

Effect of End-Capped Nanosilica on Mechanical Properties and Microstructure of LLDPE/EVA Blends

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ABSTRACT: This article describes the influence of a hexamethyldisilane-treated nanosilica (end-capped SiO₂) on morphological and tensile properties of linear low-density polyethylene (LLDPE)/ethylene vinyl acetate copolymer (EVA) blends prepared by one step melt mixing process via a twin screw extruder. The treatment replaces many of the surface hydroxyl groups on the nanosilica with extremely hydrophobic trimethylsilyl groups. Transmission electron microscopic results revealed that the treated nanosilica formed small aggregates in polymer matrix and they were mostly localized in the LLDPE matrix besides localizing in EVA droplets and at LLDPE/EVA interface. These nanoparticles had compatibilizing role on the blend system and at high content changed morphology from biphasic toward a monophasic. Addition of the end-capped nanosilica to the blend and increasing its content increased the Young's modulus, tensile strength as well as elongation at break of the nanocomposites. Different models were used to predict the Young's modulus of the nanocomposites. It was found that the experimental data were better fitted by Counto model than the other models. Melt rheological investigations on the nanosilica filled LLDPE/EVA blend system showed that incorporation of the treated nanosilica, even up to 10 wt %, did not lead to a solid-like behavior at low-frequency indicating ease of processing of such highly filled system. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

KEYWORDS: blends; mechanical properties; nanocomposites

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INTRODUCTION

Nowadays, new materials have been widely produced for industrial requirements. The polymer blending is one of the economical and easy routes for developing new materials with novel properties.¹ Linear low-density polyethylene (LLDPE)/ethylene vinyl acetate copolymer (EVA) blends are used extensively in many applications such as wire and cable coating industry as insulation or jacket, shrinkable films, and multilayer packaging. LLDPE is one of the most widely used polyethylene grades because of its good processability, low density, and low cost. Adding EVA to LLDPE improves its toughness and impact resistance, transparency, and environmental stress cracking resistance (ESCR).^{2–4}

It has been reported that blending polymeric systems (homopolymer, blends, or block copolymer) with nanoscale materials is a useful method to produce novel materials known as polymer nanocomposites. Adding a nanofiller (such as clay, nanosilica, etc.) to polymeric systems can enhance their modulus and ten-

sile strength, thermal resistance, gas-barrier properties, etc.¹ Nanosilica (SiO₂) is a spherical nanoparticle that its surface is mainly composed of silanol groups. When nanosilica particles are added into polymeric systems, these silanol groups on the surface of nanosilica particles tend to attract each other with strong hydrogen bonding. This strong hydrophilic nature of nanosilica makes it incompatible with hydrophobic polymeric matrices such as LLDPE. To improve mechanical properties of the polymeric matrix, homogenous dispersion of nanoparticles in the matrix and its adhesion with matrix are important factors that should be considered.⁵ For homogenous dispersion of hydrophilic nanofillers in the hydrophobic matrix, there are a lot of techniques including: *in situ* polymerization of monomers in the presence of nanoparticles, using compatibilizers, treatment of nanoparticles with coupling agents, or by graft polymerization.⁶ Treatment of nanosilica with hexamethyldisilane can replace many of the surface hydroxyl groups on the nanosilica with extremely hydrophobic trimethylsilyl groups and this result in a

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Table I. Composition of the Prepared LLDPE/EVA/Nanosilica Samples

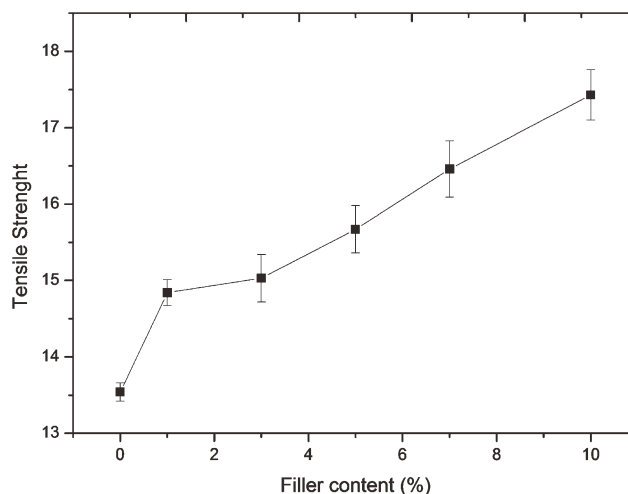
Sample codes	LLDPE (wt %)	EVA (wt %)	Nanosilica (wt %)	PE-g-MA (wt %)
1	75	25	0	0
2	74.25	24.75	0	1
3	72.75	24.25	0	3
4	71.25	23.75	0	5
5	74.25	24.75	1	0
6	72.75	24.25	3	0
7	71.25	23.75	5	0
8	69.75	23.25	7	0
9	67.5	22.5	10	0
10	72	24	3	1
11	70.5	23.5	3	3
12	69	23	3	5

