Material Science Research India Vol. **6**(1), 01-09 (2009)

Polystyrene/Carbon black nano conducting composites for PTCR thermistors and electromagnetic wave shielding applications

NADIA ABDEL AAL

Department of Chemistry, Faculty of Science, Suez Canal University, Ismailia (Egypt).

(Received: November 16, 2008; Accepted: March 03, 2009)

ABSTRACT

The network structure of the polystyrene resin/carbon black (PS/CB) nanocomposites were studied by means of scanning electron microscopy (SEM), X-ray diffraction (XRD), crosslinking density (n), interparticle distance among conducting sites (g). Mechanical properties of PS composite filled with different content of CB were investigated and the composite always exhibited higher hardness and elastic modulus than green PS. The thermal stability of nanocomposites was examined by thermal gravimetric (TG) analysis. The influences of CB content on the static conductivity, mobility carriers and concentration of charge carriers of the PS/CB nanocomposites were examined. Conductivity – temperature curves shows a positive temperature coefficient of resistance (PTCR) effect. It has been proved that the inclusion of CB into the PS/CB nanocomposites significantly enhanced the PTCR intensity and thermal stability of the nanocomposites. The electromagnetic interference shielding effectiveness (EMI), the dielectric constant, the skin depth, the reflection coefficient and the absorbance coefficient as functions of CB content of composites are investigated. In addition, the EMI, of the nanocomposites were measured and calculated in a frequency range of 1-12 GHz. The results show that PS/CB composites exhibit high EMI in the microwave band at high CB content. The composites studied are found to have a wide range of potential applications for PTCR thermistors and microwave absorber at 12 GHz.

Key words: Nanocomposites; microstructure, electrical properties; microwave properties.

INTRODUCTION

There is currently interest in the technological properties of nanoparticle reinforced polymers, because it is primarily a very efficient and cost-effective process for mass production[1,2]. Carbon black (CB) is widely used as a reinforcing filler to improve dimensional stability, a conductive filler, an ultraviolet light stabilizer, an antioxidant to prolong the lifetime of polymer, and a pigment or colorant[3,4]. However, electrically conductive polymer composite is obtained when conductive particles such as metal powder, carbon black (CB), graphite and carbon fiber etc. are implanted into an insulating polymer matrix[5,6]. The effective utilization of reinforced polymers depends strongly on the ability to disperse the particles homogeneously throughout the polymer matrix, filler aspect ratio, packing factor of filler, extent of filler reinforcement, polarity of polymers and others[7-9]. In the field of conducting polymeric composites, one main objective is to minimize the filler concentration because high concentration of the conductive filler could lead to deterioration of the physical properties of the composites[8], an increase of the melt viscosity[9], a decrease of the impact resistance[10], a contamination in clean room environment[11], and an increase of the final product cost [12]. The significant

feature of the Positive temperature coefficient of resistance (PTCR) thermistors is to show an anomalous increase in electrical resistance with temperature. PTCR thermally sensitive composite is widely used for many practical applications for examples temperature indication, control, alarm or thermal protection, compensation circuit, color TV automatic degaussing, motor starting, over current protection or limiting, and self-regulating heating[13-15]. Furthermore, the filled nanocomposites have important applications in such areas as radar absorbers and electromagnetic wave shielding at high Giga frequency[15]. The present work describes the network structure PS/CB nanocomposites has been ascertained by SEM images, x-ray, crosslinking density, interparticles distance among conductive sites, tensile strength, hardness and elongation at break. The static electrical conductivity, mobility carriers and number of charges of PS/CB nanocomposites were investigated. The effect of temperature on resistivity of PS/CB nanocomposites has also been studied in order to observe the PTCR phenomena. The dielectric constant, skin depth, reflection and absorbance coefficient as a function of CB loading of nanocomposite has also been examined. Finally, the measured and calculated electromagnetic wave shielding of the nanocomposites were tested in the range of 1 to 12 GHz. These results show a real opportunity for application of PS/CB composites as electromagnetic wave absorber.

