Research Article

Characterization and Optical and Dielectric Properties of Polyvinyl Chloride/Silica Nanocomposites Films

T. Abdel-Baset, M. Elzayat, and S. Mahrous

Physics Department, Fayoum University, Fayoum 63514, Egypt

Correspondence should be addressed to M. Elzayat; myfelzayat@yahoo.com

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Silica nanoparticles were synthesized by a sol-gel method and mixed with different amounts of polyvinyl chloride (PVC) to get nanocomposite films. The samples were characterized by XRD, HR-TEM, SEM, and FTIR. High resolution transmission electron microscopy (HR-TEM) proved that the average particle size of the nanosilica is 15 nm. The scanning electron microscopy (SEM) showed that the nanosilica was well dispersed on the surface of the PVC films. Fourier Transform Infrared (FTIR) spectra for nanocomposite films intimate a significant change in the intensity of the characteristic peaks of the functional group with addition of nanosilica. The optical band gap was found to decrease with the addition of nanosilica while the refractive index increased. The dielectric constant ϵ' , the dielectric loss modulus M'' , and AC conductivity (σ_{AC}) were also studied. It was found that ϵ' increases with temperature for all samples, clear dielectric α -relaxation observed from dielectric loss M'' around the glass temperature (T_g), and this could be related to micro-Brownian motion of the main PVC chain. The activation energy was calculated, and the AC conductivity could be a hopping one. The results of this work are discussed and compared with previously obtained data.

1. Introduction

Polymer nanocomposite, particularly polyvinyl chloride (PVC) based material, attracted worldwide attention due to its industrial applications and academic interests [1–3]. In fact, there are many reports on different PVC based nanocomposites [4–10].

Silica nanoparticles are extensively studied for many applications such as photonic crystals [11, 12], chemical sensors [13], biosensors [14], nanofillers for advanced composite materials [15–17], markers for bioimaging [18], substrate for quantum dots [19, 20], and catalysts [21, 22]. However many interesting reports indicated the uses of silica in the formation of modern polymer composites, such as poly(butylene terephthalate) (PBT) [23], poly(methyl acrylate) (PMA) [24], polyethylene (PE) [25], polypropylene (PP) [26], polystyrene (PS) [27], polyhydroxyethylmethacrylate (PHEMA) [28], polyurethane (PUR) [29], natural rubber [30], and acrylonitrile-butadiene elastomer (NBR) [31]. Motivation for the use of silica as a polymer filler comes primarily from its high thermal stability and the favorable strength properties of the resulting composites.

The mechanical properties and process ability of PVC filled with nano-SiO₂ particles are widely investigated [32, 33]. It is noteworthy that the incorporation of nanosized silica into PVC-polymer gives rise to new types of nanocomposite polymer electrolytes. Generally, extensive research is still under processing on the mechanical and process ability properties of PVC composites filled with inorganic nanoparticles and on the dispersion of inorganic particles in polymeric matrix. However, there is a notable dearth of information with respect to the optical and dielectric properties of this composite.

It seems that much more investigations of quantitative characterization of its effective interfacial interactions are required. So, it seems essential to investigate both optical properties and interfacial interactions of PVC composites filled with inorganic nanoparticles. The most important parameter governing the utilization of silica nanoparticles in the research work is the optical properties. The transparency and refractive index are important optical properties of polymer nanocomposite. From all the above we investigated the effect of the addition nanosilica to PVC matrix into the optical and dielectric properties of the nanocomposite films.

2. Experimental Work

2.1. Materials and Methods

2.1.1. Synthesis of SiO₂ Nanoparticles. Silica nanoparticles were synthesized via a sol-gel method. A desired amount of sodium silicate solution (Na₂SiO₃) with molecular weight of 122.06 (Sigma-Aldrich) was diluted with distilled water under stirring for 15 min, and diluted hydrochloric acid was used to precipitate it. The precipitate was filtered and washed several times with distilled water until complete removal of sodium chloride. This precipitate was dried in air overnight.

