Morphological and Mechanical Properties of LDPE/EVA Based TPE: Effect of both Modified and Unmodified Nanosilica

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Abstract: A comparative study between the modified and unmodified nanosilica to fine tune the morphological and mechanical properties of a model low-density polyethylene (LDPE) – ethylene vinyl acetate copolymer (EVA) thermoplastic elastomer blend system is explored in this article. The nanosilica particles were melt-blended with the LDPE/EVA system at 1.5, 3, and 5 wt % loadings through the variation of the sequence of addition. The blends were compression molded, and their morphological and mechanical properties were evaluated. The incorporation of mSiO₂ produced a drastic improvement of Young’s modulus (up to 60%) as compared to the control blend. The morphological studies clearly indicated that modified silica had a homogeneous dispersion in the bi-component polymer matrix leading to strengthening of silica-polymer interface. Interestingly, after modification the sequence did not play a major role in affecting the morphology of this system. Overall, although the properties of the unmodified nanosilica filled blends are strong functions of the sequence of addition, but, interestingly, the properties of the modified nanosilica filled blends do not depend much on the preparation procedure.

Keywords: Silica nanoparticles, blends, nanocomposites, dispersions, morphology, reinforcement

I. INTRODUCTION

The search for polymeric materials with new property profiles has stimulated a great interest into polymer blends and reactive processing. Currently, nano structured fillers become the main focus of attraction in polymer industries. The nano-particles are used in immiscible polymer blends as compatibilizers. These particles lead to unique properties resulting from the nano-scale microstructure by reducing the interfacial tension of the immiscible polymers and converting these to useful polymeric products with desired properties. Morphology plays a critical and influential role on the performance of multiphase blends. Blend morphology initially depends on the way in which the blend components interact when the individual blend components are brought into physical contact and it ends when the structure becomes frozen in only at the beginning of development of micro structure. The state of distribution and dispersion of nano particles between the two phases, the extent of interaction of the particle surface with either of the polymeric phases, and the resultant final phase morphology are believed to be the most important factors affecting the overall properties of the final blends. Recently, a new concept of compatibilization by using rigid nano-particles like layered silicate and nanosilica has been proposed by Ray et al. and Zhang et al. [1-2].

The key factors for performance improvement of nanocomposites are wide dispersion of nanoparticles over a polymer matrix and enhanced nanoparticles/matrix interaction. But homogeneous dispersion of nanoparticles in polymers is very difficult because the particles possessing high surface energy tend to agglomerate during melt blending [3-5]. In silica for example, the presence of hydroxyl groups can lead to hydrogen bonding between contiguous particles. Therefore, to remove all these difficulties many chemical approaches have been developed for the preparation of nanocomposites. Many research efforts have been devoted to the surface modification of silica leading to hydrophobic silica [5-16], among which alkyltrialkoxyxilanes, X (CH₃)₃Si(OR)₃, have been widely used. Such a surface modification reduces the high surface energy of the nanoparticles and the particle interactions. This increase in hydrophobicity of the nanoparticles leads to enhanced filler-matrix miscibility and improved interfacial interaction. Therefore the dispersibility of the filler in organic media is improved due to the more probable interactions of the polymer with the modification than with the inorganic particle surface. In this way the structure-property relationship of the nanocomposites can be tailored on purpose. Liu et al. have reported that silane-modified nanosilica disperses more efficiently in the polymer matrix, giving rise to improved impact properties of the TPO composites, compared to the unmodified filler [17]. The influence of surface modification on the structure and properties of a nanosilica filled thermoplastic elastomer has been explored by Aso et al. [18]. Bailly et al. have reported the morphology and physical properties of silane-grafted polypropylene (PP-g-VTEOS) reinforced with silica nanoparticles and toughened with an elastomeric ethylene-octene-copolymer (POE) [19]. Sequence of addition of individual
polymer and fillers also plays an important role in determining the properties of polymer blends. Effects of the blending sequence and interfacial agent on the morphology and mechanical properties of injection molded PC/PP Blends have been studied by R. A. Torres, J. Arellano- Ceja, M. E. Hernández-Hernández and R. González-Nuñez [20]. Effect of blending sequence on microstructure of Nylon 66/organoclay/SEBS g-MA based ternary nanocomposites has been studied by Aravind Dasari, Zhong- Zhen Yu and Yiu-Wing Mai [21].