EXPERIMENTAL

The polymer matrix used in the present study is polystyrene resin (PS) made by Kao, Tokyo Japan. The conductive filler is a HAF N-330 carbon black (CB) with a primary particle diameter of about 40 nm and surface area 123 m^2/g were supplied by Qinzhou Chemical Industry, China. The samples were prepared containing 4, 8, 12, 16 and 20 parts of CB per hundred parts of PS (composites are donated as CB4, CB8, CB12, CB16 and CB20 respectively). Samples of PS were centrifuge mixed for 1 min at 8000 rpm and then further sonication for an additional 30 min at room temperature. After that the composite particles were transferred to a preheated compression Teflon mold, and then hot-pressed at 200 ^{0}C under 300 KN/m^2 for 1 h. The final product was obtained in the form of sheets with a dimension of 2x1x0.3 mm^3. Scanning electron microscope (SEM) analysis of the samples was carried out using a JEOL-JSM 5800 at an accelerating voltage of 15 KV. The surfaces of the specimens were coated with silver to obtain a conductive layer. The evaluation of the structural properties of green and PS/CB nanocomposites was carried out by means of an X-ray diffractometer (XRD) (Rigaku Dmax C with Cu K α X-ray source of wavelength of 1.54 A^0). Data were collected at a scanning rate of 0.5 ^{0}/min. Thermal gravimetric (TG) analysis was carried out using thermal analyzer (Regako –Osaka, Japan) with heating rate 10 °C/min in flowing argon. The hardness of the specimen was also measured, according to ASTM D 2240-81 using Shore D type durometer. Tensile tests were carried out in an Instron 4206 tensile machine (Instron Co., UK) at a crosshead speed of 50 mm/min according to ASTM D638-98.. The dumbbell shape samples were 75 mm in length, 1 mm in thickness and 4 mm in width. Elongation at break of nanocomposites was determined from the stress–strain curves. At least five specimens were tested for each reported value. The specific electrical conductivity for the composites was performed by measuring the current through the sheet sample under a steady constant voltage using a digital Keithley 642 electrometer. The two sides of the samples were bended with Cu- rod during curing process to reduce the contact resistance[1]. The mobility carriers (μ) and concentration of charge carriers (N) of composites were measured by Hall probe[2]. The dielectric constant was measured using RLC Bridge (3535 Z-Hitester, Hioki, Japan). Electromagnetic wave shielding properties were determined by the Hewlett-Packard waveguide line containing spectroanalyzer, power meter, coefficient of reflection meter, and coefficient of attenuation meter. The measurements were carried out in the frequency ranges 1 to 12 GHz and the thickness of the sample is about 1.0 mm.

RESULTS AND DISCUSSION

Microstructure and mechanical studies

The cross sectional area surfaces of the composite were examined in order to study details of the dispersion and adhesion of CB in PS matrix. The SEM images obtained from the surface of the fabricated samples CB4, CB8, CB16 and CB20 are

shown in Fig. 1(a–d), respectively. Fig. 1(a,b) for CB4, CB8 samples; reveals that at low CB content less than 8 wt% there are weak bonds among CB particles and PS matrix. The micrographs in Fig. (1c,d) for CB16, CB20 samples clearly show that CB nanoparticles were dispersed uniformly throughout the PS matrix. Apparent bonds can be seen in nanocomposites with increasing CB more than 8 wt%, presumably due to the strong interface adhesion and cross linking density among CB and PS matrix. To confirm the above facts we measured the cross linking density (n) based on the theory of rubber elasticity by using the following equation [2].

$$E_s = nRT\left(E_r - \frac{1}{E_r^2}\right) \quad ...(1)$$

where E_S is the tensile stress, R is the universal gas constant, T is the temperature in Kelvin and E_r is the extension ratio.

