

Effect of AgNO₃-MnCl₂ Mixed Fillers on the Physical Properties of Polystyrene Films

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ABSTRACT: This study deals with the effects of various filling levels of a mixture of two transition compounds [(X)AgNO₃(10 - X)MnCl₂] on the structural, electrical, and magnetic properties of atactic polystyrene (PS) films. X-ray diffraction (XRD) scans showed two main peaks for unfilled PS films. Crystalline peaks were unexpectedly detected with the filling and could be correlated to the formation of clusters. The IR transmission spectra revealed characteristic PS peaks. Certain IR peaks could be taken as evidence for the formation of polaron and bipolaron bound states in the polymeric matrix. The direct-current (DC) electrical conduction measurements suggested that the conduction mechanism could be attributed to phonon-assisted charge carrier hopping according to the inter-polaron hopping model. The DC magnetic susceptibility results at 90–235 K obeyed the Curie–Weiss law. The negative values of the paramagnetic

Curie temperature (θ_p) indicated the possibility of an anti-ferromagnetic exchange interaction, whereas the positive values of θ_p suggested a ferromagnetic exchange interaction at low temperatures. An electron spin resonance (ESR) spectrum at $X = 0\%$ revealed a broad Lorentzian signal. This suggested the presence of aggregated Mn²⁺ and was confirmation of cluster formation found in XRD studies. On the other hand, ESR spectra at higher values of X depicted hyperfine structures characterized by the six unresolved lines of the manganese nucleus, indicating the existence of isolated Mn²⁺. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 95: 1333–1341, 2005

Key words: ESR/EPR; infrared spectroscopy; polystyrene; X-ray

INTRODUCTION

Polystyrene (PS) is a well-known commodity thermoplastic, and large quantities are produced and consumed for daily use. It has been used as a standard example for the investigation of the glassy state of matter. Moreover, PS has been chosen as a polymeric matrix because of its dielectric and mechanical properties and its low cost. During the past decades, numerous studies have been published on the physical properties of PS and its blends with other polymers.^{1–5}

Doped organic polymers display interesting phenomena similar to those of conventional semiconductors. Despite the huge amount of research on doped polymers, substantial work concerning polymers doped with rare-earth and transition-metal ions has only recently been published.^{6–16}

Manganese is well known as a magnetoactive multivalent element because of its partially filled electron shell and interesting spectroscopic properties. Consequently, using MnCl₂ as a filler may modify the structural, electrical conduction, optical absorption, and magnetic properties of a polymeric matrix. AgNO₃ has

been selected as a filler because of its good optical and electrical properties. Mixed fillers of AgNO₃ and MnCl₂ in different concentrations have been used in trials to control and improve the structural and physical properties of a PS polymeric matrix. Moreover, monotonic behavior of the filling-level (FL) dependence of certain PS properties in a fair FL range is an aim of using mixed fillers. This allows the use of PS with controllable physical properties in a variety of potential technological applications.

This article reports on the effect of mixed fillers of AgNO₃ and MnCl₂ of various FLs on the structural, electrical, and magnetic properties of PS films.

EXPERIMENTAL

Atactic PS was obtained from Aldrich Chemical Co. (Dorset, UK) in the form of pellets with a molecular weight of 100,000. Metal compounds AgNO₃ and MnCl₂ were provided in the solid state. The solvents were cyclohexanone and dimethylformamide (DMF).

The studied PS films, filled with transition-metal compounds (X)AgNO₃ and (10 - X)MnCl₂, were prepared by casting methods. Cyclohexanone was used to dissolve the polymer. The transition-metal compounds AgNO₃ and MnCl₂ were dissolved in DMF. The polymer and the transition-metal compounds were cast onto glass dishes and kept in a dry atmo-

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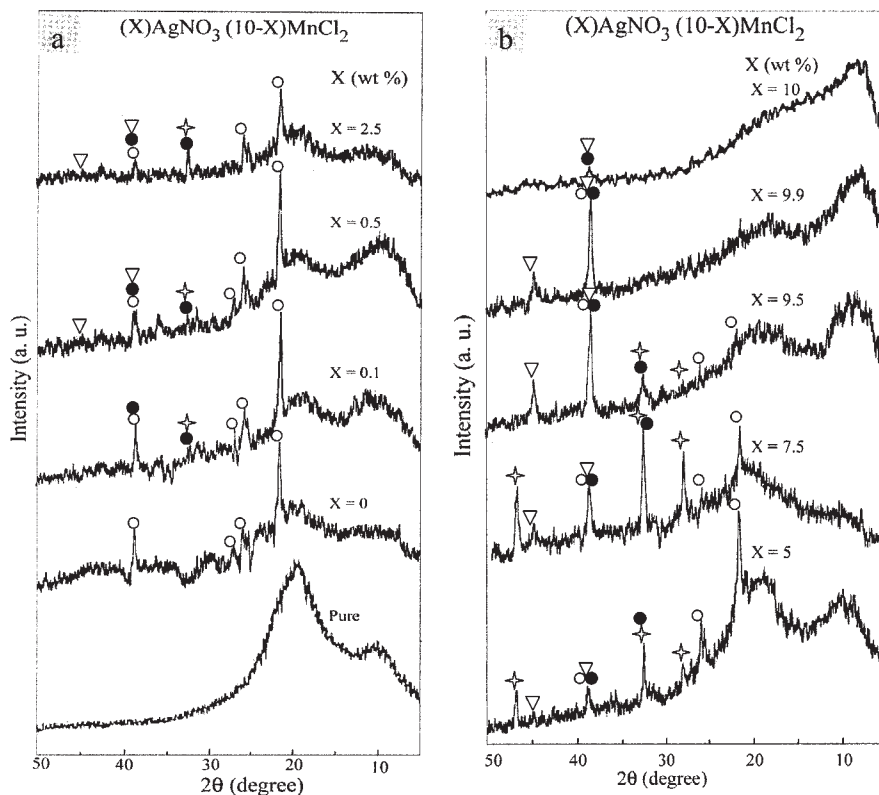


