Scientific
Research

On the Electrical and Optical Properties of Polycarbonate/MNCl₂ Composite

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Abstract

The nature of the $MnCl_2$ salt as a filler to polycarbonate, including their composition, particles dimensions and homogeneity of distribution have been studied using different spectroscopic techniques (XRD, DSC and TGA). A slight increases in the chain-chain separation due to the interaction of the $MnCl_2$ salt with the polycarbonate chains was observed, while a decrease in the optical energy gap (E_{opt}) of the polycarbonate polymer with increasing the salt concentration was detected. However employing impedance spectroscopy in the frequency range 10 Hz up to 10^6 Hz. reveals an increase in the dielectric permittivity and conductivity with increasing salt content

1. Introduction

The development of new polymers, blends, composites and advanced materials becomes necessity for modification of mechanical, electrical, optical and thermal properties to fulfill the required characteristics [1-4]. The development runs parallel with intense series of studies aiming to enlighten the structure-property relationship of the modified materials. The optical, electrical and thermal characterization of new polymeric films is an essential for the development of such films [5-9]. Transparent films can be used as optical filters, polarizers, total reflectors, narrow pass-band filters etc. Films of dielectric materials have been successfully used in some optical devices and materials [5]. However, the dielectric properties of polymeric films doped with polar/non polar filler have attracted attention. Extensive observations have been made by researchers [10-12] to explore the molecular motion and the charge carrier migration in polymeric films containing one or more fillers.

Many reports appeared in the literature dealing with the effect of the $MnCl_2$ salt concentration, frequency of the applied field and temperature on the electrical and optical properties of polymers, such as, dielectric behavior, electrical conduction and optical band gap [6-11]. Although the dielectric properties of polycarbonate thin films with $MnCl_2$ as filler forming a composite have

been worked out before [13,14], no attempt was made so far to investigate whether $MnCl_2$ form a composite or interacts chemically with the polymer.

The aim of this research is to investigate the effect of $MnCl_2$ on the electrical and optical properties of polycarbonate/$MnCl_2$ composite thin films and to make a crude answer to whether $MnCl_2$, physically dispersed or chemically attached to the polymer? Different techniques were employed to characterize the composite films including XRD, DSC, TGA and, and optical photometry as well as the impedance spectroscopy.

2. Experimental

2.1. Films Preparation

Five thin films of polycarbonate/$MnCl_2$ composite with different $MnCl_2$ salt concentrations 0, 5%, 10%, 15%, and 20% by weight were prepared by casting technique in the form of thin sheet films of thicknesses of the order of 0.2 mm. We will refer to these samples in the text as S_0 for pure polycarbonate, S_1 for sample contains 5% of $MnCl_2$, S_2 for 10%, S_3 for 15%, S_4 for 15% and S_5 for 20%.

2.2. X-Ray Diffraction

Powder X-ray diffraction (XRD) was performed using a

PW 1729 Philips diffractometer interfaced with a computer control unit model PW 1710 using Cu K_α radiation. Since no peaks were observed below 10˚ for all samples the angular range of 2θ was taken between 10˚ and 100˚. The scanning speed of the diffractometer was in the range of 0.02˚ to 0.04˚ (degrees/sec) depending on the quality of signal-to-noise ratio. The positions of the peaks were determined by curve-fitting procedure of the experimental XRD data. Special sample's holder [15] for the PC/MnCl$_2$ films was designed to eliminate scattering from glass substrate which enables us to detect small peaks due to MnCl$_2$ salt. The chain-chain separation was estimated using Bragg's law.

2.3. DSC and TGA

The thermograms were obtained using Differential Scanning Calorimeter (DSC) and Thermo Gravimetric Analysis (TGA) in the temperature range from room temperature to 350˚C in a nitrogen atmosphere with nitrogen flow rate at 10ml/min. Samples were prepared to have approximately the same weight.

2.4. Optical Absorbance Spectra

Optical absorbance spectra of PC/MnCl$_2$ composite films were obtained using [Shmadzu (UV-2401pc) UV-VIS Recording spectro photometer made in Japan] at room temperature in the UV-visible (from 200 to 800 nm).