The distance among conductive filler particles (g) is given by the following relation [3]:

$$g = D\left[\left(\frac{P}{V_{cs}}\right)^{\frac{1}{3}} - 1\right] \quad ...(2)$$

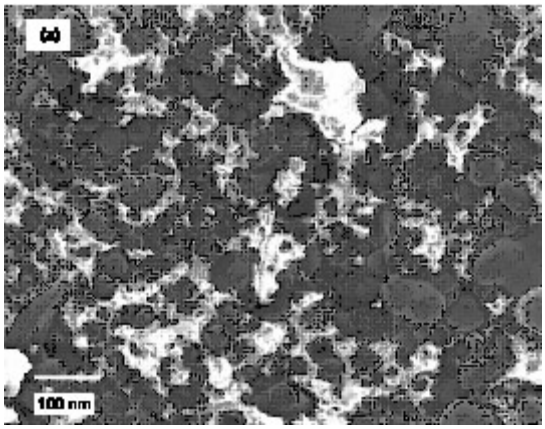

Fig. 1a: SEM of CB4 sample

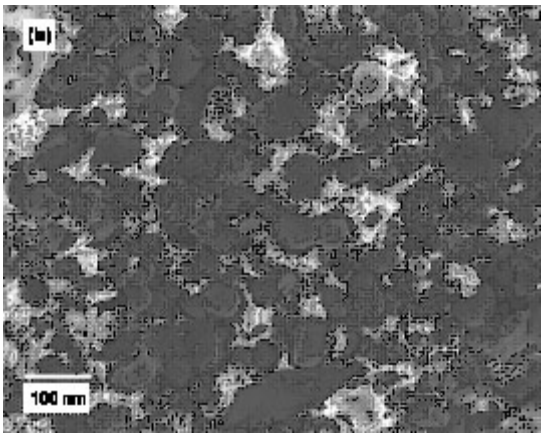

Fig. 1b: SEM of CB8 sample

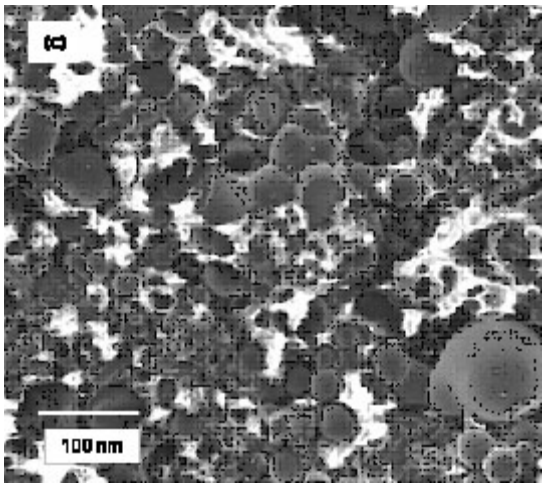

Fig. 1c: SEM of CB16 sample

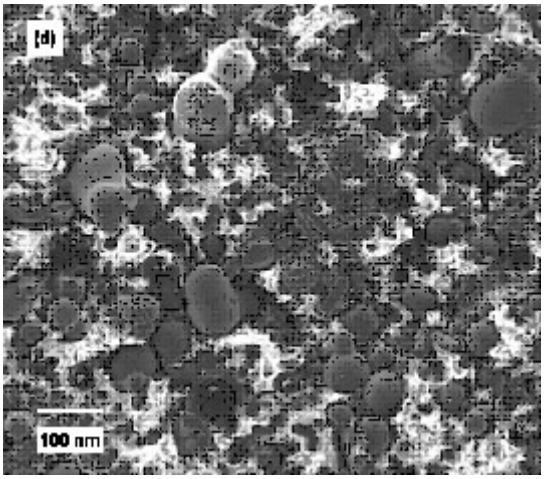

Fig. 1d: SEM of CB20 sample

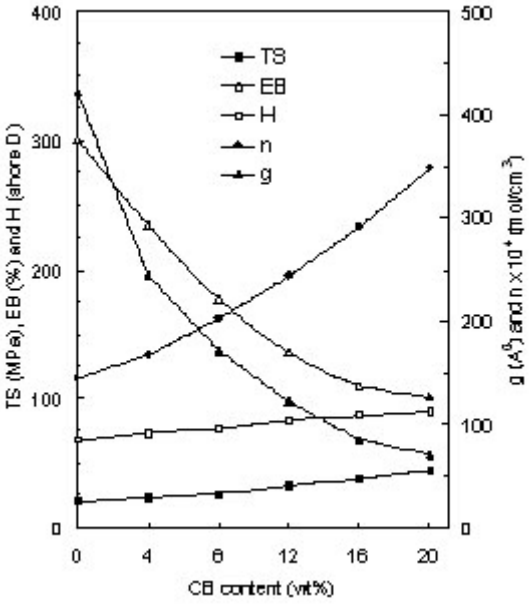

