica particles are formed in EVA matrix mainly in microscale size (about 0.2 - 0.4 μm), thereby they reduce both of tensile strength and elongation at break of EVA. Meanwhile, in the cases of pH from 4 to 6, nanoscale dispersion of silica particles in EVA matrix can be achieved. Thus, mechanical properties of EVA/silica nanocomposites has been significantly improved. Particularly in our experiment process, pH of 4 is appropriate for preparation of EVA/silica nanocomposite through sol-gel mechanism in solution.

Table 2. Mechanical properties of EVA and EVA/silica nanocomposites prepared at different pH values.

Samples and pH	σ (MPa)	ε (%)
EVA	16.91	767
EVA/silica, pH 1	13.24	560
EVA/silica, pH 2	14.58	728
EVA/silica, pH 3	14.60	742
EVA/silica, pH 4	**17.96**	**780**
EVA/silica, pH 5	**17.79**	**743**
EVA/silica, pH 6	17.48	740

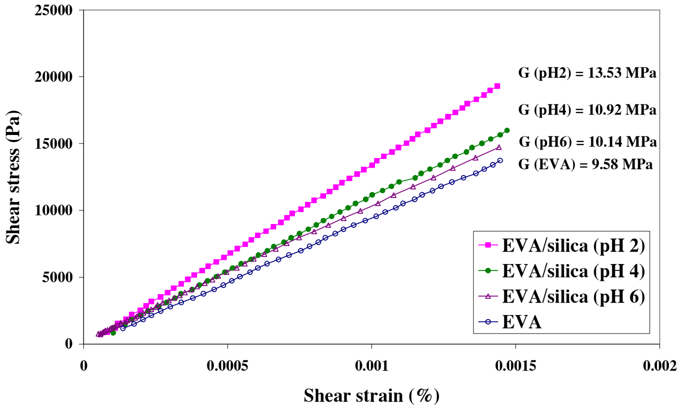

Figure 4. Shear stress-strain plots of EVA and EVA/silica nanocomposites.

Figure 4 demonstrates plots of shear strain versus shear stress applied to EVA and EVA/silica nanocomposites using stresses increased for very small shear deformation of all samples. It can be seen all shear strain-stress curves are linear, therefore, shear modulus can be determined from the slopes of curves. The obtained results show EVA exhibits the lowest shear modulus (G = 9.53 MPa), and shear modulus of EVA/silica nanocomposites are all higher than that of neat EVA. Silica particles can improve the rigidity of EVA. For EVA/silica nanocomposites prepared at lower pH values as mentioned in 3.3, the shear modulus of EVA/silica composite are higher. This phenomenon perhaps is only related to silica content in the nanocomposites but not so much related to silica particle size [17].

4. CONCLUSIONS

The EVA/silica nanocomposites has been prepared by sol-gel method used silica precusor of TEOS and the aid of HCl catalyst. The FTIR spectra show the presence of silica in EVA matrix and the shift of Si-O absorption vibrations as an evidence of hydrogen bond between C=O groups of vinyl acetate units in EVA and OH groups of the silica particles in the nanocomposites. The nanoscale of silica particles can be formed in EVA matrix at pH values of 4, 5 or 6, whereas at pH of 1 - 3, some larger agglomerates in microscale are observed. With microscale, silica particles decrease the tensile strength and elongation at break of EVA, whereas the presence of nanosize silica improves both of these mechanical properties of EVA. However, in the investigated pH values, the shear modulus of the nanocomposites increases with decreasing pH values.

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TÓM TẮT

ẢNH HƯỞNG CỦA ĐỘ pH CỦA DUNG DỊCH TEOS ĐẾN HÌNH THÁI CẤU TRÚC, ĐỘ BỀN NHIỆT VÀ TÍNH CHẤT CƠ LÍ CỦA VẬT LIỆU NANOCOMPOZIT EVA/SILICA CHẾ TẠO BẰNG PHƯƠNG PHÁP SOL-GEL

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Vật liệu nanocompozit trên cơ sở copolyme etylen-vinyl axetat (EVA) và nanosilica được chế tạo bằng phương pháp sol-gel. Silica được tạo thành tại chỗ từ tetra-etyl-ortosilicat (TEOS) với xúc tác là axit clohydric, pH của dung dịch TEOS được điều chỉnh từ 1 đến 6. Ảnh hưởng của pH đến sự hình thành của silica trong nền EVA cũng như hình thái cấu trúc, độ bền nhiệt của vật liệu nanocompozit được nghiên cứu bằng phương pháp phổ hồng ngoại biến đổi Fourier, phân tích nhiệt trọng lượng (TGA) và hiển vi điện tử quét phát xạ trường (FESEM). Phổ FTIR đã chỉ rõ sự tạo thành silica trong nền EVA và pic hấp thụ đặc trưng của nhóm Si-O trong vật liệu nanocompozit có sự dịch chuyển so với silica do sự tạo thành liên kết hydro giữa nhóm SiOH của silica và nhóm cacbonyl của EVA. Kết quả phân tích TG cho thấy silica có khả năng nâng cao độ bền nhiệt cho EVA. Khi pH dung dịch TEOS tăng từ 1 đến 4, hàm lượng silica được tạo thành trong nền EVA giảm, tương ứng là 3,78; 3,70; 2,50 và 2,09%. Với pH từ 1 - 3, các hạt silica chủ yếu được hình thành trong nền EVA với kích thước micromet, do đó làm giảm tính chất cơ lý của EVA. Các hạt silica chỉ phân tán với kích thước nano trong nền EVA khi pH dung dịch TEOS từ 4 - 6, do đó vật liệu nanocompozit thu được có tính chất cơ lý tốt hơn so với nền EVA. Modun trượt của EVA tăng theo hàm lượng nanosilica tạo thành.

Từ khóa: nanosilica, copolyme etylen-vinyl axetat, nanocompozit EVA/silica, sol-gel, ảnh hưởng của pH.