Chapter

Nanosilica Composite for Greenhouse Application

Malek Alghdeir, Khaled Mayya and Mohamed Dib

Abstract

This work represents the results of experiments on silicon dioxide insulation materials mixed with low-density polyethylene (LDPE) at a different proportion to prevent the transmittance of IR domain and to allow the transmittance of ultraviolet–visible (UV–Vis) domains, so we can keep the thermal radiation of the ground in the greenhouse. The mechanical properties of nanocomposites such as tensile were evaluated and discussed. Several ratios of nanosilica particles were employed to fabricate low-density polyethylene (LDPE) composites using melt mixing and hot molding methods. Six of composite films from different ratios (0.5, 1, 2.5, 5, 7.5, and 10 wt% nanosilica) were prepared. The obtained composite films were characterized and identified by ultraviolet–visible (UV–Vis) spectroscopy and Fourier transform infrared spectroscopy (FTIR). Thermal stability of samples was evaluated by thermogravimetric analysis (TGA). Surface morphology of samples was investigated by scanning electron microscopy (SEM). At specific mixing ratio, the ultraviolet–visible transmittance is allowed, while far infrared radiation transmittance was prohibited, and that will be explained in details. Optical measurements show that the composite films prevent the transmission of IR radiation near 9 μm and allow UV–Vis transmission during sun-shining time. The mechanical behavior was studied using tensile tests for nanosilica-reinforced LDPE composite. The sample with an addition of 1 wt% nanosilica has successfully enhanced the mechanical properties of LDPE material.

Keywords: silicon dioxide (SiO$_2$), low-density polyethylene (LDPE), composite barrier films, Fourier transform infrared spectroscopy (FTIR)

1. Introduction

Polymeric materials are widely used in greenhouses and in food packaging. Typical examples of such materials are polyethylene terephthalate (PET), polyethylene (PE), and polypropylene (PP) [1, 2].

In recent years, many studies have been done, and much effort has been devoted to polymer nanocomposites which have attracted a great attention from scientists [3]. The literature contains a plethora of experiments illustrating the thus involved parameters. At turns and among others, fabrication technique, matrix nature, nanofiller shape factor, and complex nature of the additives may be the determinants on the end-result properties of the polymer nanocomposites [4]. The dispersion of nanoparticles in the polymer matrix [5, 6] and the property of the interface between nanoparticle and polymer are regarded as key factors.
affecting the insulating properties of nanocomposites [7, 8]. Polymer nanocomposites often show superior mechanical properties compared to the conventional composites at a lower loading of the nanoparticles [9]. So far, a few researches have systematically studied the effects of different nanoparticles on the performances of composite materials [3].

The excellent properties of silicon dioxide film have attracted attention in industry and academia, due to its hardness, corrosion resistance, anti-resistance [10], dielectric properties [11], optical transparency, etc. [12]. Silicon dioxide as a thin film is widely used to improve the surface properties of materials. This is why silicon dioxide films are used in many fields as in antireflection coating field [13]. Silicon dioxide films are used as barrier layers in polymer packaging materials in the packaging industry. Most of the modern packaging materials do not provide an efficient barrier against the permeation of gases. This leads to drink and food not getting rotten quickly. Because of this, a silicon dioxide film deposited on the surface of polymer packaging becomes indispensable and popular. In addition, silicon dioxide films can be also used as corrosion protective layers of metals. Besides, the preparation of silica with high quality is always an important aim of scientific research because of the universal application of silicon dioxide films in various fields [14].

Currently, a number of different barrier coating technologies are being developed. Theoretically, a barrier function can be incorporated into a plastic-based packaging material via two different means, either by mixing a barrier material with the base polymer or by coating a layer of the barrier material [15, 16].

Presently, the traditional and simplest method of preparing polymer/silica composites is direct mixing of the silica into the polymer. The mixing can generally be done by melt blending and solution blending. This mixing process always results in the effective dispersion of the silica nanoparticles in the polymer matrix. The basic difficulty is when they usually tend to agglomerate [17].

This work represents the results of experiments on silicon dioxide insulation materials mixed with LDPE at a different proportion to prevent the transmittance of IR domain and to allow the transmittance of UV–Vis domains, so we can keep the thermal radiation of the ground in the greenhouse. The mechanical properties of nanocomposites such as tensile were evaluated and discussed.

Samples of neat LDPE and nanocomposites in different ratios (0.5, 1, 2.5, 5, 7.5, and 10 wt% SiO₂) were produced. Many material properties were investigated and will be discussed.