Figure 1 XRD scans of PS filled with various mass fractions of $(X)\text{AgNO}_3(10 - X)\text{MnCl}_2$: (○) MnCl_2 , AgCl , (●) Ag_2O , and (▽) Ag .

sphere at 323 K for 1 week to remove the solvent traces. Different concentrations of the fillers were used ($X = 0.0, 0.1, 0.5, 1.0, 2.5, 5, 7.5, 9.0, 9.5, 9.9$, or 10.0 wt %). The thickness of the films ranged from 150 to 250 μm .

X-ray diffraction (XRD) scans were carried out with a Seimens type-F diffractometer with $\text{Cu K}\alpha$ radiation and an LiF monochromator. A PerkinElmer 883 IR spectrophotometer (England) was used to measure the IR spectra of the different films at room temperature in the wave-number range of $4000\text{--}600\text{ cm}^{-1}$. We obtained IR spectra in the range of $2000\text{--}600\text{ cm}^{-1}$, in which the main characteristic spectral features were found. The electrical resistivity was measured with a TM 14 insulation tester and a 175A autoranging multimeter (Keithley, USA) with an accuracy of $\pm 0.2\%$.¹⁷ The direct-current (DC) magnetic susceptibility (χ) was measured, from 90 to 280 K, with a Faraday pendulum balance.¹⁸ The accuracy of the measurements was better than $\pm 3.5\%$. Diamagnetic corrections were performed. The electron spin resonance (ESR) spectra were recorded at room temperature on a Bruker (EMX) spectrometer operating in the X-band frequency ($\approx 9.7\text{ GHz}$) with a field modulation frequency of 100 KHz. The microwave power and modulation amplitude were 10 mW and 0.1 mT, respectively. A standard sample of MgO doped with Mn^{2+} was used as a calibrant.

RESULTS AND DISCUSSION

XRD

The XRD scans for PS films filled with various mass fractions of a mixture of AgNO_3 and MnCl_2 are shown in Figure 1. The observed spectrum characterizing the virgin PS sample showed two main peaks at $2\theta \approx 19.5^\circ$ and $2\theta \approx 10^\circ$. The first peak, the most intense one, was the amorphous halo and corresponded to the van der Waals distance.^{19–21} The second peak, located at $2\theta \approx 10^\circ$, was the polymerization peak and could be attributed to the intermolecular backbone–backbone correlation and to the size of the side group, which corresponded to an approximately hexagonal ordering of the molecular chains.²¹ At $X = 0\%$, an unexpected appearance of crystalline peaks at 2θ values of approximately $21.7, 25.8, 27,$ and 38.5° was observed. These peaks were not easily assigned to the formation of bulk crystalline materials. On the other hand, these peaks at these values of X could be correlated to the formation of clusters of Mn^{2+} due only to the MnCl_2 filler.²² The microclusters displayed curious crystallographic anomalies that could not be found in the bulk.²³ The formation of manganese clusters was confirmed by our ESR study at $X = 0\%$, which led to the absence of isolated Mn^{2+} and the presence of aggregated Mn^{2+} .^{9,14,24} This aggregation was evidence of the formation of Mn^{2+} clusters.²⁵ Because the total