2.1.2. Preparation of PVC/SiO₂ Nanocomposite. Different concentrations (1, 2, and 4 wt.%) of the synthesized SiO₂ nanoparticles were added to PVC (Polymer Laboratories, Essex, UK) according to the relation

$$x \text{ (wt.\%)} = \left(\frac{w_f}{w_p + w_f} \right) \times 100, \quad (1)$$

where w_f and w_p represent the weights of SiO₂ and PVC, respectively. We get the nanocomposite films through the following steps: 1 g of PVC was dissolved in 25 mL tetrahydrofuran (THF, Aldrich, Germany) with stirring until a transparent solution was watched. The calculated weight of the prepared SiO₂ nanoparticles was added to the solution under ultrasonic stirrer at room temperature (RT) for 30 min to prevent the agglomeration of the nanoparticles. The different solutions of the mixtures were then casted in Petri dishes and kept for 24 h to dry in air at RT.

2.1.3. Characterization Techniques. X-ray diffraction (XRD) was used to characterize the sensitized SiO₂ powder, the films of pure PVC, and the films of PVC loaded with SiO₂ nanoparticles. Analysis of the samples was achieved using a Rigaku miniflex diffractometer with CuK α radiation ($\lambda = 1.5406 \text{ \AA}$). The particle size of the as-synthesized nanosilica was determined using high resolution transmission electron microscopy (HR-TEM; JEM 2100, JEOL, Japan). Scanning electron microscopy (SEM; Inspect S, FEI, Holland) images were taken for the nanocomposite films. The FTIR spectra were taken using a Shimadzu 8201 PC spectrophotometer in the range of 4000–400 cm⁻¹. A Shimadzu UV-3600 UV-VIS-NIR spectrophotometer was used to study optical characterization in the wavelength range of 200–850 nm. LCR meter (model 3532, HIOKI, Ueda, Nagano, Japan) was used to investigate the temperature dependence of the dielectric characterization. A T-type thermocouple was used to measure the temperature (with an accuracy of $\pm 1^\circ\text{C}$).

3. Results and Discussions

3.1. X-Ray Diffraction. X-ray diffraction spectra of pure PVC, pure SiO₂ nanoparticles, and 4 wt% PVC-SiO₂ nanocomposite films are shown in Figure 1. The amorphous nature of the nanosilica was clearly observable, consistent with previous reports [34, 35]. Also, the amorphous nature of pure PVC is indicated through a broad peak in the region

FIGURE 1: X-ray diffraction pattern for pure PVC, pure SiO₂ nanoparticles, and 4 wt% SiO₂-doped PVC.

of 15–30° [36]. Moreover the spectra for the composite intimate a wide and shallow peak, suggesting an amorphous structure of the nanocomposite. This shows that the addition of silica nanoparticles causes a decrease in the degree of crystallinity and a simultaneous increase in the amorphicity of the composite.

3.2. Characterization. The average size and shape of the as-prepared SiO₂ nanoparticles were tested through HR-TEM image. It can be seen from Figure 2(a) that the average particle size is about 15 nm. Also, SEM was used to examine the morphology and dispersion of SiO₂ nanoparticles on the surface of PVC films. Figures 2(b) and 2(c) show the SEM images of selected nanocomposite films, showing a good dispersion of SiO₂ on the surface of the PVC films. This proves the validity of our synthesis process for obtaining nanosilica.