Fig. 2: Tensile strength (TS), elongation at break (EB), hardness (H), gap distance among conductive sites (g) and crosslinking density (n) as a function of CB content of composites.

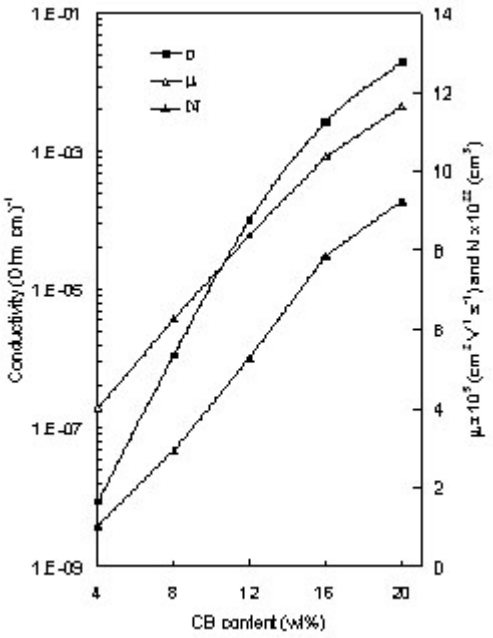

Fig. 4: The conductivity (σ), mobility carriers (μ) and concentration of charge carriers (N) as a function of temperature for different CB content of PS/CB nanoomposites

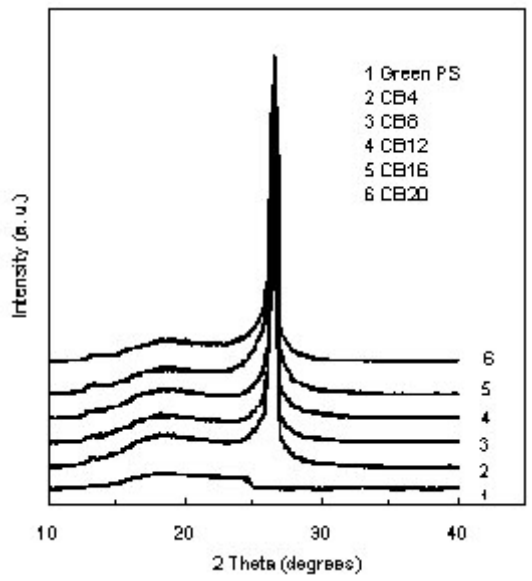

Fig. 3: X-ray patterns of the nanocomposites

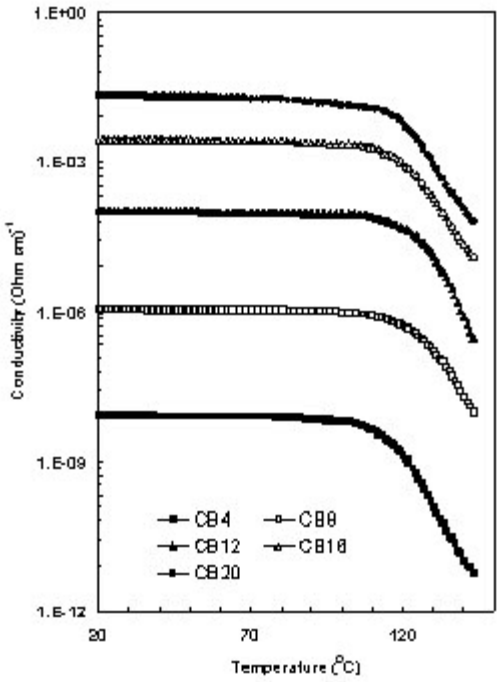

Fig. 5: temperature dependence of the electrical conductivity of the PS/CB nanocomposites