2.5. AC Measurements

The impedance measurements were carried out on thin discs of approximately 0.2 mm thickness and 13 mm in diameter, the discs were cut from the composite sheets containing different concentrations of MnCl$_2$ salt, sandwiched between two copper circular discs to ensure good ohmic contacts with the electrodes .The measurements were performed in the frequency range between 10 Hz and 10^6 Hz at room temperature using a 1260 Impedance Gain Phase Analyzer (Solarton Analytical). The system was controlled using the Z-60 and Z-View Packages which maximize the performance and data handling of the system. The generator amplitude was kept at 0.5 rms volt and zero volt dc bias. The complex ac impedance and the phase angle were measured, from these measurements imaginary and real components of impedance and permittivity can be determined.

3. Results and Discussion

The XRD spectrums obtained have two main peaks which is a common feature of all composite films as shown in the **Figure 1**: The broad peak appears near θ ~20˚ which is usually used to measure the chain-chain separation, and a second broad peak at about 45˚ which is used to estimate the chain length [16-19]. The chain-chain separation was calculated using Bragg's law for data obtained from the position of the first peak. The result of the calculations is shown in **Table 1**. It is clear that increasing the MnCl$_2$ concentration in the system increases slightly the chain-chain separation and increases the intensity of the X-rays reflected from the sample. The slight increase in the chain-chain separation may be due to the interaction of the MnCl$_2$ salt with the polycarbonate chains, and that the intake of the polycarbonate to MnCl$_2$ approaches saturation for salt concentrations above 20%, in consistent with our previous findings in other polymers [16].

Figure 2 shows the TGA results (weight loss vs. temperature) in the temperature range from room temperature up to 300˚C for S$_5$ sample. A very small weight loss below 50˚C was observed in all samples due to traces of the solvent trapped in the system during the samples preparation. In order to show the effect of the solvent on the physical properties of the composite the natural logarithm, ln(σ) versus 1/T was plotted for S$_5$ as shown in **Figure 3**. From which we can conclude that ionic conduction dominates at temperatures up to 50˚C, followed with the insulating behavior (electron hopping) at temperatures higher than 50˚C. Hence, to insure that all samples are stable and suffer no significant weight losses or phase changes in the temperature range from room temperature to 100˚C, all samples were kept in an oven at temperature of 70˚C for twenty four hours prior to measurements.

Figure 4 shows the DSC thermogram for sample (S$_5$) together with sample S$_0$ in the temperature range from room temperature to 300˚C. The figure shows a small decrease in the glass transition temperature (T$_G$). This decrease in T$_G$ with the increase in MnCl$_2$ concentration was observed for all other samples. Moreover it was clear that sample S$_5$ shows a distribution of sizes in the composite as observed in successive minima in the DSC thermogram, indicating that polycarbonate polymer cannot tolerate high concentrations of MnCl$_2$.