3.3. FTIR Spectroscopy. Figure 3 shows the FTIR spectra for the nanocomposite films. The characteristic peaks of the saturated C–H groups on PVC chains appeared at 2970–2800 cm⁻¹, 1428 cm⁻¹, and 1327 cm⁻¹ absorption. For both the pure PVC and PVC-SiO₂ nanocomposite films, C–H band at 2953 cm⁻¹ appeared. Unexpectedly, C–H band at 2907 cm⁻¹ surpasses the band at 2953 cm⁻¹, which might be due to the presence of isooctyle groups on the surface. The peaks at 695 cm⁻¹ and 615 cm⁻¹ are attributed to C–Cl bond stretching [36]. The observed peak at 1250 cm⁻¹ is attributed to the C–C swing vibration in the group CH₂–CHCl. Also, at 945 cm⁻¹ an absorption peak is seen which could be related to the Si–OH group (Si–O– stretching). At about 797 and 1095 cm⁻¹, the absorption peaks are initiated by Si–O–Si symmetric and asymmetric stretching vibration, respectively, demonstrating the generation of Si–O–Si in the system [37].

FIGURE 2: (a) HR-TEM of SiO₂ nanoparticles and SEM images for (b) 1 wt% SiO₂-doped PVC and (c) 4 wt% SiO₂-doped PVC.

FIGURE 3: FTIR spectra for the PVC-SiO₂ nanocomposite films.

Usually, the long-range coupling Coulomb interactions cause the splitting of the peak of the Si–O–Si asymmetric stretching vibration into two components: a transverse optical (TO) and a longitudinal optical (LO) component. The peak close to 1095 cm^{−1} has been generally caused by the TO component, whereas the shoulder at 1186 cm^{−1} under the peak of 1095 cm^{−1} is denoted as the LO component [38]. The absorption peak at about 1000–1430 cm^{−1} is related to the overlap of Si–O–Si (1000–1100 cm^{−1}), Si–O–C (1080–1120 cm^{−1}), and C–O–C (1000–1300 cm^{−1}). The observed FTIR data are in good agreement with the results of [39].

Also, as is seen in Figure 3, the FTIR bands of PVC-SiO₂ nanocomposite films intimate a regular increase in the intensity of the absorption peaks with SiO₂ particle loading. This was related to the formation of bonds between the constituents of the composite materials.

3.4. Optical Properties

3.4.1. Optical Band Gap and Urbach Energies for and PVC-SiO₂ Nanocomposite Films. The optical behavior of materials is described by optical constants. Figure 4(a) shows the absorbance spectra of pure PVC and PVC-SiO₂ nanocomposite films. It is obvious that the absorbance increases with increasing SiO₂ nanoparticles ratio in PVC-SiO₂ nanocomposite. As is known, PVC is transparent in the visible region. This is clearly shown in Figure 4(b), while the transmittance decreases in the PVC-SiO₂ nanocomposite sample. It is known that sol-gel method causes many lattice defects in the silica, resulting in a decrease in the transparency of the nanocomposite with increasing nano-SiO₂ content. The formula (α = absorbance/films thickness) was used to calculate the dependence of the absorption coefficient (α) on frequency. The optical band gap (E_g) is determined by Tauc's relation [40, 41]:

$$\alpha h\nu = B(h\nu - E_g)^m, \quad (2)$$

where $h\nu$ is the incident photon energy, B is the probability parameter for transition, and m adopts being 1/2 and 2 for allowed direct and allowed indirect transitions [42],

FIGURE 4: (a) The absorbance spectra for pure PVC and PVC-SiO₂ nanocomposite films. (b) The transmittances spectra for pure PVC and PVC-SiO₂ nanocomposite films.

TABLE 1: The direct energy band gap, E_g , Urbach energy, E_U , and various optical dispersion parameters for pure PVC and PVC/SiO₂ nanocomposite films.

Samples	E_g (eV)	E_U (eV)	E_0 (eV)	E_d (eV)
Pure (PVC)	3.93	0.37	6.6	8.6
1% SiO ₂	3.81	0.85	6.8	187.1
2% SiO ₂	3.76	0.85	6.8	199
4% SiO ₂	3.87	0.82	6.4	138.4

respectively. The direct band gaps were obtained from the plots of $(\alpha h\nu)^2$ versus $h\nu$ at RT as shown in Figure 5, and the E_g values were estimated by extrapolating the linear part of $(\alpha h\nu)^2$ to zero. The obtained E_g values are given in Table 1. It was found that the E_g values decrease with the addition of nanosilica which indicates that the position of the electronic band gap of the nanocomposite depends on the concentration of SiO₂ on it.

