Effect of both Modified & Unmodified Nanosilica on Morphological and Thermal Properties of Model TPE Blend Systems

Dr.Shalmali Hui[1*]

Assistant Professor, Department of Chemistry, Achhruram Memorial College, Jhalda, Purulia-723202, West Bengal, India

Abstract

A comparative study between the modified and unmodified nanosilica to fine tune the morphological and thermal 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 through the variation of the sequence of addition. The blends were compression molded, and their morphological and thermal properties were evaluated. The incorporation of nanosilica particles produced a drastic improvement in thermal stability as compared to the control blend. The morphological studies clearly indicated that modified nanosilica 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

Introduction

During the last two decades polymer systems are widely used due to their unique attributes, e.g., ease of production, light weight and ductility. In performance characteristics, applications and diversity, polymer blends offer a degree of versatility which is not found in any other kind of materials. At present, nano structured fillers become the center of attention in polymer industries. Nanotechnology is now recognized as one of the most promising fields of research in the 21st century. These nanoparticles 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. The performance of multiphase blends depends on morphology. In the case of nanocomposites based on polymer blends, the microscale morphology as well as the nanoscale filler distribution could dictate the resultant properties of the composites [1-3].The interfacial interaction between polymer and nanofiller strongly affects the mechanical, thermal, and otherproperties of the nanocomposites.

These particles possess high surface energy. So they tend to agglomerate during melt blending. As a result, homogeneous dispersion of nanoparticles in polymers is very difficult [4-8]. In silica, forexample, the silanol groups residing on adjacent particles, in turn, form hydrogen bonds and lead to construction of aggregates. Therefore, to enhance the compatibility between polymer and the nanosilicamany chemical approaches have been developed for the preparation of nanocomposites. Many research efforts have been devoted

Corresponding author
Email address; mamoni06@gmail.com
Tel no.: +919433442653

to the surface modification of silica leading to hydrophobic silica [8-14], among which alkyltrialkoxysilanes, $X(CH_2)_n Si(OR)_3$, have been widely used.

Such a surface modification greatly improves the dispersion and distribution of nanosilica particles in polymeric matrices. In this way the structure-property relationship of the nanocomposites can be tailored on purpose. The influence of surface modification on the structure and properties of a nanosilica filled thermoplastic elastomer has been explored by Aso et al. [15]. An overview on the degradability of polymer nanocomposites has been studied by Pandey et al. [16]. Aspects of the thermal oxidation of EVA have been investigated by Allen et al. [17]. Sequence of addition of individual polymer and fillers also plays an important role in determining the properties of polymer blends [18].

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 thermal properties of LDPE/EVA TPE systems by following the different procedure of mixing sequence.

Experimental

Materials

The plastic used for this work was LDPE (16MA400) supplied by Reliance Industries Limited, India (0.918 g/cm^3 density, MFI as per ASTM D is 30 g/10 min). The elastomer used was EVA-40 (0.967 g/cm^3 density, MFI as per ASTM D 1238 is 3 g/10 min) purchased from DuPont, India. Pristine silicon dioxide nanopowder and modified Nanosilica ($mSiO_2$), treated with trimethoxyoctylsilane, Aerosil® R805 (particle size ~10–15 nm) were procured from Degussa Chemical.

Sample Preparation

Melt blending of polymers and nanosilica powder (3 wt% loading) was carried out in a BrabenderPlasticorder at 130°C and 80 rpm rotor speed. Two different sequences of addition were used. In sequence-1, initially LDPE and EVA were mixed, and then the nanosilica particles were added to the mixture. The total mixing time was 10 min. In sequence-2, initially EVA and nanosilica particles were mixed at 110°C to prepare a master batch. Thereafter LDPE was melt blended with this master batch at 130°C. The total mixing time was 10 min. The control blend was prepared by allowing the LDPE to melt for 4 min at 130°C, followed by EVA for 6 min. All these mixtures were remixed again in the BrabenderPlasticorder for another 2 min at 130°C to get more homogeneity. All the nanocomposites prepared were compression molded between two Teflon sheets for 4 min at 150°C with a preheat time of 1 min 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.

Field Emission Scanning Electron Microscopy (FESEM)

The nanoscale bulk morphology of the nanocomposites was observed using a Leo 1530 FESEM instrument (Germany). The samples were vacuum-dried and then about 20

micrometer scales from the surface of 1 mm thick film was removed in room temperature using the diamond knife.