better dispersion of the treated nanoparticles in non-polar polymeric systems such as polyolefins. Incorporation of nanoparticles into immiscible polymer blends also can refine the morphology of the blends and this change in morphology can significantly affect mechanical properties of nanocomposites. Basically, three methods have been reported for producing polymeric nanocomposites: melt mixing, solution technique, and *in situ* polymerization.⁷ The melt mixing process is favorable from industrial view point. Literature survey shows that there are a lot of interest on LLDPE/EVA blend and LLDPE/nanosilica and EVA/nanosilica composites. Liu et al. described effect of nanosilica on mechanical properties of LLDPE/LDPE blend.⁸ Moly et al. studied melt rheology and correlation between the morphology and dynamic mechanical properties of EVA/LLDPE blend by investigating effects of blend ratio and compatibilization on those properties.⁹ Huang et al. characterized dynamic mechanical properties of LLDPE/nanosilica composite,¹⁰ Chaichana et al. studied thermo mechanical properties of zLLDPE/nanosilica and mLLDPE/nanosilica.⁶ Kiachan et al. characterized effects of nanosilica particle size on the formation of LLDPE/nanosilica composite synthesized via *in situ* polymerization with a metallocene catalyst.⁷ Sadeghi et al. studied gas permeation properties of EVA/nanosilica composite membrane.¹¹ Dorigato et al. characterized rheological properties of LLDPE with various types of micro and nanoscale silica.¹² The literature survey indicates the importance and the high interest in incorporating nanosilica in different PE-based systems. However, the studies on nanosilica filled LLDPE/EVA blends are rare. In this work, we study the influence of a hexamethyldisilane-treated nanosilica (end-capped SiO₂) on microstructure and mechanical properties of LLDPE/EVA system. The effect of high content of nanosilica on processability and thermal properties of the nanocomposites will also be assessed. An attempt is made to find an appropriate model to predict the mechanical properties of the system.

EXPERIMENTAL

Materials

LLDPE 1004YB FILM, MFR 2.8 g/10 min at 190°C was supplied by ExxonMobil Chemical, EVA Elvax[®] 3173SHB, MFR 2.5 g/10

**Figure 1.** Effects of nanosilica contents on tensile strength of LLDPE/EVA/nanosilica composites.

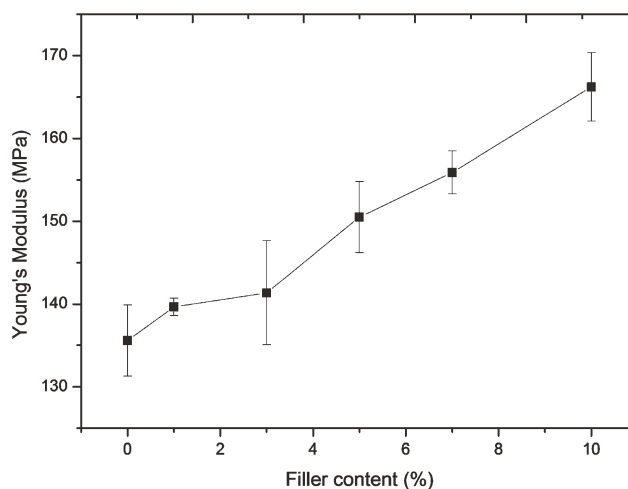
min at 190°C /2.16 kg, was supplied by DuPont, Germany. Hydrophobic nanosilica with specific surface area of 150–200 m²/g and particle size of 20–30 nm, modified with hexamethyldisilane, was obtained from Gelest, Germany. The compatibilizer used in this study was Fusabond E226 which was an anhydride modified polyethylene (PE-g-MA) from DuPont with MFR 1.75 g/10 min at 190°C and density of 0.93 g/cm³.

Sample Preparation

Nanocomposites were prepared via a one step melt compounding. All components were introduced simultaneously in a ZSK30 co-rotating twin screw extruder. All temperature zones were fixed at 170°C. The details of the prepared samples are given in Table I

Transmission Electron Microscopy

The extruded samples were ultramicrotomed down to approximately 70 nm thickness under cryogenic conditions at –120°C via EM UC/FC6 ultramicrotome (Leica) equipped with a