The absorption coefficient near the fundamental absorption edge is exponentially dependent on $h\nu$ and obeys the empirical Urbach relation. The Urbach energy (E_U), which is the width of the tails states in the band gap associated with the structural defects and disorder within the polymer matrix, can be calculated by the relation [43]

$$\alpha(h\nu) = \alpha_o \exp\left(\frac{h\nu - E_1}{E_U}\right), \quad h\nu < E_g, \quad (3)$$

where $\alpha(h\nu)$ is the absorption coefficient as a function of the photon energy (E) and α_o and E_1 are constants determined

from $\ln(\alpha)$ versus $h\nu$ plot (Figure 6). E_1 approximately coincides with the energy of the lowest free exciton state at zero temperature. The value of E_U was obtained from the inverse of the slope of $\ln \alpha$ versus $h\nu$, and the obtained values are listed in Table 1. The E_U values change inversely with optical band gap. The increase of E_U suggests that the atomic structural disorder of PVC increases by nanosilica doping; this increase would lead to a redistribution of states, from band to tail, thus allowing for a greater number of possible bands-to-tail and tail-to-tail transitions [44]. E_U is often interpreted as the width of the tail of localized states in the gap region associated with the tailing of the valance band density of states and is broader than the conduction band tail.

3.4.2. Refractive Index Dispersion of Pure PVC and PVC/SiO₂ Nanocomposite Films. The refractive index (n) could be calculated using the reflectance (R) and the extinction coefficient, k , (where $k = \alpha\lambda/4\pi$) of films as follows [44]:

$$n = \left(\frac{1+R}{1-R}\right) + \sqrt{\frac{4R}{(1-R)^2} - k^2}, \quad (4)$$

where $R = 1 - \sqrt{(T * \exp(A))}$ is the reflectance calculated from the absorbance (A) and transmission (T) spectra [44].

Figure 7 shows the refractive index distributions of pure PVC and PVC-SiO₂ nanocomposite films. The refractive index are found to increase with the addition of SiO₂ nanoparticles. Such increase in n may extend the usability of these materials as antireflection coating.

We used the Wemple-DiDomenico model describes that the dielectric response for transitions below the optical gap

FIGURE 5: Plot of $(\alpha h\nu)^2$ versus $h\nu$ for pure PVC and PVC-SiO₂ nanocomposite films.

was used to calculate the single-oscillator parameters. The dispersion data of the refractive index can be described by a single-oscillator model, where E_0 and E_d are single-oscillator constants [45]:

$$n^2 - 1 = \frac{E_0 E_d}{E_0^2 - E^2}. \quad (5)$$

E_0 is the single-oscillator energy and E_d is the dispersion energy which measures the average strength of interband optical transition, E_0 and E_d values can be determined as the slope and the intercept of Figure 8, according to (5), and the obtained values are listed in Table 1. It is found that $E_0 \approx 2E_g$; this result agrees with the single-oscillator model [45].

3.5. Dielectric Properties

3.5.1. Dielectric Permittivity. The dielectric behavior of polymer nanocomposite materials is a powerful technique for studying the relaxation and conduction mechanisms in polymeric materials [46].

Figure 9 displays the temperature dependence of ϵ' at selected frequencies for pure PVC and PVC-SiO₂ nanocomposite films. It is shown that ϵ' varies slowly with increasing the temperature up to T_g and then increases with further increase in temperature till reaching a saturation region and then it decreases again. The relaxation process observed near the glass transition temperature for the prepared nanocomposite (α -relaxation) is attributed to the cooperative dipolar orientations. This relaxation process corresponds to the segmental relaxation associated with the glass transition at

FIGURE 6: Plots of $\ln(\alpha)$ versus $h\nu$ for pure PVC and PVC-SiO₂ nanocomposite films.