The calculated values of the real component of impedance (Z') from the measured complex impedance and phase angle as a function of frequency for all samples are shown in **Figure 5**. The figure shows a decrease in Z' with increasing the salt concentration in the frequency range 10 Hz up to about 10^4 Hz. *i.e.*; the composite conductivity increases, this may indicate that the main contribution to the conduction mechanism in the composite system is ionic conduction, While at higher frequencies, increasing the salt concentration has a negligible effect
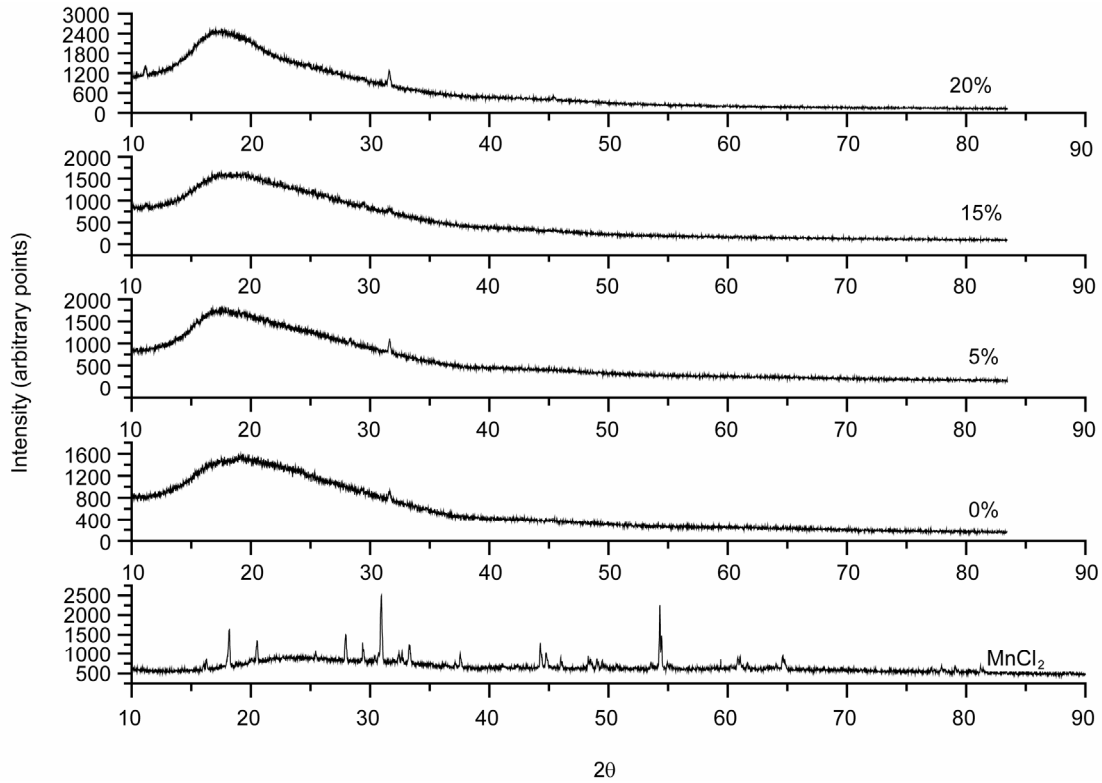
Figure 1. The XRD spectrum for the polycarbonate films and the MnCl₂ salt.

Table 1. Chain-chain separation and intensity as a function of concentration.

Wt%	d(Å)	I(arbitrary units)
0	4.57	1524
5	5.08	1750
15	5.15	2124
20	5.17	2490

on the impedance of the composite where ionic conduction is not active in this range of frequency so we can conclude that the addition of MnCl₂ salt in polycarbonate films results in a cross-linked polycarbonate polymer, forming isolated blocked clusters with space charges at their boundaries [15,18].

Figure 6 shows the plot of Z'' versus frequency for all samples; two features can be noticed from the figure,
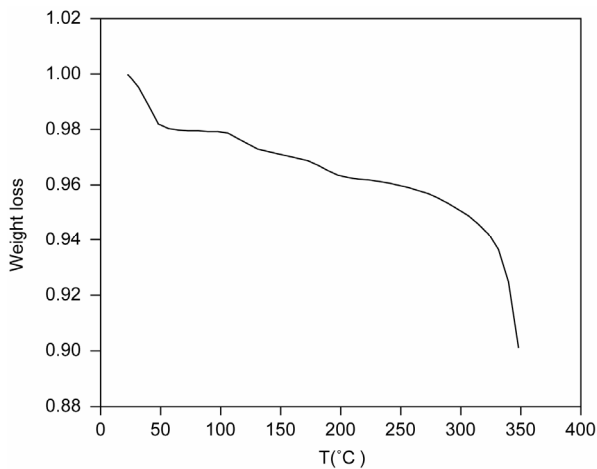
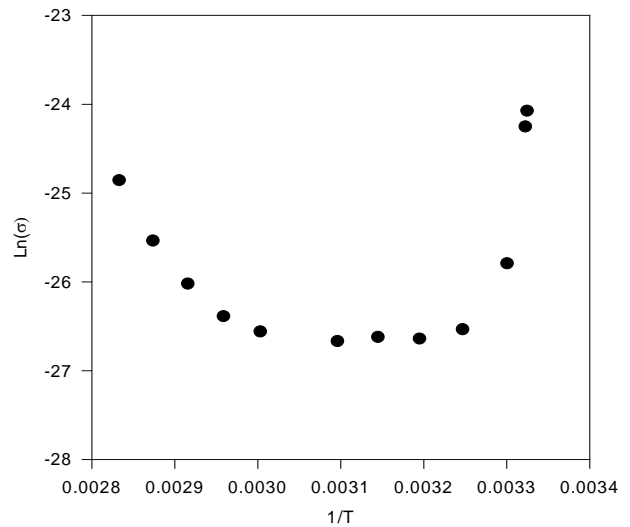**Figure 2. Normalized weight loss versus temperature for the S_5 sample.**
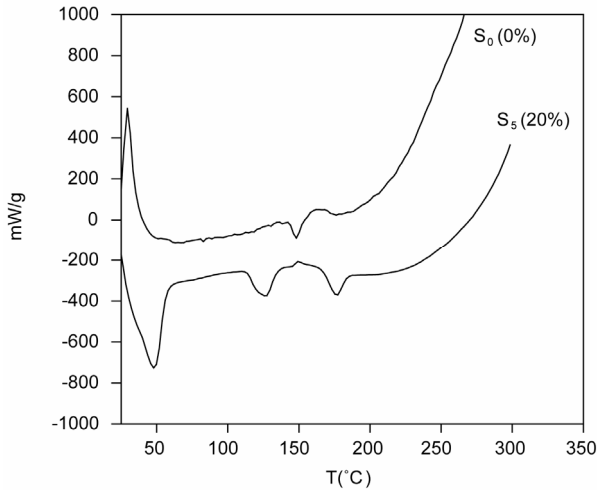