By studying blackbody thermal radiation, all objects with a temperature above absolute zero emit energy in the form of electromagnetic radiation. A blackbody is a model or theoretical body which absorbs all radiation falling

Figure 1.
Blackbody radiation spectra at 273, 293, 313, 333, 373, 393, 413, 433, and 453 K [14].
on it. It is a hypothetical object which is a “perfect” absorber and a “perfect” emitter of radiation. The electromagnetic radiation emitted by a blackbody has a specific intensity and spectrum that depend only on the body’s temperature; the thermal radiation spontaneously emitted by ordinary objects, for example, plants and land, can be approximated as blackbody radiation. Figure 1 shows the blackbody radiation spectrum at different several temperatures. We are interested in the vicinity of 10 μm (9–11 μm), because at the temperatures near 0°C (273 K), the thermal radiation from the ground is maximum at 10 μm while at the temperature 30°C (303 K), thermal radiation from the ground is maximum at 9.5 μm [14].

2. Material and methods

2.1 Materials

Low-density polyethylene (LDPE) which is a thermoplastic made from the monomer ethylene with a density of 0.922 g/cm³ was purchased from Saudi Basic Industries Corporation (SABIC). High-purity fumed nanosilica (purity >99%) with the trademarks of A200 with an average particle size of ~12 nm was obtained from Evonik Degussa AG (Germany). Table 1 shows the information on basic physical and chemical properties for fumed nanosilica.

2.2 Sample preparation

Samples were prepared by blending LDPE in different ratios (0.5, 1, 2.5, 5, 7.5, and 10 wt% SiO₂) and making plates from composite material. In different nanosilica ratios, nanosilica composites were mechanically mixed with LDPE granules at the processing temperature of 130°C and speed at 50 rpm min⁻¹ for 10 min using the internal mixer (Brabender Plasti-Corder PL-2200, W50, Germany). Films of the neat LDPE with dimension of 10 cm × 10 cm × 120 μm and nanocomposites were prepared by a hot press method at the temperature of 140°C and the pressure of 50 bars.

| Properties                   | Value                     |
|------------------------------|---------------------------|
| Physical state               | Solid                     |
| Color                        | White                     |
| Form                         | Powder                    |
| pH                           | 3.7–4.5                   |
| Melting point/range          | Approx. 1700°C            |
| Surface area                 | 200 ± 25 m²/g             |
| Density                      | Approx. 2.2 g/cm³         |
| Thermal decomposition        | >2000°C                   |
| Water solubility             | >1 mg/l                   |
| Loss on drying               | ≤1.5% (2 h at 105°C)      |
| Silica content based on ignited material | >99.8%                 |

Table 1. Information on basic chemical and physical properties for nanosilica.
3. Results and discussion

3.1 Infrared spectroscopic study

The transmittance of samples was examined by Fourier transform infrared (FTIR) spectroscopy (FTIR spectrometer, VERTEX 70/70v from Bruker™ Optics) in the wavelength range of 1–25 μm. Figure 2 shows the transmittance spectra of the SiO₂/LDPE films in different ratios.

Different absorption peaks could be identified in the MIR range. The first one at ~3 μm caused by OH group and other peaks at ~9 μm, ~12 μm, and ~21 μm, due to Si—O—Si resonance mode of vibrations [18]. Some of these peaks also involve the LDPE substrate in the IR absorption spectra. The peak at 9 μm gives the SiO₂ its importance and allows it to be used in this application. We observe a decrease in transmittance when the mixing ratio of SiO₂ increases. The changes in the average transmittance for wavelengths ranging from 7 to 10.5 μm are shown in Figure 3. We notice a sharp decline in transmittance when the ratio of SiO₂ is increased.

3.2 Ultraviolet-visible spectroscopy study

The optical transmittance measurements of LDPE/silica nanocomposite substrate films were carried out with a UV–Vis–NIR spectrophotometer (UV Spectrophotometer A560AOE instruments) at normal incident of light in the wavelength range of 200–1100 nm. Figure 4 shows the transmittance spectra of the samples. The UV spectra show that the composite substrates (0.5, 1, 2.5, 5, and 7.5 wt% SiO₂) have no significant effect on the transmittance. On the other hand, a significant decrease in the transmittance is observed with a mixture ratio of 10 wt% SiO₂ compared to the LDPE without mixing. This decrease is addressed in Section 3.