**Figure 2.** Effects of nanosilica contents on Young's modulus of LLDPE/EVA/nanosilica composites.

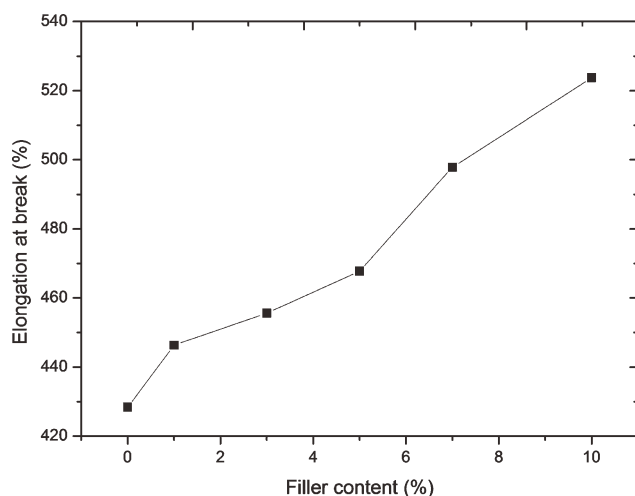


Figure 3. Effects of nanosilica contents on elongation at break of LLDPE/EVA/nanosilica composites.

diamond knife. Transmission electron microscopy (TEM) images were then recorded using a LEO 910 TEM (Carl Zeiss) at an accelerated voltage of 120 kV.

Mechanical Properties

Standard tensile test samples (ISO 527-1) were prepared by injection molding operated at 170°C with the mold temperature of 30°C. After molding, the molded specimens were conditioned at room temperature for at least 24 h to allow for any relaxation of elasticity within the specimens. The tensile testing was performed on a tensile tester (Zwick/Roell, Germany) according to the standard method (ISO 527-1 : 1993) at room temperature. For all samples the crosshead speed was 50 mm/min and the average values of at least five measurements were reported.

Rheological Properties

Rheological measurements were performed on a parallel plate MCR300 (Paar physica) at 170°C in oscillation mode under nitrogen atmosphere to prevent oxidative degradation. Linear viscoelastic region was found using strain sweep test. Frequency sweep experiments were then carried out over 0.03–100 rad/s at a strain of 10% and rheological characteristics were then recorded.

Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) analysis was performed on a TA instrument Q1000 from –80 to 200°C. All samples were heated with a constant heating rate of 10°C/min from –80 to 200°C to release previous thermal histories and then they were cooled with a rate of –10°C/min from 200°C to –80°C and again they were heated from –80°C up to 200°C with a rate of 10°C/min. The holding times between heating and cooling processes were 2 min. The sample weight was about 5 mg.

RESULTS AND DISCUSSION

Mechanical Properties

It is known in nanocomposites that extent of improvement of mechanical properties of the matrix depends on the adhesion between matrix and nanofiller. To better transfer applied load

from matrix to nanofiller, a homogeneous dispersion of nanofillers in the matrix is needed.⁵ Since LLDPE in the current study is the major phase, for improving of mechanical properties, a hydrophobic nanosilica was chosen which has good interactions with LLDPE. Tensile strength versus nanosilica content for LLDPE/EVA blends loaded with different amounts of nanosilica is shown in Figure 1. It is seen that the tensile strength of the nanocomposite increases with incorporation of nanosilica to the blend. It further increases with increasing the content of nanosilica. As is shown in Figure 2, Young's modulus increases with increasing the content of nanosilica too. This may be because of the inherent high modulus of SiO₂ and the physical crosslinking effects of the nanosilica on the matrix.¹³ Nanosilica and polymer chains have relatively the similar time motion scale, because their size is comparable. Because of their mobility, the nanosilica particles can act like temporary physical crosslinks within polymer segments, making localized regions of improved strength, which in turn can delay growth of cracks or cavities at