Figure 3. Ln(σ) versus 1/T for sample S_5.

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Figure 4. DSC spectrum for S_0 and S_5 samples.

Figure 6. Z'' Versus Frequency for Polycarbonate/MnCl$_2$ composite.

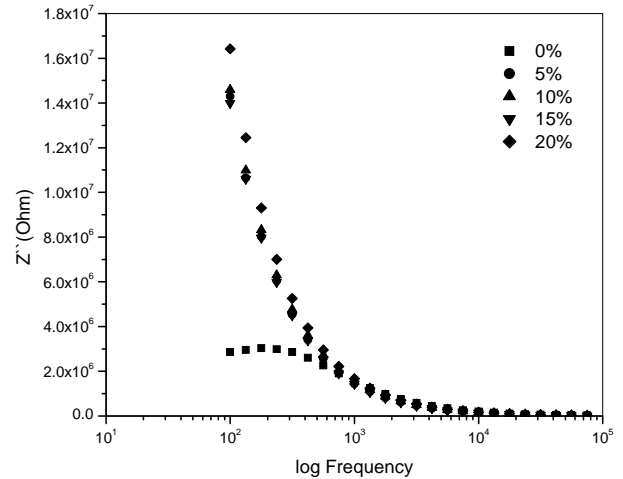**Figure 5. Real component of impedance Z' Vs. frequency for Polycarbonate/MnCl$_2$ composite.**
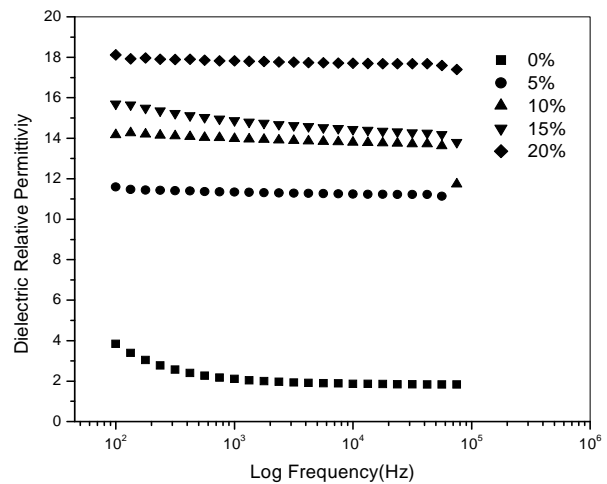
Figure 7. Dielectric permittivity versus frequency for Polycarbonate/MnCl$_2$ composite.