Table 1: Sample Designation (* C: Control EVA (60 wt%)/ LDPE (40 wt%) Blend, S: Silica, m: modified)

Sample code *	LDPE (wt%)	EVA (wt%)	Nanosilica (wt%)	Sequence of addition of ingredients
C	40	60	0	-
CS/3-1	40	60	3	1
CS/3-2	40	60	3	2
CmS/3-1	40	60	3	1
CmS/3-2	40	60	3	2

Microscopy Studies

Transmission Electron Microscopy (TEM)

The microstructure of the nanocomposites was imaged using a high-resolution transmission electron microscope (HRTEM) (JEOL JEM 2100, Japan). The specimens were cut into ~50 nm thick sections with a diamond knife.

Thermal Properties

Thermogravimetric Analysis (TGA)

The thermogravimetric analysis was conducted on a TA Instrument (USA), model Q 50 under O_2 flow from ambient temperature to $600^{\circ}C$. In the present study, the temperature corresponding to 5% degradation, taken as the degradation onset temperature (T_{onset}) and the temperature corresponding to the maximum value (peak) in the derivative thermogram (T_{max}) were recorded.

Results and discussion

Evaluation of Morphology

Field Emission Scanning Electron Microscopy (FESEM)

FESEM photomicrographs of the unmodified and modified nanosilica-filled LDPE/EVA systems are shown in Figure (1).The average diameter of dispersed pristine SiO_2 nanoparticles spans from 12 to 200 nm along with the appearance of aggregates of higher length scales [Figure 1 (a) and 1 (c)] whereas in case of $mSiO_2$ nanoparticles it spans from 4 to 46 nm [Figure 1 (b) and 1 (d)] (by image analysis using image J software, NIH, USA). The silica particles are dispersed in both phases as well as in the interface in case of CS/3-1 [Figure 1 (a)]. 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. The deformation of EVA phase is greater for CS/3-2 [Figure 1(c)]. This indicates that in this case dispersion of silica in the interface is not as good as that of previous one. In all the 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 [Figure 1(b) and 1 (d)]. Interestingly, here most

of the $mSiO_2$ particles are strongly confined at the interface, leading to more interfacial strength.
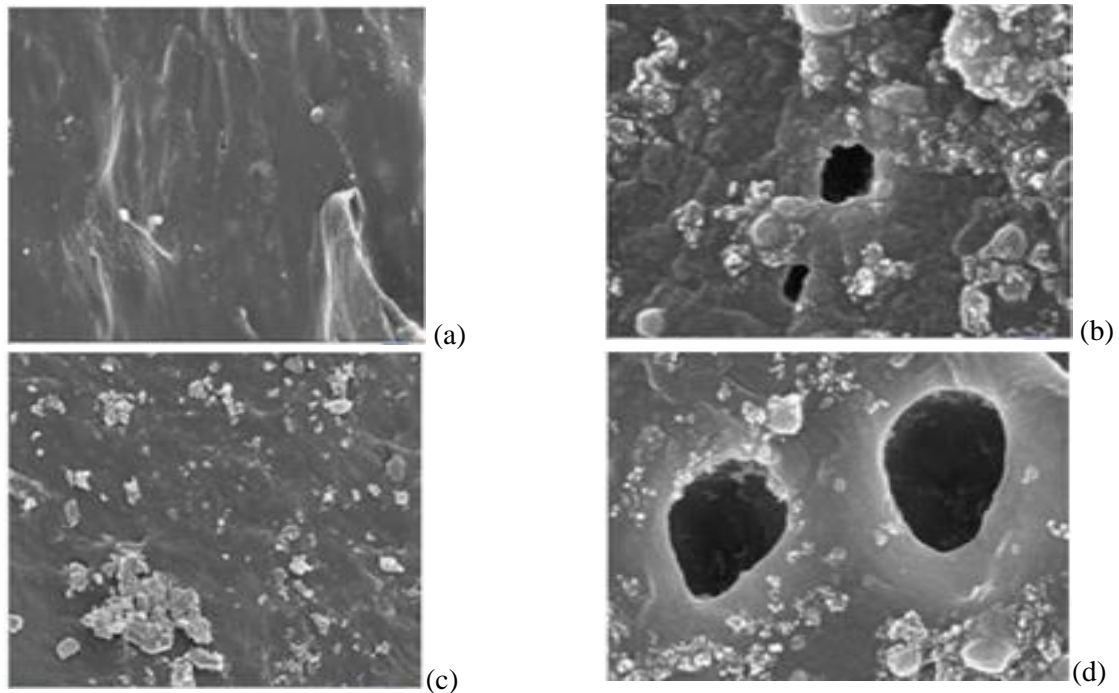