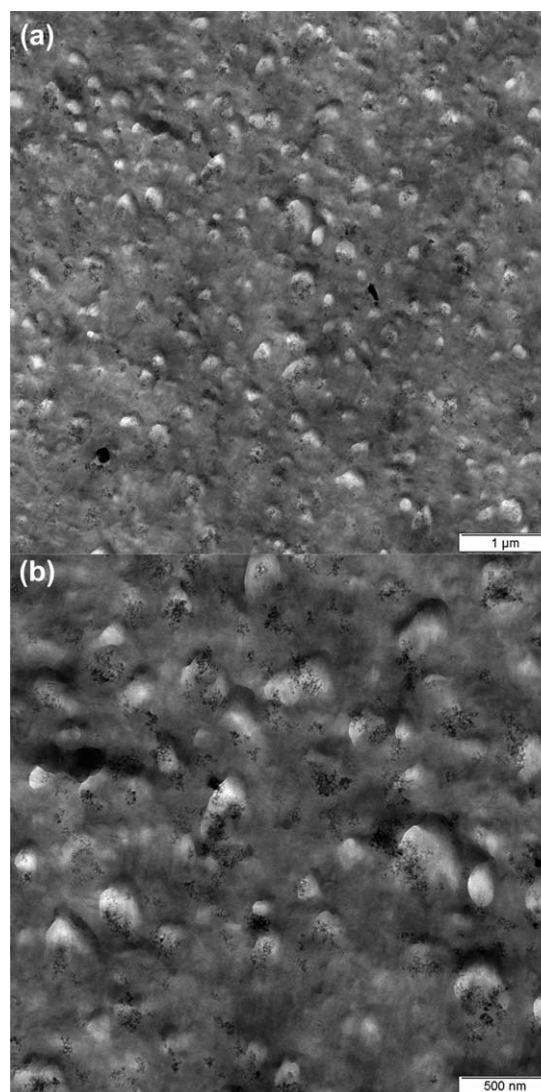


Figure 4. (a,b) TEM micrographs of LLDPE/EVA/nanosilica composite with 3 wt % of nanosilica.

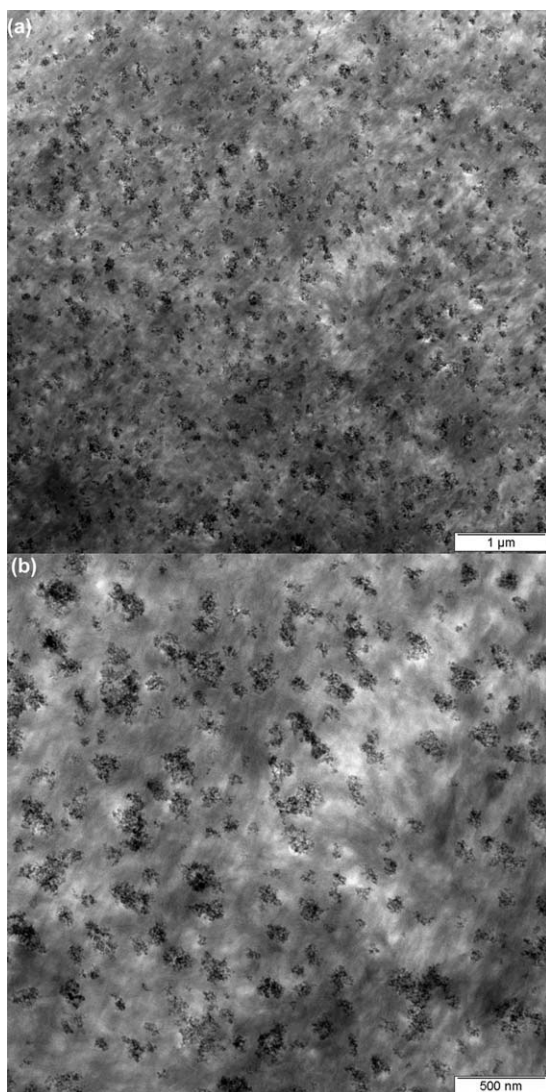


Figure 5. (a,b) TEM micrographs of LLDPE/EVA/nanosilica composite with 10 wt % of nanosilica.

weak points of composites.⁶ From Figure 3, it is also seen that elongation at break increases with increasing nanosilica content. Considering the increased area under the stress–strain curves (not shown here) and the observed increased in the elongation at break it can be deduced that the nanosilica particles increase toughness of LLDPE/EVA blend besides improving its stiffness.

Kontou et al. reported increasing of elongation at break with increasing of nanosilica content in LLDPE/nanoSiO₂ composite. They reported that homogenous dispersion of nanoparticles and strong interactions with matrix are important factors for improving of toughness.⁶ Since in the current work the matrix is LLDPE/EVA blend, change in morphology of the blend due to incorporation of nanosilica could be one of the reasons for increasing of elongation at break with increasing of the nanosilica content. Figures 4(a,b) and 5(a,b) show TEM micrographs of LLDPE/EVA with 3 and 10 wt % nanosilica. These TEM images confirm a dramatical change in the morphology with increasing nanosilica content. When the nanoparticle loading

increases from 3 to 10 wt %, EVA big droplets, white areas are EVA phase and gray areas are LLDPE, disappear that means compatibility of LLDPE and EVA phases has improved. Different mechanisms may be responsible for this phenomenon, including changed viscosity ratio of the blend components influencing the balance between break up and coalescence of the minor phase and enhanced stress transfer to the minor phase. Another mechanism is that nanosilica particles act as effective physical barriers and hinder coalescence of big droplets of the minor phase. If the nanoparticles are located at the interface of two phases, adsorption of polymer segments of the minor and major phases on the filler surface and reduction of interfacial tension between two phases can improve their compatibility.⁵ The magnified TEM image presented in Figure 6 shows that nanoparticles are located at LLDPE, EVA, and also at the interface of two phases, and as a result, all of the mentioned mechanisms can affect the phase morphology. Generally, the localization of nanoparticles in a polymer blend is controlled by both thermodynamic and kinetic factors such as interfacial tension between components, viscosity ratio during mixing, applied shear stress, time of mixing, and so on.¹⁴ Yang et al.¹⁴ and Elias et al.¹⁵ worked on localization of nanosilica particles in the PP/EPDM and PP/EVA blends, respectively. On the basis of their works, when nanosilica particles are localized in two phases and also at interface it indicates that the localization of nanosilica particles has been affected by kinetic parameters otherwise, nanosilica particles should be localized in one of this phase. On the basis of our TEM results and considering the Yang et al. and Elias et al. works, it can be concluded that the kinetic factors are the main controlling parameters in localization of nanosilica in LLDPE/EVA system.