FIGURE 7: The refractive index (n) curve for pure PVC and PVC-SiO₂ nanocomposite films.

which the micro-Brownian motion of long chain segments in the amorphous regions of PVC [47].

At lower temperatures, the thermal energy that is absorbed by the polymeric material, at a certain fixed frequency, is small and a small number of dipoles can rotate with

FIGURE 8: Plots of $(n^2 - 1)^{-1}$ against $(E)^2$ for pure PVC and PVC-SiO₂ nanocomposite films.

small angles. With increasing temperatures, ϵ' value is determined by the number of orienting dipoles per unit volume and their dipole moments [46]. As the temperature increased, the viscosity of polymeric films is decreased and the dipoles gain sufficient energy and can orient themselves easily in the direction of the applied electric field; thus ϵ' increase with increasing temperatures. Also, the chain segments get sufficient thermal energy to speed up its rotational motion and consequently polarization increases [48]. However, the specific volume of the polymer increases with the further increase in temperature, and hence ϵ' value is increased at higher temperatures [49, 50].

It is also clear that ϵ' decreases with the increase of frequencies for all samples. The decreases may be attributed to the decreasing of the number of dipoles, which contribute to polarization, or dipole structure is no longer able to respond to the applied electric field; this leads to reduction in the ϵ' value.

Moreover, ϵ' seems to decrease to lower values after adding the nanosilica to PVC matrix. Silica nanoparticles have more surface area whose effect combined with the resulting change in PVC morphology and the space charge distribution leads to reduction in the internal field. This reduction could be the cause of the ϵ' reduction for pure PVC and PVC-SiO₂ nanocomposite films.

3.5.2. Electric Modulus. At low frequencies and high temperatures the observed values of dielectric permittivity do not refer to the bulk of the material; this is related to the so-called “interfacial polarization” dominant in these composites polymeric materials [51]. To avoid contributing of the interfacial polarization, the modulus formalism can be used for analyses of the dielectric behavior of PVC.

In addition, the recorded dielectric data can be expressed in terms of the complex electric modulus (M^*) [52], which is defined as the inverse of the complex permittivity (ϵ^*):

$$M^* = M' + iM'',$$

$$M^* = \frac{1}{\epsilon^*} = \frac{\epsilon'}{\epsilon'^2 + \epsilon''^2} + i \frac{\epsilon''}{\epsilon'^2 + \epsilon''^2}, \quad (6)$$

where M' and M'' are the real and imaginary parts of the dielectric modulus, respectively. Figures 10(a)–10(d) show the temperature dependence of M' for PVC and PVC-SiO₂ nanocomposite films at different frequencies; it is observed that the values of M' decrease with increasing temperatures for pure PVC and PVC-SiO₂ nanocomposite films; at high temperatures M' tends to reach a constant value indicating the removal of the electrode polarization for the investigated samples owing to thermally activated nature of dielectric constant [52].

The temperature-dependent behavior of M'' for pure PVC and PVC-SiO₂ nanocomposite films at different frequencies is displayed in Figure 11. The M'' spectrum shows asymmetric peak corresponding to α -relaxation process which is related to the micro-Brownian motion in the amorphous region of the main polymer chain [47]. The M'' peaks shift to higher temperatures with increasing frequency because the increase of temperature releases more dipoles; hence the density of dipoles contributing the relaxation process increases with increasing temperature. The region to the left of M'' peak is where the dipoles rotate faster, and the region to the right is where the dipoles are spatially confined to their equilibrium positions.