Figure 1. FESEM photomicrographs of the microtome surface of samples of 40:60LDPE: EVA blends filled with nanosilica particles: (a)CS/3-1 (b)CmS/3-1 (c)CS/3-2 (d)CmS/3-2

Transmission Electron Microscopy (TEM)

TEM photo-micrographs of pristine and modified nanosilica filled samples are shown in Figure (2). The gray region corresponds to LDPE matrix and the intermixed (LDPE-EVA) portion is indicated by the white section. Besides gray LDPE matrix and bright EVA phase, a dark phase is also appeared. It represents intermixed portion of silica filled EVA domains. Besides all these, the typical silica network is observed in all the samples.

In CS/3-1, most of the particles are arbitrarily dispersed in both phases as well as in the interface [Figure 2(a)]. This further proves the occurrence of intermixing. In CS/3-2 [Figure 2(c)], the pristine nanoparticles are organized in a three-dimensional network-type structure. Here most of the particles are concentrated in the EVA phase.

As a result of intermixing the $mSiO_2$ particles are more uniformly dispersed in both phases as well as in the interface in CmS/3-1 [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 [Figure 2 (d)]. The surface treatment of nanosilica renders it more hydrophobic, therefore reducing its polar nature and increases its affinity towards more hydrophobic polymer matrix. This 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 LDPE/ EVA interface and in both phases.

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Figure 2. TEM photomicrographs of (a) CS/3-1, (b) CmS/3-1 (c) CS/3-2, (d) CmS/3-2
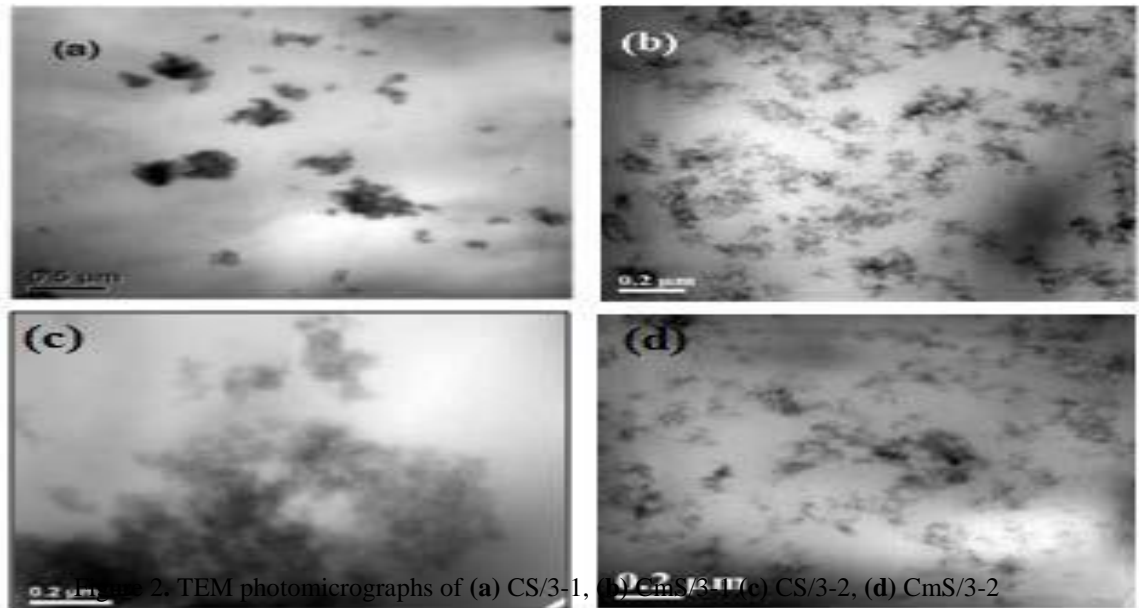
Thermal Properties