The mechanical properties of compatibilized LLDPE/EVA blends at different compatibilizer loadings are summarized in Table II.

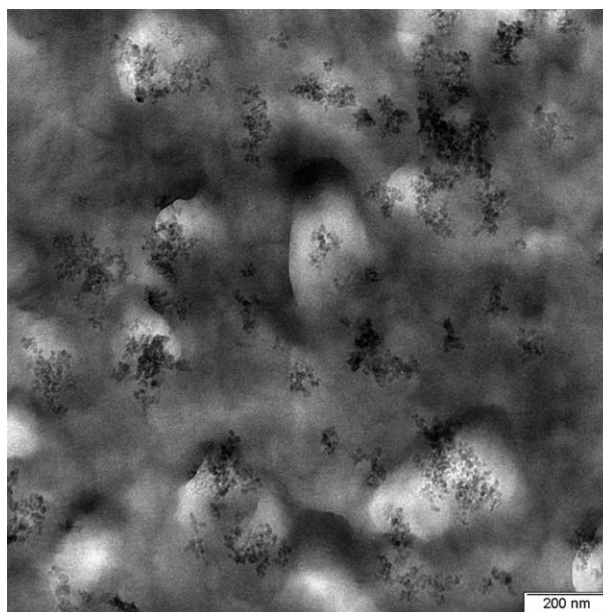


Figure 6. Magnified TEM micrographs of LLDPE/EVA/nanosilica with 3% of nanosilica. This image shows that nanosilica particles located at LLDPE phase, and EVA and also at interphase of the two phases.

Table II. Tensile Properties of Blends with Various Contents of Compatibilizer

LLDPE/EVA/ nano-SiO ₂ / compatibilizer	Young's modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
75/25/0/0	135.60	13.45	428.4
74.25/24.25/0/1	141.59	14.15	437.0
72.75/24.25/0/3	139.80	14.28	427.2
71.25/23.75/0/5	141.79	14.09	422.7

Incorporation of compatibilizer to LLDPE/EVA blend generally improves the stiffness, strength, and toughness of the blend to some extent. The sample with 1 wt % of compatibilizer content shows the maximum improvement in toughness. This finding is in agreement with the results reported by Moly et al.⁹ The influence of compatibilizer on the mechanical properties of the filled-blend, i.e. LLDPE/EVA blend loaded with 3 wt % nanosilica, is shown in Table III. The results indicate that the compatibilizer does not have remarkable effect on the improvement of mechanical properties of the filled system.

Predication of Modulus

There are many empirical or semi-empirical equations for predicting of the modulus of polymer microcomposites in literature, in fact, most of these models do not describe satisfactorily the experimental behavior of nanocomposites.¹⁶ The main reason for deviation of theoretical results from real data is that the models assume a complete adhesion between the filler surface and the matrix which is not entirely true.⁶ In this work, the most appropriate models where used for predicting of the modulus of LLDPE/EVA/nanosilica (E_C) system. It is assumed that LLDPE/EVA is an isotropic matrix, its modulus is denoted by E_m , especially at the high content of nanosilica (see Figure 5). The distribution of nanoparticles in the matrix is homogeneous. The modulus of nanosilica particles (E_p was taken equal to 70 GPa.¹⁷

Einstein equation's¹⁸ for prediction of the modulus for composites with spherical particles with perfect dispersion and adhesion are as follows:

$$\frac{E_C}{E_m} = 1 + 2.5V_p \quad (1)$$

where E_C and E_m are modulus of composite and matrix, respectively. V_p is filler volume fraction. Guth,¹⁹ reformed Einstein equation's by adding a particle interaction term:

Table III. Tensile Properties of Nanocompaties with 3 wt % of Nanosilica and Various Contents of Compatibilizer

LLDPE/EVA/ nano-SiO ₂ / compatibilizer	Modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
72.75/24.25/3/0	141.36	15.03	455.8
72/24/3/1	143.53	14.92	449.5
70.5/23.5/3/3	147.10	15.04	437.9
69/23/3/5	147.53	14.73	437.5