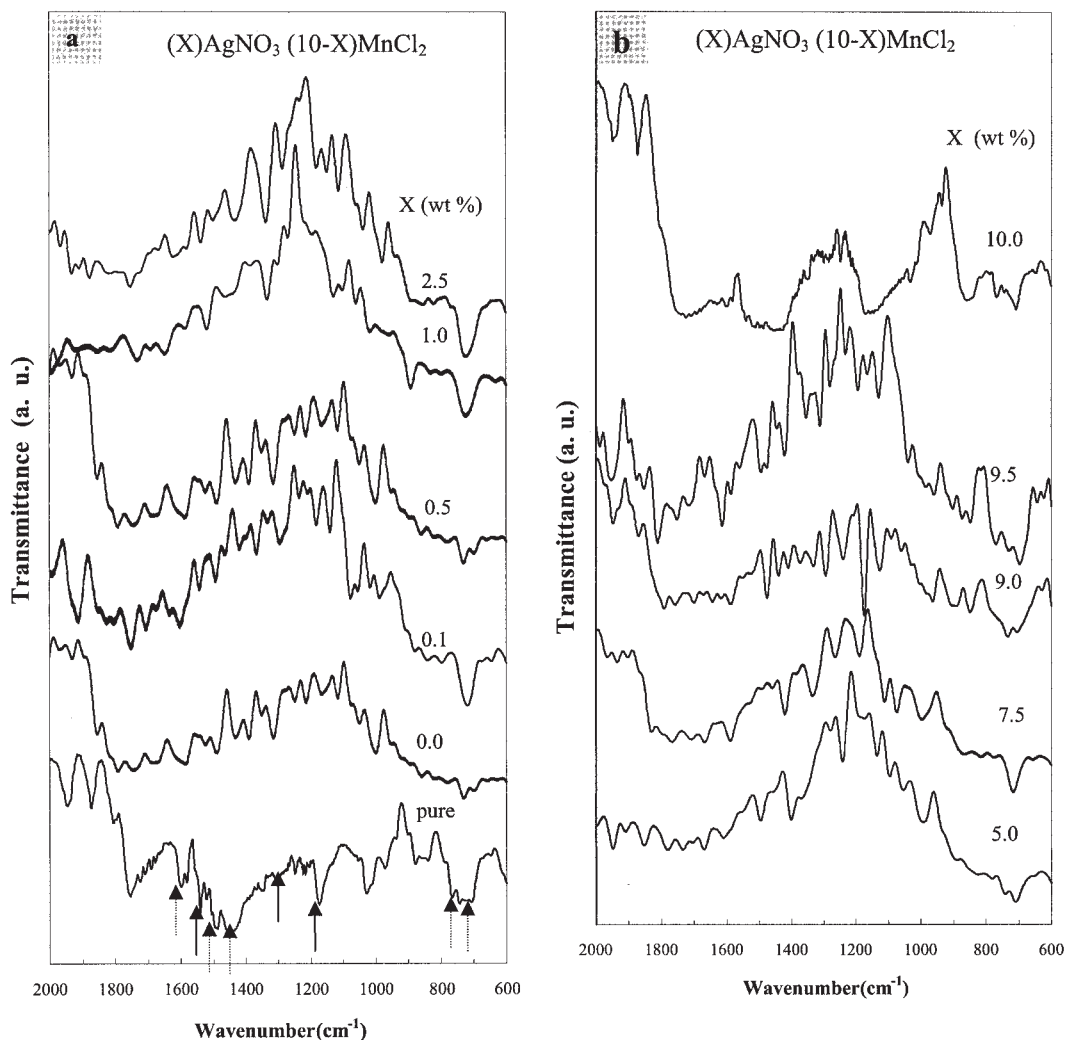


Figure 2 IR transmission spectra of PS films with various FLs.

concentration of the fillers was always constant and equal to 10%, we could assume that at low values of X , the clusters were basically due to the MnCl₂ filler, whereas at higher values of X , the clusters were basically due to the AgNO₃ filler. Finally, at $X = 10\%$, the almost complete disappearance of all the crystalline peaks was observed, except for a small peak (hump) at $2\theta \approx 38.5^\circ$, which could be attributed only to the AgNO₃ filler. Generally, the change in the intensity of different peaks at different values of X could be attributed to the change in the contents of the two fillers, AgNO₃ and MnCl₂. The unexpected appearance of the crystalline peaks occurred over a fair FL range, and this was the aim of using the mixed fillers.

IR spectroscopy

The IR transmission spectra for PS films filled with different mass fractions of $(X)\text{AgNO}_3(10 - X)\text{MnCl}_2$ are shown in Figure 2. The most obvious observed

peaks were assigned. The aromatic ring (C₆H₅) gave rise to a group of bands above 3010 cm⁻¹ (not shown here). The aromatics displayed distinctive double-bond C=C stretching at about 1600 cm⁻¹,²⁶ which in combination with unsaturated C-H stretching above 3000 cm⁻¹ identified polymers containing aromatics. The C-C stretching mode of phenyl rings at 1480 cm⁻¹ and the C-H out-of-plane deformation modes of monosubstituted phenyl rings at 765 and 695 cm⁻¹ were noted.^{26,27}

The IR transmission decreased with increasing doping content over the entire studied frequency range. This may have been due to free or weakly bound charge carriers.²⁷ The peaks at 1530, 1275, and 1180 cm⁻¹ (solid arrows) are interesting. These peaks were found in doped polyacetylene²⁸ and FeCl₃-doped polyparaphenylene (PPP).²⁷ Moreover, Shacklette and coworkers^{29,30} found dopant-induced peaks at exactly the same wave numbers as those for AsF₅-doped PPP. However, Kuivalainen et al.²⁷ and Fincher et al.²⁸