From the literature review it is realized that, no comparative study has been made to understand the effect of both modified and unmodified nanosilica on the structure-property relationship of LDPE/EVA based TPE system. A thermoplastic elastomer (TPE) blend system derived from low-density polyethylene (LDPE) and ethylene vinyl acetate copolymer (EVA) has been chosen for this study. In the present work we aim at making a comparative study by taking the advantage of addition of pristine nanosilica and trimethoxyoctylsilane modified nanosilica to fine tune the morphological and mechanical properties of LDPE/EVA TPE systems by following the different procedure of mixing sequence.

II. METHODS AND MATERIAL

The plastic used for this work was LDPE (Indothene MA 400) supplied by IPCL, Vadodera, India (0.918 g/cm³ density as per ASTM D 1505, MFI as per ASTM D 1238 at 190°C using 2.16 kg load 30 g/10 min melt index). The elastomer used was EVA containing 40% vinyl acetate (EVA-40) (0.967 g/cm³ density as per ASTM D 792, MFI as per ASTM D 1238 at 190°C using 2.16 kg load: 3 g/10 min) purchased from Bayer (Leverkusen, Germany). Silicon dioxide nanopowder was procured from Aldrich Chemical Co. Ltd. Modified Nanosilica (mSiO₂), treated with trimethoxyoctylsilane, Aerosil ® R805, having a specific surface of 150 m²/g (particle size ~10–15 nm) was procured from Degussa Chemical.

A. Sample Preparation

Melt blending was carried out with EVA (60 wt%) and LDPE (40 wt%) with various loadings of nanosilica (1.5, 3, and 5 wt%, respectively) in a Brabender Plasticorder (PLE-330) (Duisburg, Germany) at 130°C and 80 rpm rotor speed by varying two different sequences of addition of ingredients. In Sequence-1 LDPE was initially allowed to melt for 4 min, followed by EVA addition. Thereafter, the nanosilica particles were added to the mixture. The total mixing time was 10 min. The mixes so obtained were sheeted out via passing through an open mill set at a 2-mm nip gap. In Sequence-2, initially EVA was made soften for 4 min, which was followed by the addition of nanosilica particles (various loadings) for another 4 min at 110°C to prepare the master batch comprising EVA and nanosilica. Thereafter, LDPE was allowed to melt for 4 min at 130°C, followed by the addition of EVA–silica particle mixture (that was previously mixed at 110°C). Mixing was carried out for 2 min at 130°C. The mixes so obtained were also sheeted out via passing through an open mill set at a 2-mm nip gap. For both the sequences after the initial mixing (as depicted earlier), the mixtures were remixed again in the Brabender Plasticorder for another 2 min at 130°C to get more homogeneity. The control (unfilled) blend (C) was prepared by first allowing the LDPE to melt for 4 min at 130°C, followed by EVA for 6 min. The mixes from the first pass were also sheeted out using a two-roll mill set at a 2-mm nip gap. This was then remixed for another 2 min. All the nanocomposites prepared were compression molded between two Teflon sheets for 3 min at 150°C with a preheat time of 1 min and with a load of 5 Tons on platens (18x15 cm²) in an electrically heated hydraulic press to obtain films of 0.03–0.04 cm thickness. The moldings were cooled under compression to maintain the overall dimensional stability. The details of the samples and their appropriate designations are given in Table-1.

<table>
<thead>
<tr>
<th>Sample code *</th>
<th>LDPE (wt%)</th>
<th>EVA (wt%)</th>
<th>Nanosilica (wt%)</th>
<th>Sequence of addition of ingredients</th>
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<tbody>
<tr>
<td>C</td>
<td>40</td>
<td>60</td>
<td>0</td>
<td>–</td>
</tr>
<tr>
<td>CS/3-1</td>
<td>40</td>
<td>60</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>CS/1.5-2</td>
<td>40</td>
<td>60</td>
<td>1.5</td>
<td>2</td>
</tr>
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<td>60</td>
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<td>1</td>
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<td>40</td>
<td>60</td>
<td>5</td>
<td>2</td>
</tr>
</tbody>
</table>

* C: - Control EVA (60 wt%) + LDPE (40 wt %) Blend, S: - Silica, m: - modified
B. Microscopy Studies

1) Field-emission scanning electron microscopy (FESEM): The nanoscale bulk morphology of the composite was observed with FESEM. The samples were vacuum-dried and then about 20 micrometer scales from the surface of 1mm thick film was removed in room temperature using the diamond knife of a LEICA ULTRACUT UCT (Austria) microtoming device. The samples were then coated with a thin layer of gold with a sputter coater equipped with a quartz crystal microbalance thickness controller. They were then imaged at high magnifications (e.g., 160,000x) with a Leo 1530 field emission scanning electron microscope (Carl Zeiss, Oberkochen, Germany).