Table IV. Weight and Volume Percent of LLDPE/EVA/Nanosilica System

Nanosilica content (wt %)	Volume percent (vol %)
1	0.41
3	1.274
5	2.15
7	3.04
10	4.43

$$\frac{E_C}{E_m} = 1 + 2.5V_p + 14.1V_p^2 \quad (2)$$

Kontou et al.⁶ used Cheng's equation for predication of the Young's modulus of nanocomposite.

$$C^* = C_m \cdot [I + f_1 B \cdot (I + f_1 E)^{-1}]^{-1} \quad (3)$$

where

$$B = A \cdot T \quad (4)$$

$$A = I - C_m^{-1} \cdot C_f \quad (5)$$

and

$$T = (I + S \cdot C_m^{-1} \cdot C_f - S)^{-1} \quad (6)$$

$$E = (S - I) \cdot A \cdot T \quad (7)$$

where f_1 is filler volume fraction, C_f is the stiffness moduli of the filler, C_m is elastic modulus tensor of matrix, and I is identity matrix tensor. In this model S is Eshelby tensor, and its components for spherical inclusions are:

$$S_{11} = S_{22} = S_{33} = \frac{7 - 5\nu_0}{15(1 - \nu_0)} \quad (8)$$

$$S_{12} = S_{23} = S_{31} = \frac{1 - 5\nu_0}{15(1 - \nu_0)} \quad (9)$$

$$S_{44} = S_{55} = S_{66} = \frac{4 - 5\nu_0}{15(1 - \nu_0)} \quad (10)$$

where ν_0 is Poisson ratio of matrix.

Counto²⁰ proposed the following equation by assuming perfect bonding between filler and matrix:

$$\frac{1}{E_C} = \frac{1 - V_p^{0.5}}{E_m} + \frac{1}{(1 - V_p^{0.5}) / (V_p^{0.5} \cdot E_m) + E_p} \quad (11)$$

Results of this equation have been in good agreement with a wide range of experimental data.

For composite including spherical particles, Kerner equation's can be used to calculate the modulus of composite if the particles are much more rigid than the polymer martrix¹⁹

$$\frac{E_C}{E_m} = 1 + \frac{V_p}{(1 - V_p)} \frac{15(1 - \nu_m)}{(8 - 10\nu_m)} \quad (12)$$

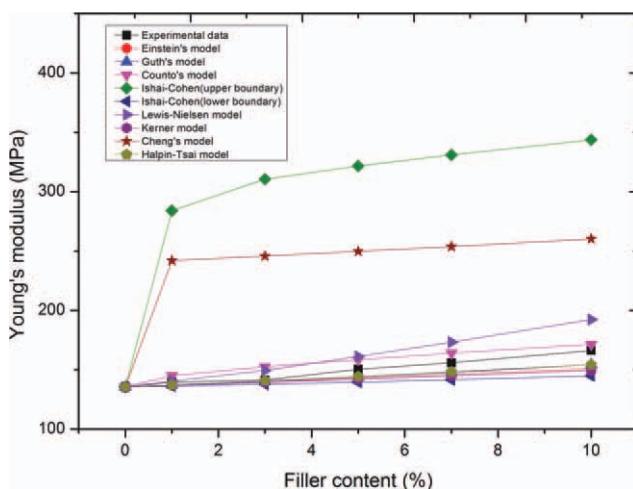


Figure 7. The prediction of Young's modulus with various models, this figure shows that Counto model can predicts the experimental data better than the other models. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

In this equation, ν_m is Poisson ratio of matrix.

The Halpin–Tsai model includes the shape factor of the filler, for nanosilica particles Jumahat et al. assumed that the length of particle, w , equals the thickness of the particle, t , and therefore shape factor is 2.¹⁷

$$E_C = \frac{1 + \zeta \eta V_P}{1 - \eta V_P} E_m \quad (13)$$

$$\eta = \frac{E_p/E_m - 1}{E_p/E_m + \zeta} \quad (14)$$

in this equations, ζ is the shape factor.

Ishai and Cohen²¹ equations for upper and lower boundary area are:

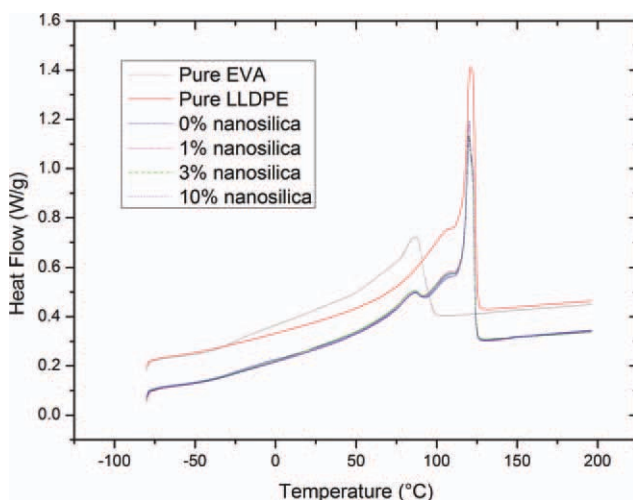


Figure 8. DSC thermograms of pure LLDPE and EVA, and their blends with various loadings of nanosilica. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

$$\frac{E_C}{E_m} = 1 + \frac{1 + (1 - \delta)V_P^{2/3}}{1 + (1 - \delta)(V_P^{2/3} - V_P)} \quad (15)$$

$$\frac{E_C}{E_m} = 1 + \frac{V_P}{(\delta/1 - \delta)V_P^{2/3}} \quad (16)$$

in this equation, δ is equal to $\frac{E_p}{E_m}$.