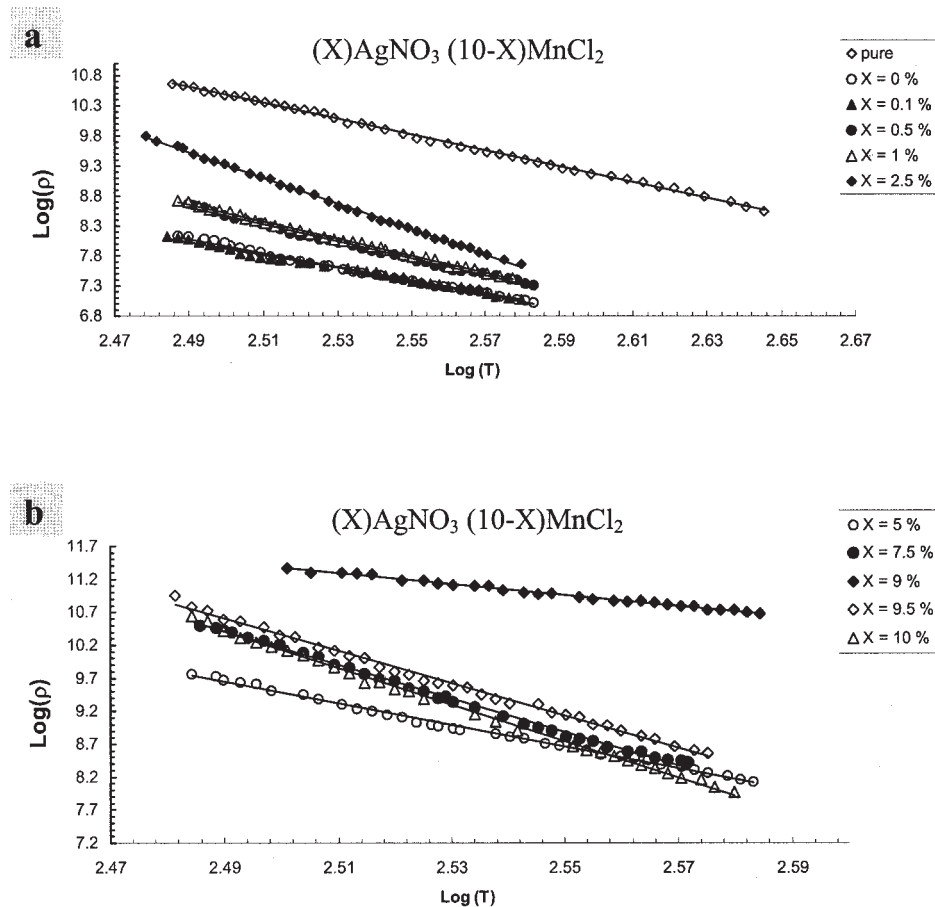


Figure 3 Log ρ versus log T for PS with various FLs.

stated that these modes of vibrations were not due to specific vibrations of the dopant molecules but were intrinsic vibrations of the polymer chain. According to Kuivalainen et al., the mode at 1275 cm^{-1} , which also appeared at 1298 cm^{-1} according to Racovics et al.,³¹ was related to the deformations of the benzene ring structure, which was typical of the polaron and bipolaron defect states.^{32,33}

DC electrical conduction

The study of the DC electrical resistivity (ρ) was recorded in the temperature range of 300–390 K for PS films filled with various mass fractions of $(X)\text{AgNO}_3(10 - X)\text{MnCl}_2$. The deformation in the benzene ring and the double bond $\text{C}=\text{C}$, detected by the IR analysis, were evidence for the formation of polarons and bipolarons in the polymeric matrix. Accordingly, these results could be discussed on the basis of Kuivalainen et al.'s²⁷ modified inter-polaron hopping model, in which the conduction mechanism could be interpreted on the basis of phonon-assisted charge carrier hopping between the polaron and bipolaron bound states in the polymer. According to this model, ρ could be expressed as follows:

$$\rho = [kT/A_1 e^2 \gamma(T) (R_0^2/\zeta)] [(Y_p + Y_{bp})^2 / Y_p Y_{bp}] \exp(2B_1 R_0/\zeta) \quad (1)$$

where A_1 is 0.45 and B_1 is 1.39; Y_p and Y_{bp} are the concentrations of the polarons and bipolarons, respectively; $R_0 = (3/4\pi C_{\text{imp}})^{1/3}$ is the typical separation between impurities and C_{imp} is the impurity concentration; and $\zeta = (\zeta_{\parallel} \zeta_{\perp}^2)^{1/3}$ is the average decay length of a polaron and bipolaron wave function, ζ_{\parallel} and ζ_{\perp} being the decay lengths parallel and perpendicular to the polymer chain, respectively. The rate of transition of an electron between the polaron and bipolaron states [$\gamma(T)$] could be expressed as follows:

$$\gamma(T) = \gamma_0 (T/300\text{K})^{n+1} \quad (2)$$

where n is a constant (~ 10) and γ_0 is a prefactor estimated to be $1.2 \times 10^{17}\text{ s}^{-1}$ by Kivelson.³⁴ With a computer-aided program, the order of magnitude of ρ in this work was adjusted with C_{imp} , which actually was the fitting parameter. The parameters $\zeta_{\parallel} = 1.06\text{ nm}$ and $\zeta_{\perp} = 0.22\text{ nm}$ ³⁵ depended on the interchain resonance energy and the interchain distance. As a reasonable approximation and for simplicity, Y_p was