Figure 3 shows the TGA thermograms of control blend and modified & unmodified nanosilica filled systems with variation of sequences.
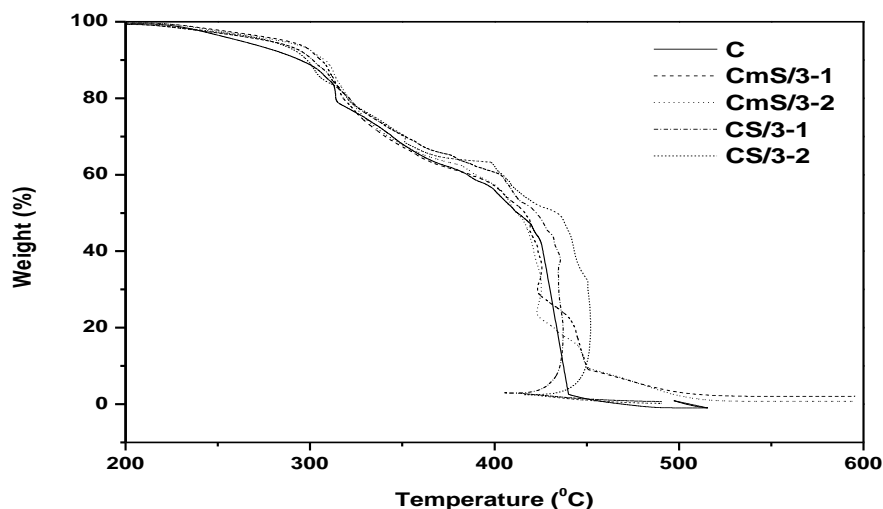

Figure 3. Typical TG Trace of LDPE/EVA systems filled with modified and unmodified

nanosilica in O_2 atmosphere

Two distinct and well separated steps are observed. The first step (306-316°C) for all samples (unfilled and. filled) possibly corresponds to deacetylation of vinyl acetate group of EVA with the elimination of acetic acid and the formation of double bonds [19]. The second step (420-443°C) may be assigned to the further degradation of polyacetylene-ethylene chains formed in the first step accompanied with the degradation of LDPE [19]. The parameters obtained from TGA thermograms are summarized in Table 2.

The onset of degradation of CS/3-1 and CS/3-2 are quite similar. But upto 20% conversion, the thermal stability of CS/3-1 is higher than that of CS/3-2. This again

reflects the possibility of intermixing of EVA and LDPE in the continuous matrix for CS/3-1 leading to strengthened silica-polymer interface. The intermixing of LDPE and EVA for such systems has been proven by FESEM and TEM analyses in the earlier section. As a result of intermixing, O2 diffusion through the polymer matrix is initially restricted. The significant delay of weight loss in O_2 has been attributed to the barrier effect due to diffusion of both the volatile thermo-oxidation products to the gas phase and oxygen from the gas phase to the polymer matrix [20].

The thermal stability increases significantly upon addition of modified nanosilica in all samples. Most importantly, as compared to unmodified fumed silica, the onset of degradation of CmS/3-1 increases considerably. In CmS/3-1, due to intermixing the hydrophobic silica particles are dispersed more uniformly in both EVA and LDPE phases as well as in the interface as compared to unmodified silica. Thus O_2 diffusion through the polymer matrix is restricted more. As a result onset of degradation increases. However, in case of $mSiO_2$, comparing sequence 1 and 2 at the same loading (CmS/3-1 and CmS/3-2) it is noticed although the onset of degradation is more in sequence 1 but overall thermal stability is similar in both sequences. Thus it is again evident from here that just like morphological properties, the thermal stability of $mSiO_2$ filled samples does not depend considerably on the preparation procedure.

Table 2: Characteristic parameters obtained from the thermo-oxidative degradation of both modified and unmodified silica filled TPE systems in oxygen atmosphere at the heating rate of $10\,^{o}C$

Sample ID	T_{onset} (^{o}C)	T_1 (^{o}C)	T_2 (^{o}C)	Residues (%)	Maximum rate of decomposition (%/^{o}C)
C	260±1*	312±1	420±1	0	0.58±0.12
CS/3-1	278±1	313±1	431±1	2.95±0.05	1.21±0.10
CS/3-2	279±1	311±1	444±1	2.97±0.01	1.24±0.09
CmS/3-1	289±1	315±1	422±1	2.06±0.01	1.27±0.09
CmS/3-2	287±1	316±1	421±1	0.79±0.01	1.27±0.09
*Standard deviation T_1 = First decomposition temperature (^{o}C) T_2 = Second decomposition temperature (^{o}C)					

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 thermal properties. The final dispersion state of $mSiO_2$ 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 thermal stabilities of pristine nanosilica filled TPE nanocomposites are the strong function of sequence of nanosilica addition. Apart from the role of $mSiO_2$ in blend morphology development, the hydrophobic silica can considerably change the thermo-oxidative stability of this blend system. The thermal stability is increased more significantly upon addition of $mSiO_2$ in all samples irrespective of the sequence of addition.

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