The Lewis–Nielsen model²² for prediction of modulus of composites is one of the most generalized equations:

$$\frac{E_C}{E_m} = \frac{1 + BV_P(K_E - 1)}{1 - B\psi V_P} \quad (17)$$

in this equation, K_E is Einstein coefficient of filler and B is 1 for very large filler/matrix modulus ratio. The ψ parameter which depends on maximum particle packing fraction V_{pmax} can be obtained from the following equation²²:

$$\psi = 1 + \frac{V_m}{V_{pmax}} [V_{pmax}v_p + (1 - v_{pmax})v_m] \quad (18)$$

where V_m is the matrix volume fraction. Lewis and Nielsen reported the maximum particle packing fraction V_{pmax} and Einstein's coefficient factor K_E are 0.37 and 6.76 for large agglomerates with spherical particles in random packing.²² The weight and volume percent of samples are given in Table IV. The weight fractions of nanocomposites were converted to volume fraction by using density of 2.2 g/cm³ for nanosilica, 0.95 g/cm³ for EVA, and 0.918 g/cm³ for LLDPE, these information are obtained from materials datasheets. This procedure was used by Bailly for calculation of nanosilica volume fractions at PP/EOC/nanosilica composites.⁵

The predicted Young's modulus values versus nanosilica content and its comparison with the experimental data are shown in Figure 7. It is seen that most of the predicted results are in good agreement with the experimental data especially at low nanosilica contents. Moreover, it is found that the results of Counto model is in better agreement than other models over a wide range of nanosilica content.

DSC Results

DSC heating endotherms (second heating cycle) for the pure LLDPE and EVA and blends with 0, 1, 3, and 10 wt % of nanosilica are shown in Figure 8. These DSC thermograms were analyzed and the results are presented in Table V. The results show

Table V. DSC Data of LLDPE/EVA/Nano-SiO₂ with Various Contents of Nanosilica

LLDPE/EVA/ nano-SiO ₂	T_{m1} (°C)	T_{m2} (°C)	Change in the first melting enthalpy ΔH (J/g)	Change in the second melting enthalpy ΔH (J/g)
75/25/0	86.8	120	-	-
74.25/24.75/1	86.5	120.14	+0.332	+1.573
72.75/24.25/3	86.3	120.09	+3.66	+1.479
67.5/22.5/10	86.6	120.2	+2.22	-0.67

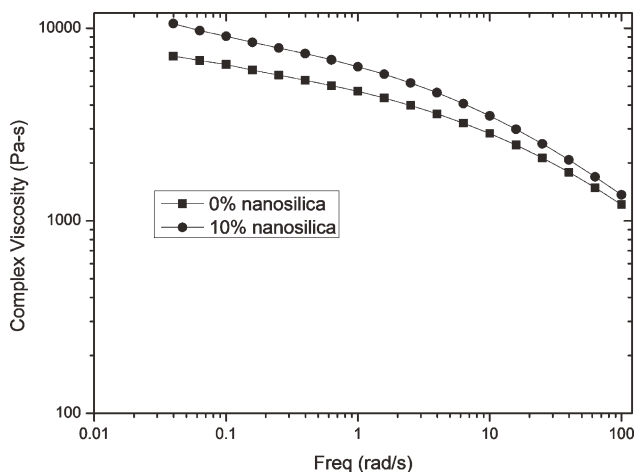


Figure 9. Complex viscosities of LLDPE/EVA blend and nanocomposite with 10 wt % of nanosilica.

that melting temperatures of LLDPE and EVA in the blend without nanosilica are not affected by the treated nanosilica particles. Melt enthalpy of the first peak increases with nanosilica contents that may be because of the nucleating effect of nanosilica particles. Table V indicates melt enthalpy of the second peak, assigned to the LLDPE component, initially increases that can be because of the nucleating effect of nanoparticles at low contents, i.e. 1 and 3 wt % of nanosilica, and then decreases that can be because of the preventing effects of nanoparticles at high contents, 10 wt % of nanosilica, on the motion of polymer segments. Crystallization process is affected by two procedures, nucleation and growth. At low composition of nanosilica, melt enthalpy of nanocomposites is higher than that of the neat blend. This implies that the nucleating role of nanosilica is more effective than its role in reduction of polymer chain movements. At high nanosilica contents, because chain movements are strongly affected by nanoparticles, reduction of the growth process is more than nucleating effect of nanosilica particles, as a result melts enthalpy of nanocomposites decreases.⁶ These results show that nanosilica particles are residing in both