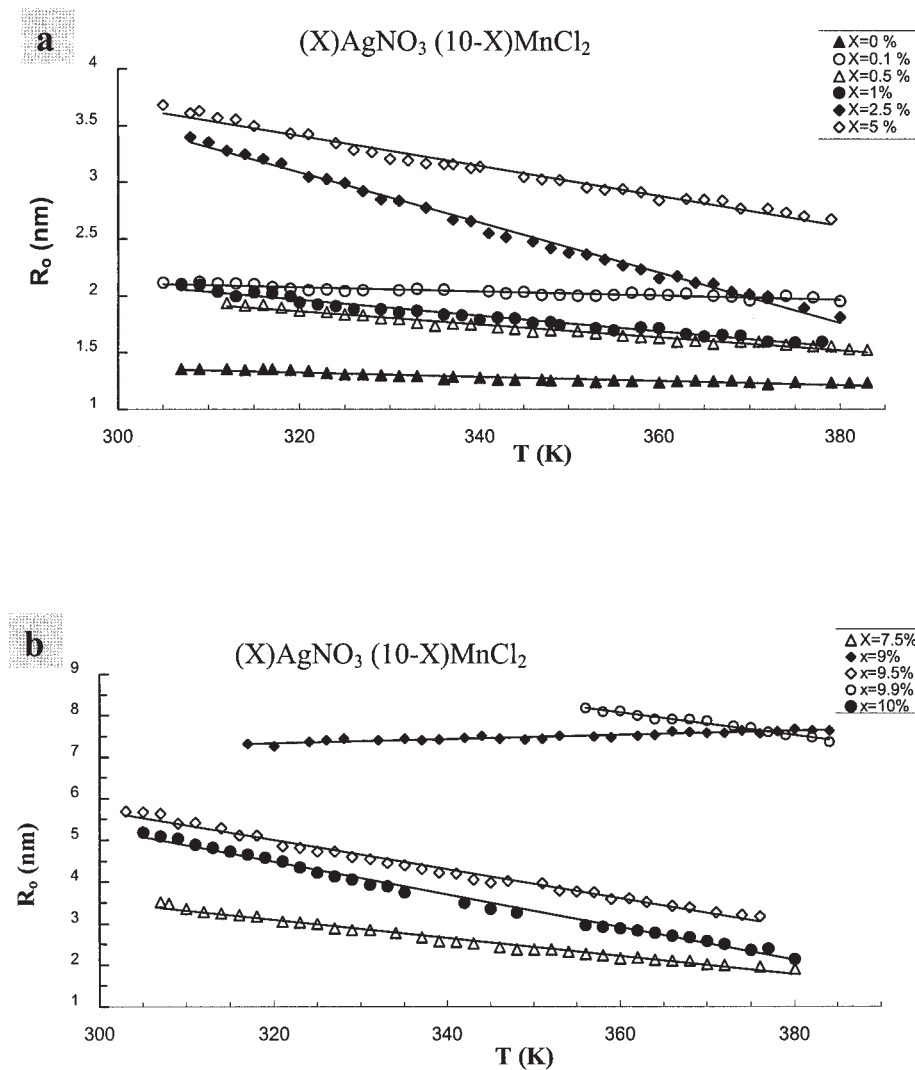


Figure 4 Temperature dependence of R_0 for PS with various FLs.

set equal to Y_{bp} ,⁷ with eqs. (1) and (2), the values of the separation between impurities, which was considered the hopping distance (R_0) of the charge carriers, could be obtained.

According to eqs. (1) and (2), the plotting of $\log \rho$ versus $\log T$ (where T is the temperature) should give a straight line if the measured $\rho(T)$ value is dominated by interpolymer hopping.^{7,27} Figure 3 shows this plot for variously filled PS films. The linear behavior of these plots corresponds to the temperature ranges in which the interpolymer hopping proceeds.^{7,27} Moreover, a linear temperature dependence of R_0 for various FLs is revealed in Figure 4. This is a confirmation that the conduction mechanism is predominated by an interpolymer hopping model.^{7,27} The FL dependence of $\log \rho$ is shown in Figure 5. A fair FL range (0–7.5%) has been noted; the electrical resistivity behaves nearly monotonically, and this has led to important electrical technological applications.