first there is a dramatic increase in Z'' for pure polycarbonate and the composite sample contains 5% of MnCl$_2$, however this dependency decreases with increasing the MnCl$_2$ concentration, indicating that increasing the salt content may hinder the mobility of such ions and yields to a drop in the values of Z'', the second feature is observing a relaxation transition at low frequency for pure polycarbonate this is due to dipole polarization and as the frequency increases the dipole polarization will tend to zero. However, the low values of ε` at higher frequencies as shown in **Figure 7** emphasizing the insulating behavior of our samples, while at low frequencies, large values of ε' were reported due to space charges and electrode effect, which is typical in this type of measurements [20]. Increasing the concentration of MnCl$_2$ tends to decrease ε'. This also indicates that the MnCl$_2$ salt being encapsu-

lated inside polycarbonate chains, and tends to increase the chain-chain separation due to the size of MnCl$_2$, as observed in the XRD data, lowering the tendency of electron hopping, and tends to decrease electron conduction.

At low frequencies, the imaginary part of the dielectric function ε'' as shown in **Figure 8** has high values and decreases at high frequencies. The low frequency dispersion in ε'' is attributed to charge carriers, associated with large losses at low frequencies.

Optical Analysis

The product of optical absorption coefficient and photon energy versus photon energy for all thin film samples in the UV-visible range (200 - 800 nm) are shown in **Figure 9**. The absorption spectrum reveals a band to band transition. The fundamental absorption manifests itself
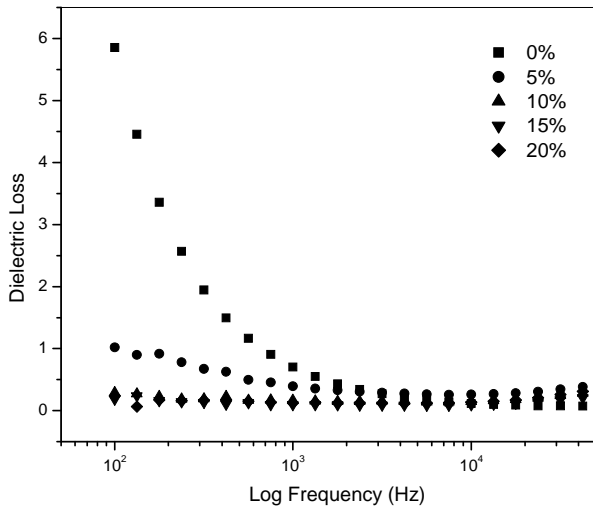
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Figure 8. Dielectric loss versus Frequency for Polycarbonate/MnCl$_2$ composite.

by a rapid rising in absorption, known as absorption edge, which can be used to determine the optical energy gap.

The experimental values of the absorption coefficient $\alpha(\omega)$ are calculated using the relation [21];

$$\alpha(\omega) = \frac{2.303}{x} A(\omega)$$

where $A(\omega)$ is the absorbance and x is the sample thickness.

The absorption edge of non-crystalline materials gives a measure of the band strength or optical energy band gap. The usual method of determining band gap is to plot a graph between $(\alpha \hbar \omega)^{\frac{1}{r}}$ and $\hbar \omega$ [22,23], and looking for that value of r which gives best linear relation over the band edge. The values of E_{opt} can be obtained from extrapolating a straight line in the upper energy portion of the spectrum to the value of $(\alpha \hbar \omega)^{\frac{1}{r}} = 0$, [21-25]. A good straight line was obtained with ($r = 1/2$) which indicates that the transition mechanism for electrons follow the direct allowed transition process.

The optical energy gap E_{opt} was calculated from the curves representing the square of quantity ($\alpha \hbar \omega$) versus photon energy ($\hbar \omega$) using the equation [25]:

$$\alpha(\omega) \hbar \omega = \beta (\hbar \omega - E_{opt})^r$$

The linear part of each curve in **Figure 9(a)**, is extrapolated to the energy axis to give the value of the optical band gap E_{opt} as shown in **Figure 9(b)**. The calculated values of E_{opt} are given in **Table 2** and plotted on **Figure 10**.