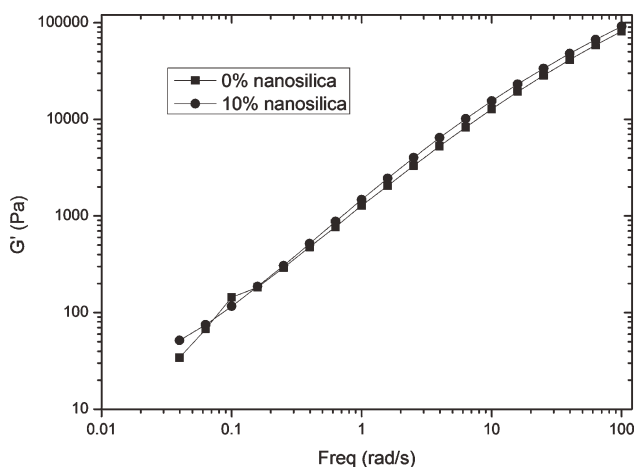


Figure 10. Storage modulus of LLDPE/EVA blend and nanocomposite with 10 wt % of nanosilica.

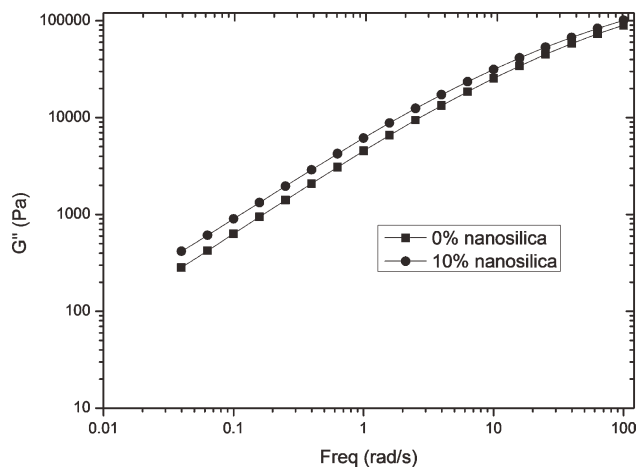


Figure 11. Loss modulus of LLDPE/EVA blend and nanocomposite with 10 wt % of nanosilica.

LLDPE and EVA phases that can change both the melting enthalpy. Results also indicate that increasing of the modulus with the nanosilica content cannot be due to increasing of the crystallinity because the melt enthalpy of the second peak which is related to the LLDPE major phase decreases with nanosilica content.

Rheological Properties

Figure 9 shows the influence of nanosilica on complex viscosity of LLDPE/EVA blend. It is seen that complex viscosity increases with increasing the nanosilica content. Figures 10 and 11 show the effects of nanosilica on loss modulus (G'') and storage modulus (G') as a function of the angular frequency. Comparing the G'' with G' data at low frequency region it is seen that $G'' > G'$ indicating that the nanocomposite containing 10 wt % nanosilica does not show any solid like behavior. Because of the small size and high surface area, untreated nanosilica particles tend to self-aggregate and form network in molten polymer matrix. Due to the strong particle-particle interaction unmodified nanosilica particles show the solid like behavior in terminal zone.¹² These strong interactions can be related to hydrogen bonds among silanol groups on the surface of unmodified particles. However, in our case since the treated nanosilica was used the solid like behavior was not seen even in the system with 10 wt % nanosilica. This means that treatment of silica particles with HMDS has delayed formation of the solid like behavior, consequently processing of these nanocomposites is easier than composites that show the solid like behavior. Figure 11 also show that incorporation of the treated nanoparticles into LLDPE/EVA blend do not have remarkable effect on G' as a function of the angular frequency.

CONCLUSIONS

For LLDPE/EVA blend the results of the mechanical properties indicated that nanocomposite with 10% content of nanosilica had the best tensile properties. Increasing of the elongation at break with nanosilica content was an unusual phenomenon which could be because of the change in the morphology of blends. Adding the compatibilizer did not have any dramatic effect on the mechanical properties of nanocomposites. For this

nanocomposite, our study showed the results of Contou model for prediction of the modulus were better than other models. DSC results showed nucleating effect of nanoparticle on crystallization process that increased the melting enthalpy. The rheological analysis did not show the solid-like behavior even at 10% of nanosilica, which means the particle–particle interactions had been decreased dramatically with treatment of the nanosilica surface.

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