DC magnetic susceptibility

The investigation of χ of PS films filled with various mass fractions of $(X)\text{AgNO}_3(10 - X)\text{MnCl}_2$ was studied from 90 to 270 K. The temperature dependence of

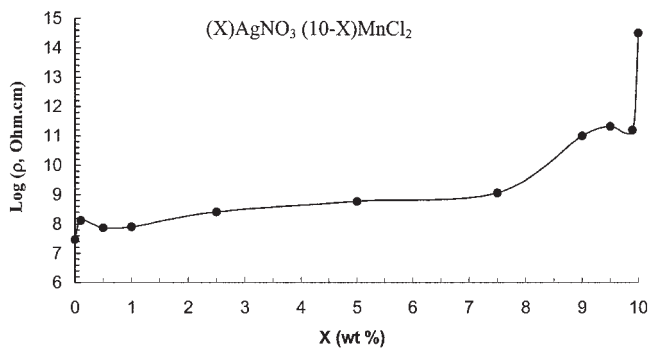


Figure 5 FL dependence of $\log \rho$ at 348 K.

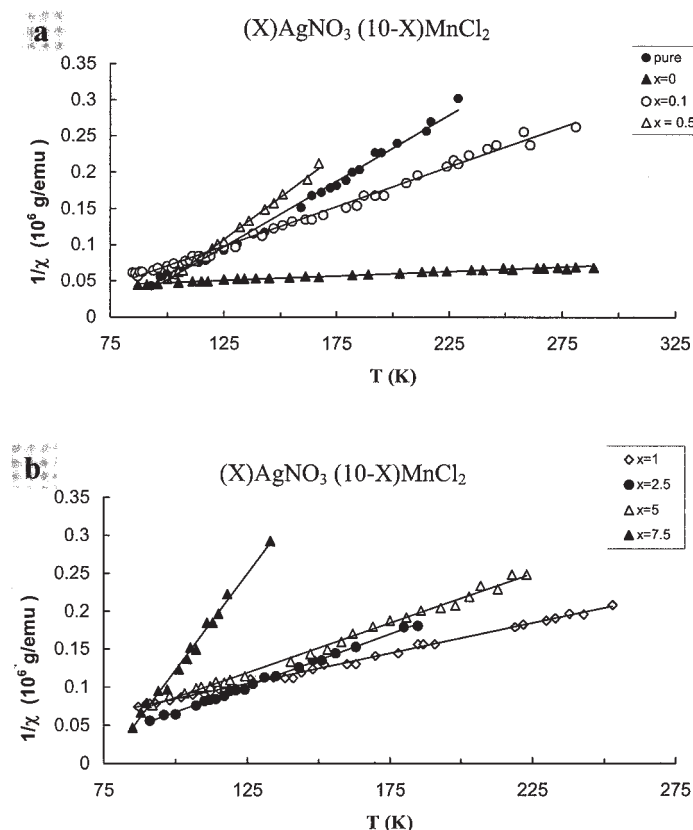


Figure 6 Temperature dependence of the reciprocal of χ for variously filled PS.

the reciprocal of χ is plotted in Figure 6. These plots are linear and obey the Curie–Weiss law:

$$\chi = C/(T - \theta_p) \quad (3)$$

where C is the Curie constant and θ_p is the paramagnetic Curie temperature.

Ferromagnetic materials behave as normal paramagnetics at high temperatures, and as T approaches the magnitude of θ_p (θ_p has positive value), there is a marked increase in χ . The critical temperature obtained for this process is called the Curie temperature. Once the material becomes ordered, the susceptibility behaves in a very complicated way and no longer has a unique value for a given field strength. On the contrary, antiferromagnetic materials also behave as normal paramagnetics at high temperatures, and as T approaches the value of θ_p (θ_p has a negative value), χ becomes small and attains its maximum value at a certain critical temperature called the Néel temperature. Below this temperature, the spins have antiparallel orientations.^{36,37}

In this study, the values of θ_p were calculated for different values of X with eq. (3) and are plotted in Figure 7. The negative values of θ_p at X values of 0 and 1% indicate the possibility of an antiferromagnetic exchange interaction between magnetic centers at low

temperatures. On the other hand, the positive values of θ_p suggest a ferromagnetic exchange interaction between magnetic centers at low temperatures. Moreover, the effective paramagnetic moment (μ_{eff}) was calculated at 100 K as follows:

$$\mu_{\text{eff}} = 2.828[\chi_m(T - \theta_p)]^{1/2} \quad (4)$$

where χ_m is the molar susceptibility of the filled polymer. The obtained values were plotted as a function of X in Figure 8. The calculated values of μ_{eff} indicated that these fillers affected the magnetic response of PS. The FL dependence of μ_{eff} almost behaved like a pla-

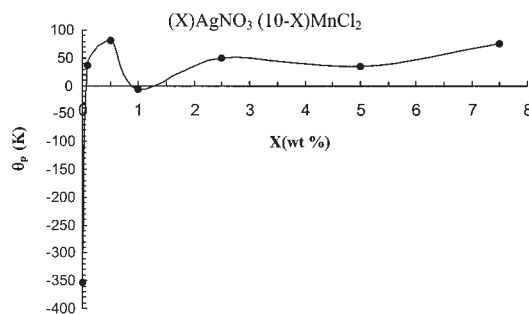


Figure 7 FL dependence of θ_p .