3.3 Mechanical property study

For mechanical property studies, the test specimens for tensile was molded and cut according to the dimensions specified in Table 2. The tensile test was measured using a traction compression machine Adamel Lhomargy DY34 under atmospheric conditions. Average five samples were tested and the stress-strain curves were recorded. Crosshead speed for tensile tests was carried at 5 mm/min. Table 3 shows the summary of tensile data for the control sample and six composites of LDPE.
Figure 5 shows the stress–strain curves from tensile tests for LDPE/silica nanocomposites. Figure 5 shows that the stress at break gradually increasing with the increase of silica loading up to 1 wt%. This result suggests that the fine silica particle

Table 2.
Specified dimension of samples for tensile test.

| Specifications                      | Dimensions (mm) |
|-------------------------------------|-----------------|
| Sample length                       | 75              |
| Display ends                         | 12.5 ± 1        |
| Length of the active part           | 25 ± 1          |
| Display the effective part          | 4 ± 0.1         |
| External radius                      | 8 ± 0.5         |
| Internal radius                      | 12.5 ± 1        |
would reinforce and orient along the direction of stress and this has contributed to the increase of tensile strength of the nanocomposite with the addition of 1 wt% of nanosilica particles.

The stress–strain curves also illustrate that there was a significant increase of elongation at break values of LDPE with the incorporation of nanosilica particle into the nanocomposite. This result indicates that the incorporation of nanosilica particle would improve the interaction between the molecules. At lower weight percentage, the addition of nanosilica in LDPE matrix increases surface interaction bonding between the molecules. The nanoparticles may be trapped inside entanglements resulting in a restriction on the polymer overall chain mobility.

**Figure 5** shows that both of the stress at break and elongation at break (strain) of nanocomposite achieved the highest values with 1 wt% loading of silica particles.

**Table 3.**
Summary of tensile data for the control sample and six composites of LDPE.
Above 1 wt% silica loading, both the stress and elongation at break showed a gradual drop. These results are attributed to the reinforcing effect of the silica particles. A higher amount of silica particles would reduce the reinforcing effect and mechanical properties of the nanocomposites due to poor dispersion and agglomeration of silica particles. The agglomerated silica particles with larger particle size would serve as flaws and stress concentration for crack initiation, resulting in poor tensile properties.

In this study, the nanoparticles were well dispersed at lower loading (0.5 to 1 wt%) of silica particles. The reinforcing effect of this small amount of nanoparticle loadings with the huge specific surface area has a dramatically larger total interface area for reinforcement efficiency.

In Figure 6 all nanocomposites show the same average tensile strength compared to that of LDPE. This is not unexpected as large changes in tensile strength and extensibility and cannot be expected at a loading below of 10 wt.% of nanofiller [9]. Figure 6 illustrates the effect of nanosilica particles to Young’s modulus of LDPE matrix. As shown in Figure 6, Young’s modulus increased with the addition of silica nanoparticles. This suggests that the incorporation of silica nanoparticles would improve the stiffness of LDPE. At low silica contents of 1 wt%, the nanocomposite exhibits an interactive structure with the matrix. Strong interfacial interaction will enable the load to be transferred easily across the nanoparticle-matrix interface. This will contribute to the increase of Young’s modulus and tensile strength of the nanoparticle-reinforced composites. However, the agglomeration of particles occurred with the increase of silica loadings. The high amount of nanoparticle loadings did not participate in homogeneous interactive bonding with LDPE. The weak interaction between particle and matrix has caused lower tensile properties due to the debonding of particle from matrix prior to the plastic deformation of the matrix.

### 3.4 Greenhouses thermal study

We built a mini greenhouse of LDPE without mixing and another of LDPE mixed with 2.5 wt% SiO₂. We also built a third mini greenhouse of silica glass...
window (glass thickness is 6 mm, the transmittance from 350 to 1100 nm is 88% approximately) (see Figure 7). All the three greenhouses are cubic with a side of 20 cm. Inside each greenhouse, we put a small plant. This plant was previously grown under similar conditions.

The temperature inside each greenhouse was measured using identical temperature sensors (Tecnologic with resolution 0.1°C). The external temperature was also measured using an identical sensor. All the measurements were made at the same moment every 30 minutes starting from 1:00 PM until 6:00 AM the next day. Figure 8 shows the temperature variations inside the three greenhouses along with the external air temperature. An increase in the temperature inside the greenhouse mixed with 2.5 wt% SiO$_2$ is noticed. This increase is estimated to be more than 2°C than the LDPE greenhouse without mixing (2°C overall and 2.2°C between 11:00 PM and 5:00 AM). We also noticed that the transmittance of the greenhouse mixed with 2.5 wt% SiO$_2$ approaches that of the glass house very much (see the green and blue triangles in Figure 8). In fact, the average temperature difference is about 0.14°C overall, and the two temperatures between 11:00 PM and at 5:00 AM match to each other very well.