2) Transmission electron microscopy (TEM): For the transmission electron microscopic (TEM) observation, the compression molded specimens were dried in a vacuum oven overnight at ambient temperature. Then the specimens were cut into ~50 nm thick sections on a Leica ULTRACUT UCT (Austria) microtoming apparatus equipped with a diamond knife. The preparation of the sections was conducted at 1.0 mm/s at approximately -50°C in liquid N2 atmosphere. The ultra thin sections were mounted on 300-mesh copper grids and dried in desiccators and examined using a high-resolution transmission electron microscope (HRTEM) (JEOL JEM 2100, Japan) operated at an accelerating voltage of 200 kV with a resolution of 1.9Å.

C. Mechanical properties

The specimens for the measurement of mechanical properties were punched out from the molded films using ASTM Die-C. The measurement was carried out in a HIOKS-HOUNS FIELD universal testing machine (Test Equipment, Ltd., Surrey, England) at a crosshead speed of 100 mm/min at 25°C. The average of three tests is reported here. The force-elongation curve was plotted with Lab Tensile software, from which the tensile strength and elongation percentage were calculated. The tension set properties were measured with a similar tensile sample by elongation up to 100% elongation for 10 minutes, and the percentage set were measured after equilibration for another 10 minutes.

III. RESULTS AND DISCUSSION

A. Microscopy Studies

Field Emission Scanning Electron Microscopy (FESEM)

FESEM photomicrographs of the unmodified and modified silica-filled EVA/LDPE system are shown in Fig. 1.

![FESEM photomicrographs of the microtome surface of samples of 60:40 EVA: LDPE blends with various loading of nanosilica particles:](image-url)
For morphological analysis, intentionally FESEM was performed on samples prepared at room temperature (to enhance the contrast of the deformed rubbery phase and comparatively non-deformed plastic matrix) to visualize the dispersion-aggregation of silica particles. It is important to note that the room temperature modulus of pure EVA is considerably less than that of pure LDPE. Thus at room temperature EVA is more ductile than LDPE.

It is found that the average diameter of dispersed pristine SiO$_2$ nano particles spans from 12 to 200 nm along with the appearance of aggregates of higher length scales [Fig. 1 (a) – (d)] whereas in case of mSiO$_2$ nanoparticles it spans from 4 to 46 nm [Fig. 1 (e) – (h)] (by image analysis using Image J software, NIH, USA). A fine dispersion of silica is observed in the polymer matrix with 1.5 wt% pristine silica, with very little aggregated structure along with distorted EVA domains [Fig. 1(a)]. For CS/3-1, silica particles are dispersed in a nano- to micro scale range [Fig. 1(b)] in both phases as well as in the interface. Some spherical lumps are also noticed which may be the deformed EVA phase. However, in this case deformation of EVA phase is less as compared to CS/3-2, which indicates the possibility of intermixing of both phases and strengthening of EVA phase. This will be also explained in light of TEM observation in the following section. For CS/3-2, greater deformation of EVA phase is observed [Fig.1(c)]. This indicates that in this case dispersion of silica particles in the interface is not as good as that of previous one. Obviously, with 5 wt% loading, more silica particles are distributed in the polymer matrix along with aggregated structure [Fig. 1(d)]. In all modified silica loaded samples, a fine, homogeneous and uniform dispersion of mSiO$_2$ is observed both in the polar EVA phase and in the non-polar LDPE matrix with very tiny aggregated structure [Fig. 1 (e) – (h)]. Interestingly, here most of the mSiO$_2$ particles are strongly confined at the interface, leading to more interfacial strength. These nanoparticles, very present at the interface, thus provoke a small but yet very important physical compatibilization of the phases.

1) Transmission Electron Microscopy (TEM): To investigate the state of dispersion of silica particles in the bi-component polymeric matrix, TEM analysis was performed for some selected samples. TEM photo-micrographs of pristine and modified silica filled samples are shown in Fig. 2. The gray and the white regions correspond to LDPE matrix and intermixed (LDPE-EVA) portion respectively. Besides gray LDPE matrix and bright EVA phase, a dark phase is also appeared which represents intermixed portion of silica filled EVA domains. In all cases, the intensity of the black color varies among the dispersed particles. The change in the intensity of black color is attributed to the presence of silica particles in the EVA phase. Besides all these, the typical silica network is observed in all samples.