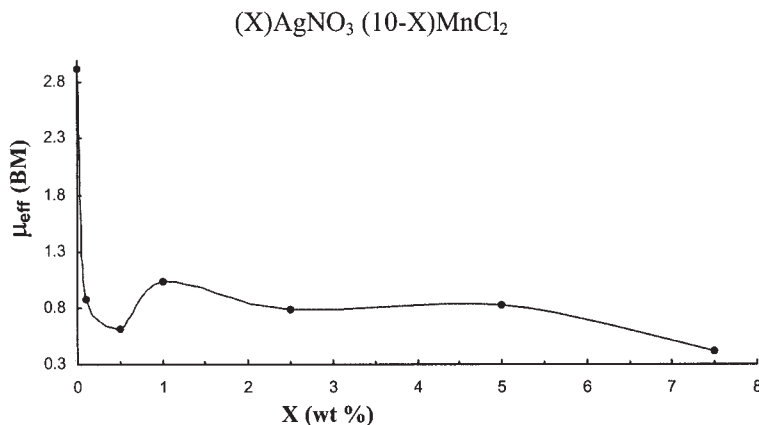


Figure 8 FL dependence of μ_{eff} at 100 K.

teau region for the magnetic properties at $X > 0\%$. The aim of using the mixed fillers was monotonic behavior for the FL dependence of certain PS properties over a fair FL range. Furthermore, the Curie-Weiss behavior indicated that the energy band diagram of this filled PS system was characterized by magnetic localized energy states.³⁷ The order of magnitude of μ_{eff} confirmed the divalent state of Mn²⁺. The unexpected appearance of the crystalline peaks at $X = 0\%$ from the XRD scan could be correlated with the negative value of θ_p noted at the same value of X from the χ results.

ESR

Figure 9 reveals an unresolved complicated ESR spectrum of the pure PS film. This complicated spectrum can be attributed to the hyperfine structure resulting from the interaction of the unpaired electrons with the nuclei of the virgin sample.³⁸ The ESR spectra for PS

films filled with various mass fractions of (X)AgNO₃(10 - X)MnCl₂ are depicted in Figure 10. At $X = 0\%$, the spectrum characterizing the virgin PS film basically disappeared, and the ESR spectrum revealed a nearly broad Lorentzian signal characterized by a Lande splitting factor (g) of approximately 2.002, a peak-to-peak line width (ΔH_{pp}) of approximately 500 G, and an asymmetry ratio (A/B) of approximately 1. This suggests that the filler affected the magnetic properties of the polymeric matrix. On the basis of the g and ΔH_{pp} values, the observed ESR signal was assigned to polarons formed during filling.^{7,27,39} Moreover, the formation of the polarons was confirmed from our DC electrical conduction results; the conduction mechanism was interpreted on the basis of the phonon-assisted charge carrier hopping between polaron and bipolaron bound states. It is well known that the broadening of ΔH_{pp} (≈ 500 G) depends on the relaxation time of the spin state under study. The two

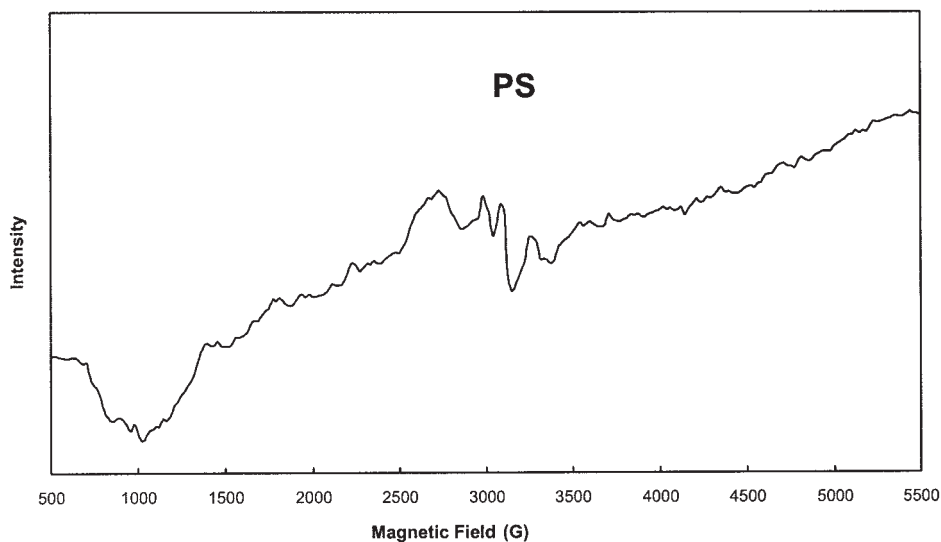


Figure 9 ESR spectrum of a pure PS film.