3.5.3. The AC Conductivity. To investigate the influence of adding the silica nanoparticles on the AC conductivity (σ_{AC}) for pure PVC and PVC-SiO₂ nanocomposite films, the σ_{AC} values were calculated using the relation ($\sigma_{AC} = \omega \epsilon_0 \epsilon''$), where ω is the angular frequency, ϵ_0 is the permittivity of the free space, and ϵ'' represents the dielectric loss. The activation energy (E_a) for all samples was calculated according to the Arrhenius relation [53]: $\sigma_{AC} = \sigma_0 \exp(-E_a/kT)$. Figures 12(a)–12(d) represent the measured ac conductivity ($\ln \sigma_{AC}$) as a function of the reciprocal of temperature ($1000/T$) for pure PVC and PVC-SiO₂ nanocomposite films. It is clear that σ_{AC} for each sample increases with increasing the applied frequency. This may be due to the increase of the absorbed energy which leads to increase of the number of the charge carriers that contribute to the conduction process. These observations agreed with the published data for different polymers and amorphous nanoparticles [53–55].

The values of E_a for all investigated samples at $f = 60$ kHz to 2 MHz and their corresponding temperature range ($300 \text{ K} \leq T \leq 370 \text{ K}$) are summarized in Table 2. We show that the values of E_a for PVC are decreased with increasing the content of silica nanoparticles; moreover the increase of σ_{AC} with temperature may have been caused by an increase in the absorbed energy, which leads to an increase in the number of charge carriers that contribute to the conduction process. This reveals that the conduction mechanism could

FIGURE 9: The variation of dielectric constant ϵ' as a function of temperature for pure PVC and PVC-SiO₂ nanocomposite films with different concentrations at different frequencies.

FIGURE 10: The variation of dielectric modulus M' as a function of temperature at some fixed frequencies for pure PVC and PVC-SiO₂ nanocomposite films.

FIGURE 11: The variation of dielectric modulus, M'' , for pure PVC and PVC-SiO₂ nanocomposite films with temperature at different frequencies.

FIGURE 12: The variation of AC conductivity for pure PVC and PVC-SiO₂ nanocomposite films with temperature at different frequencies.

TABLE 2: Activation energies of pure PVC and PVC/ SiO₂ nanocomposite films according to the Arrhenius relation within the temperature range of 300–370 K.

Frequency	Activation energy E_a (eV)			
	Pure PVC	1% NS	2% NS	4% NS
60 kHz	0.727	0.36	0.26	0.29
90 kHz	0.68	0.34	0.25	0.28
0.3 MHz	0.44	0.34	0.2	0.20
0.5 MHz	0.38	0.24	0.18	0.20
1 MHz	0.42	0.24	0.17	0.19
1.4 MHz	0.16	0.21	0.11	0.11
2 MHz	0.10	0.12	0.08	0.09

be a hopping one [56]. Also, the variation of the conductance with temperature can be attributed to a combined effect of the change in the conductance with temperature and to the nature of the trap distribution inside the polymer networks.

4. Conclusions

Silica nanoparticles with an average particle size of 15 nm were successfully prepared and used for synthesis of PVC/SiO₂ nanocomposite films with 1, 2, and 4 wt% silica. It is found that the PVC-silica nanocomposite films were homogenous. The XRD analysis indicated that both the prepared silica nanoparticles and PVC-SiO₂ nanocomposite films have amorphous nature. The values of the optical band gap and Urbach energy were calculated using the optical method. The optical band gap was found to decrease with addition of nanosilica, while the Urbach energy E_U values change inversely with optical band gap. The dispersion curves of the refractive index obey the single-oscillator model. The refractive index increased by increasing the silica nanoparticles content. These results may suggest the important applications of these nanocomposite films as optical devices.

The dielectric constant ϵ' increase with increasing temperatures and the α -relaxation obtained around T_g due to micro-Brownian motion were observed on the dielectric loss behavior. The temperature dependence behavior of the AC conductivity indicated that the conduction mechanism for all samples could be hopping. The activation energy E_a for all samples was found to be decrease with addition of nanosilica; these results could be helpful for many applications of the nanocomposite films.

Competing Interests

The authors declare that they have no competing interests.

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