In CS/3-1, most of the particles are randomly distributed in both phases as well as in the interface [Fig. 2 (a)] which proves the occurrence of intermixing. In CS/3-2 [Fig. 2(c)], the pristine nanoparticles are organized in a three-dimensional network-type structure and most of the particles are concentrated in EVA phase.

![Fig. 2: TEM photomicrographs of (a) CS/3-1, (b) CmS/3-1 (c) CS/3-2, (d) CmS/3-2](image-url)
For all the modified silica loaded samples the covalent bonding between the polymer and the modified filler improves the stress transfer to the filler during melt compounding, resulting in more efficient breakup of the filler aggregates. Further, the silane consisting of long alkyl chains replace silanol groups of silica tends to reduce the size of the aggregates, by breaking the hydrogen bonds between the particles, therefore improving the dispersion of the fillers. As a result of intermixing the mSiO$_2$ particles are more uniformly dispersed in both phases as well as in the interface in sequence-1 [Figure 2(b)]. Interestingly, in contrast to the untreated silica, in CmS/3-2, mSiO$_2$ particles are well distributed in both phases as well as in the interface like CmS/3-1 [Fig. 2 (d)]. The similar morphology is observed in all the samples prepared by sequence-2 that is not shown here. The surface treatment of nanosilica renders it more hydrophobic, therefore reducing its polar nature and increases its affinity towards more hydrophobic polymer matrix. This further contributes to the improved dispersion of the mSiO$_2$. Ultimately mSiO$_2$ increases the compatibility between EVA and LDPE. One important observation noticed here is that as the silica particles are modified, so the sequence does not play a major role in affecting the morphology of this system. It is evident from these morphologies that the modified silica has a homogeneous dispersion in the bi-component polymer matrix. In sequence-2, the hydrophilic silica tends to confine in the EVA phase whereas the hydrophobic one is located at the EVA/ LDPE interface and in both phases.

B. Mechanical Properties

Tensile tests were performed to investigate mechanical properties of the samples with varying composition and method of preparation. The average mechanical properties of pristine silica loaded samples are given in Table 2.

Table 2: Effect of filler loading on the mechanical properties of the films made from unmodified silica filled EVA/LDPE TPE system

<table>
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<tr>
<th>Sample code</th>
<th>T.S. (MPa)</th>
<th>E.B. (%)</th>
<th>Modulus (MPa)</th>
<th>Set (%)</th>
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<tr>
<td></td>
<td></td>
<td>100%</td>
<td>200%</td>
<td>300%</td>
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<tr>
<td>C</td>
<td>3.4</td>
<td>480</td>
<td>2.63</td>
<td>2.90</td>
</tr>
<tr>
<td>CS/1.5-2</td>
<td>3.8</td>
<td>478</td>
<td>2.62</td>
<td>2.93</td>
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<tr>
<td>CS/3-1</td>
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<td>479</td>
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<td>450</td>
<td>2.28</td>
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Within the sequence-2, the tensile strength initially increases with silica loading, reaches its maximum value at a loading of 3 wt% followed by a decrease with further increase in silica loading. On the contrary, both high and low strain modulus decreases with increase in filler loading. Elongation at break is only improved in case of samples with 3 wt% silica loading. At a constant loading of 3 wt% silica, maximum tensile strength is observed in sequence-2. Modulus decreases with the variation of sequence at a constant loading and the trend remains similar to that of tensile strength. Elongation at break of sequence-1 & 2 are comparable with the control sample. But in all cases, tension set is improved as compared to the control one. Initial increase in tensile strength up to 3 wt% loading of silica is possibly due to the increase in the interfacial interaction which eliminates the possibility of formation and propagation of crack at interface during stretching. Also at 3 wt% loading, the unmodified silica particles are optimally dispersed in the elastomeric phases compared to other loadings, providing better reinforcement effect. On the other hand, since surface of the silica particles are not modified, filler-polymer interaction is not manifested in the increase of percent elongation and modulus. At higher loading, tensile strength and modulus are not affected greatly. This can be ascribed due to aggregation of fillers leading to occurrence of low energy deformation modes e.g., aggregate breakage, aggregate-polymer interface breakage and from the defect sites. Thus it dilutes the reinforcement effect.