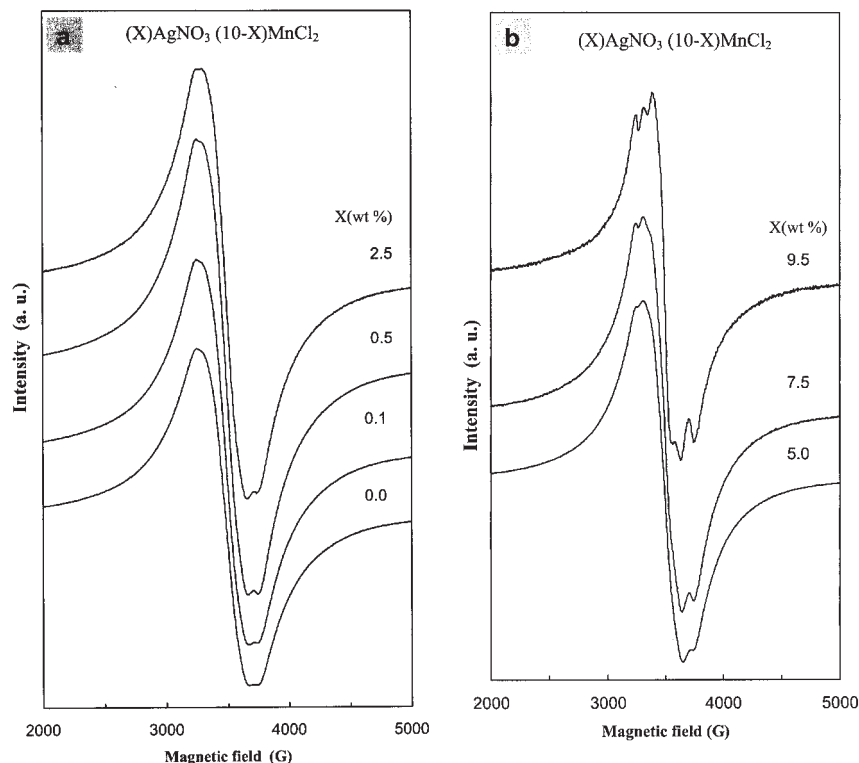


Figure 10 ESR spectra of PS filled with various FLs.

possible relaxation processes are spin–spin relaxation and spin–lattice relaxation. The spin–spin interaction is usually very efficient unless the sample is extremely dilute. The spin–lattice relaxation is efficient at room temperature but becomes progressively less efficient at reduced temperatures.⁴⁰ It is remarkable that Mn^{2+} has a nuclear spin of $I = 5/2$, which leads to hyperfine splitting of $2I + 1 = 6$ possible magnetic orientations with respect to the applied magnetic field. The absence of the hyperfine structure characterized by the well-known six lines of the manganese nucleus can be attributed to the Mn^{2+} – Mn^{2+} exchange interaction. This interaction was caused by the proximity of the manganese ions, suggesting the absence of isolated Mn^{2+} and the presence of aggregated Mn^{2+} and leading to the formation of Mn^{2+} clusters in the polymeric matrix.^{9,14,24,25,38,41} Moreover, the unexpected appearance of the crystalline peaks, observed in XRD studies, confirmed the formation of Mn^{2+} clusters. At $X = 0.1\%$, the ESR spectrum mainly consisted of a broad signal characterized by the unresolved hyperfine structure superimposed on it and a narrow signal due to AgNO_3 filler.²⁵ On the other hand, at higher values of X and at $X = 9.5\%$, the six unresolved lines due to the hyperfine structure of the manganese nucleus became clearer, and this indicated the existence of isolated Mn^{2+} and the absence of aggregated Mn^{2+} .

There was a critical FL ($X = 0\%$) at which there occurred an unexpected appearance of the crystalline

peaks from XRD studies, an antiferromagnetic exchange interaction from χ results, and a Lorentzian signal characterized by $g \approx 2.002$, $\Delta H_{pp} \approx 500$ G, and $A/B \approx 1$ from ESR investigations. This suggested that there were certain energy states with a common contribution to the structural and magnetic properties of this system.

CONCLUSIONS

XRD of virgin PS film revealed two main characteristic peaks at 2θ values of approximately 19.5° and 10° , which corresponded to amorphous and polymerization peaks. An unexpected appearance of crystalline peaks was observed with the filling. The assignment of these peaks was correlated to the cluster formation. This was confirmed with the ESR investigations. The unexpected appearance of the crystalline peaks occurred over a fair FL range. The most notable characteristic PS peaks were shown in the IR transmission spectra. Certain IR peaks could be taken as evidence of the formation of polaron and bipolaron bound states in the polymeric matrix. These DC electrical conduction measurements were interpreted on the basis of phonon-assisted charge carrier hopping between the polaron and bipolaron bound states in the polymeric matrix. The χ results obeyed the Curie–Weiss law. The negative values of θ_p indicated the possibility of an antiferromagnetic exchange interaction, whereas the

positive values of θ_p suggested a ferromagnetic exchange interaction at low temperatures. The ESR spectrum at $X = 0\%$ revealed a broad Lorentzian signal characterized by $g \approx 2.002$ and $\Delta H_{pp} \approx 500$ G. This suggested the presence of aggregated Mn²⁺, indicating cluster formation. At higher values of X , the ESR spectra depicted a hyperfine structure characterized by six unresolved lines of the manganese nucleus, which suggested the existence of isolated Mn²⁺.

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