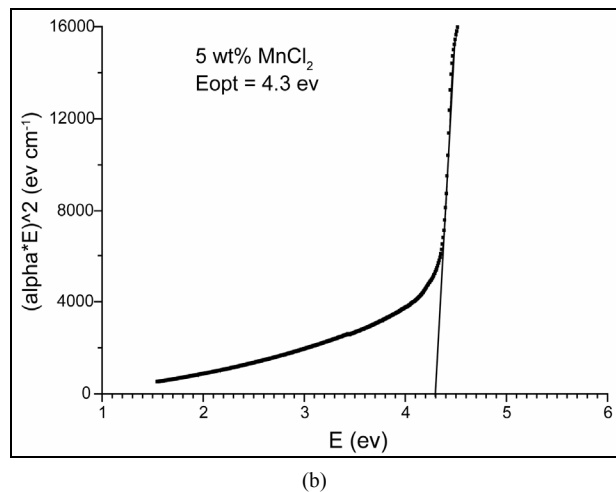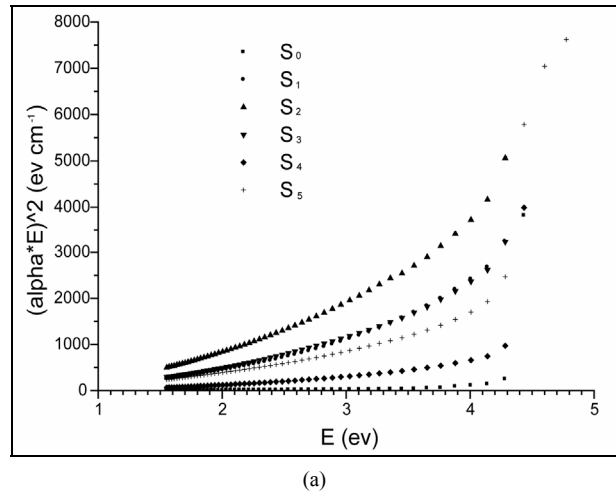A general decrease in the optical energy gap is ob-

(a)

(b)

Figure 9. (a) The product of optical absorption coefficient and photon energy versus photon energy for Polycarbonate/MnCl$_2$ Composite; (b) Optical energy gap versus photon energy for Polycarbonate/ MnCl$_2$ Composite.

Table 2. Optical energy gap for Polycarbonate/MnCl$_2$ Composite.

Sample	Concentration Wt%	Energy gap (eV)
S$_0$	0	4.45
S$_2$	5	4.30
S$_4$	15	4.25
S$_5$	20	4.23

served with the increase in the content of MnCl$_2$ as shown in **Figure 10**. This decrease is attributed to the impurity levels localized in the band gap which ultimately decreases the energy band gap width, this is in consistent with the analysis of the XRD and the AC results.
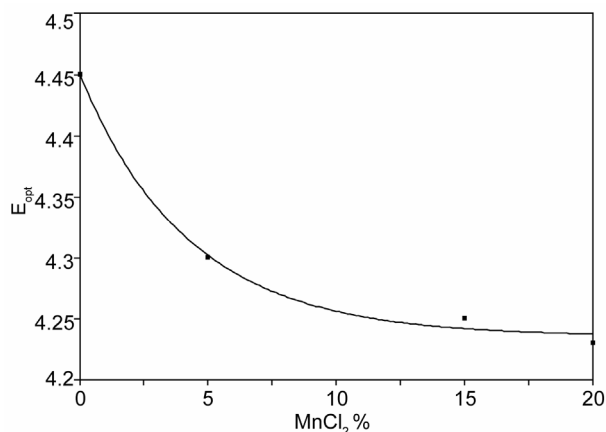
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Figure 10. Optical energy gap versus MnCl$_2$ concentration for Polycarbonate/MnCl$_2$ composite.

4. Conclusions

Electrical and optical properties of PC/ MnCl$_2$ thin films composite with different concentration of MnCl$_2$ were studied. Electrically the polycarbonate Films behave as an R-C network connected in parallel enhancing electron hoping to be the main source of conduction. The increase in MnCl$_2$ concentration was found to decrease the optical energy gap while the electric conductivity increases.

5. Acknowledgements

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