By studying the IR transmission in Figures 2, 3, and 9, a decrease in the transmittance near 9 μm with increasing mixture ratios is noticed. This result explains the rise in temperature inside the mini greenhouses (shown in Figure 9). The LDPE/silica nanocomposite barrier films preserve the thermal radiation of the ground. Thus, the internal temperature inside the greenhouse is maintained.

One can also notice that in the vicinity of 9 μm, the transmittance of the sample with a ratio of 5 wt% SiO$_2$ is very close to that with a ratio of 2.5 wt% SiO$_2$. We deduce that it may not be very beneficial to go beyond a ratio of 2.5 wt% SiO$_2$.

By studying the UV–Vis transmission in Figure 4, a significant decrease is noticed in the transmittance of the film with a ratio of 10 wt% SiO$_2$, compared with the other films of less ratios (0.5, 1, 2.5, 5, and 7.5 wt% SiO$_2$). These five composite barrier films do not have any significant effect on the transmittance compared with that of the LDPE without mixing. Thus, the film with a ratio of 2.5 wt% SiO$_2$ composite film was adopted to build the mini greenhouse. It has no effect on the UV–Vis transmission but it reduces a maximum transmission of the IR radiation around 9 μm.

![Figure 6.](image)

*Figure 6.* The tensile strength, elongation at break and Modulus of elasticity as a function of different ratios of SiO$_2$. 
The refractive index of LDPE in the visible domain is 1.51, while the imaginary part is $k = 0$ [19]. It is very close to the real part value of the refractive index of SiO$_2$ which is equal to 1.43 [20]. Therefore, there should not be any significant change in the transmittance of the LDPE, in the visible range, when mixed with SiO$_2$. This is clearly seen in Figure 4 except for the last case where the ratio of SiO$_2$ is 10 wt%. Consequently, there should not be any significant change in the greenhouse temperature during sun-shining time. The significant reduction in the transmittance in the case where the ratio of SiO$_2$ is 10 wt% is probably due to Mie scattering [21–23].

3.5 SEM study

Figure 10 shows the SEM images at a magnification of $\times 2000$ that show no obvious signs of agglomeration of the filler. At this magnification, significant agglomeration should be discernible. While some idea of the level of dispersion might be ascertained by scanning electron microscopy (SEM), the small areas
sampled by this technique do not yield an average picture of the sample. Also, transmission electron microscopy (TEM) is better suited than SEM for studying nanoparticle dispersion [9].

### 3.6 Thermal analysis

The decomposition temperatures (Td) for LDPE and LDPE nanocomposite were obtained by thermogravimetric analysis (TGA). Samples (10 mg) placed in
an alumina holder were submitted to a heating cycle at a rate of 10°C/min starting from room temperature (25°C) up to 600°C, under nitrogen atmosphere.

**Figure 11** shows the decomposition profile (percentage of weight loss with temperature) for LDPE and LDPE/silica nanocomposites performed in one step. The presence of SiO$_2$ in the nanocomposite confers thermal stability to it shown by the continuous shifting of the curve to higher temperatures as the SiO$_2$ content increased. These results may be attributed to the silica layers acting as an insulator and a barrier to mass transport from volatile substances generated during the decomposition [24].

### 4. Conclusion

Throughout this study, silicon dioxide films with different ratios (0.5, 1, 2.5, 5, 7.5, and 10 wt% SiO$_2$) were mixed with low-density polyethylene (LDPE) polymer, using melt mixing technique.

The effect of incorporation of 0.5–10 wt% of silica particles to a tensile property of LDPE matrix was investigated. The results showed that the addition of 1 wt% of nanosilica has successfully enhanced the tensile and elongation at break of the nanosilica-filled LDPE material. The incorporation of >1 wt% of nanosilica particles had caused agglomeration and uneven distribution of the particles throughout the LDPE matrix.

These LDPE/silica nanocomposites were used to build a mini greenhouse. SiO$_2$ reduces the transmission of radiation near 9 μm and allows the transmission of the ultraviolet and visible radiations to pass through them during daytime (period of sunshine, without being exposed to direct sunshine.) Thus, we were able to preserve the thermal radiation of the ground by raising the internal temperature of the greenhouse up to more than 2°C than that of the same greenhouse without mixing. The temperature inside the LDPE/silica greenhouse was found to be almost identical to that inside the glass greenhouse.
Statistically speaking the conclusions are acceptable because the experiment was replicated many time. The main gain is the fact that the LDPE/silica greenhouse has the same temperature as the glass-made greenhouse.

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