As compared to sequence-1, in sequence-2, property enhancement is maximum. Since in this particular sequence silica was initially blended to the more polar EVA phase, silica distribution is more uniform here, leading to strengthening of the weaker phase of the
blend system (as observed in morphological analysis). In sequence-1 on the other hand, equivalent probability of distribution of silica particles in both the LDPE and EVA phases exists. These explain the difference in mechanical properties.

Improvement of set properties can be explained on the basis of improvement of the recovery of the polar EVA matrix in presence of silica fillers. The average mechanical properties of modified silica loaded samples are given in Table 3. Significant reinforcement is achieved upon mSiO₂ addition with respect to the control blend. This indicates that for this modified silica the extent of particle modification is balanced, so that filler/filler interactions can be reduced enough to prevent particle agglomeration and to facilitate dispersion while leaving a sufficient amount of hydroxyl groups available to form covalent bonds. Within sequence-2, the tensile strength increases with increase in mSiO₂ loading and this increase is much more significant as compared to untreated silica. The increase in tensile strength is possibly due to the increase in the interfacial interaction which eliminates the possibility of formation and propagation of crack at interface during stretching. Due to fine dispersion and good hydrophobic nature of mSiO₂ the interface can transfer more stress from polymeric matrix to the inorganic particles, which may improve the tensile strength. At a constant loading of 3 wt% silica in both sequences, property enhancement is more in sequence-1. This further proves the occurrence of intermixing between EVA and LDPE in the continuous matrix of LDPE that becomes more significant upon mSiO₂ addition. Overall, the property enhancement is maximum in case of CmS/5-2. This is due to the destruction of aggregated network structure and fine dispersion of modified silica in the bi-component polymeric matrix as well as in the interface [evidenced from earlier morphological analysis]. Thus interfacial adhesion between polymer-polymer and polymer-filler is improved. So the reinforcement effect is more significant than the other samples prepared by sequence-2. The incorporation of mSiO₂ results in a drastic improvement of Young’s modulus (up to 60%) as compared to the control blend. As interfacial stress transfer efficiency depends on the stiffness and area of the interface, higher interfacial stiffness favors improvement of the composite modulus. This higher modulus of the nanocomposites reflects their higher interfacial area. Additionally all samples retain remarkably higher values of elongation. It is a result of interfacial viscoelastic deformation and matrix yielding which is again attributed to the significantly better dispersion of mSiO₂. Improvement of set properties can be explained on the basis of improvement of the recovery of the polar EVA matrix in presence of silica fillers.

### Table 3: Effect of filler loading on the mechanical properties of the films made from modified silica filled EVA/LDPE TPE system

<table>
<thead>
<tr>
<th>Sample code</th>
<th>T.S. (MPa)</th>
<th>E.B. (%)</th>
<th>Modulus (MPa)</th>
<th>Set (%)</th>
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<td>200 %</td>
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<tr>
<td>C</td>
<td>3.4</td>
<td>480</td>
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<tr>
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<td>667</td>
<td>2.72</td>
<td>3.10</td>
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</table>

Overall, the mechanical properties are remarkably increased in mSiO₂ filled samples as compared to the untreated silica. In case of untreated hydrophilic silica filler-filler interaction leads to the formation of agglomerates. But in case of treated hydrophobic silica, a combination of formation of covalent bonding and good dispersion leads to substantial improvement in mechanical properties at the same loading.

### IV. CONCLUSIONS

Nanoscale modified and unmodified silica, when dispersed in LDPE/EVA-based TPE systems, alter the nanoscale morphology of the blend systems as well as their mechanical properties. The final dispersion state of mSiO₂ and morphology of the blend do not depend much on the preparation procedure in contrast to untreated silica where the morphology is a strong function of sequence and
extent of nanosilica addition. The surface treatment of nanosilica renders it more hydrophobic, therefore reducing its polar nature and increases its affinity towards more hydrophobic polymer matrix. Significant reinforcement is achieved upon mSiO₂ addition with respect to the control blend. Within sequence-2, the tensile strength increases with increase in mSiO₂ loading and this increase is much more significant as compared to untreated silica. At a constant loading of 3 wt% silica in both sequences, property enhancement is more in sequence-1. Overall, the property enhancement is maximum in case of CmS/5-2. The incorporation of mSiO₂ results in a drastic improvement of Young’s modulus (up to 60%) as compared to the control blend. Additionally all samples retain remarkably higher values of elongation.

REFERENCES