where D is the diameter of filler particles, P is the packing density coefficient of fillers, which is about 0.64 for statistically packed monodispersed spherical particles of any size and (V_{CB}) is the volume fraction of filler.

Fig. (2) depicts the values of n and as functions of CB of nanocomposites. As expected the inclusion of CB nanoparticles into PS matrix enhanced the crosslinking density and number of elastically effective chains within nanocomposites. The gap distance among conducting sites decreases with increasing CB loading as observed in Fig. (2). This indicates that the interfacial bonding among CB particles and PS chains increases with CB loading level.

The increase in hardness with the increase in CB content has been noticed for PS/CB nanocomposites as shown in Fig. (2). The increase in hardness with the increase in CB content suggests that the inclusion of CB has substantially accelerated the interlink among filler and matrix and has also increased the crystallinity of the nanocomposites as confirmed by measuring the X-ray patterns of the nanocomposites in Fig. (3).

It was observed that the tensile strength increases with increase in the CB content into composites as shown in Fig. (2). The increase of tensile strength with increasing CB content is attributed to the increase of the interfacial adhesion of nanocomposites as depicted in the SEM Figures. We see that with increasing CB content in the composites more and more polymer chains are expected to link or attach and are in the vicinity of the CB surface. However, with increasing CB content, the free volume of the polymer decreases leading to an increasing the tensile strength. The elongations at break (EB) of nanocomposites are found to decrease with the increase in CB content as shown in Fig. (2). The decrease in elongations is a typical characteristic for inorganic filled composite[3,9]. The initial slow decrease in elongations at break in nanocomposites corresponds to a region of good dispersion of CB nanoparticles of low loading and good interfacial adhesion between the nanoparticles and the PS matrix. In addition the mobility of the PS is not restricted under low CB content.

Electrical properties and conduction transport

The bulk dc conductivity at room temperature of the PS/CB composites as a function of CB filling is plotted in Fig. (4). It can easily be seen that the conductivity of the composites significantly depends on the content of CB. When 4 wt% of CB was incorporated into PS matrix, the volume conductivity of the composite is four as much as the initial of green PS. Then with the increase in the amount of CB; the volume conductivity of the composite increases slowly. This phenomenon demonstrates that the percolation threshold in conductivity of the composite is lower than 8 wt%. The low percolation threshold ascribed to the CB is more homogeneity disperse and interconnected to form conductive nets into composites see SEM images Fig. 1 (a-d). Mobility carriers (μ) and concentration of charge carriers (N) as a function of CB content is shown in Fig. (4). It is seen that both μ and N increases with increasing CB content into composites leading to an increase of the whole conductivity of composites.

The experimental data obtained in Fig. (5) are fitted using the following equation [12]:

were ϕ is the volume fraction of CB, ϕ_c is the percolation threshold and is the critical exponent.

$$\sigma \alpha (\phi - \phi_c)^F \quad ...(3)$$

The estimate of calculated from the slope of the linearity is in the range of 1.56 for the PS/CB composites. This indicates that the CB particles formed a three dimentional network throughout the composites.

The temperature dependence of the electrical conductivity of the PS/CB nanocomposites is depicted in Fig. (5). It is seen that at relatively small temperature the conductivity slightly decreases up to certain temperature (denoted by percolation temperature) after which a sharp decrease of conductivity is observed. This is usually called positive temperature coefficient of resistivity (PTCR) effect[11]. This anomalous PTCR behavior is mainly due to the two reasons. First at percolation temperature the volume thermal expansion of PS

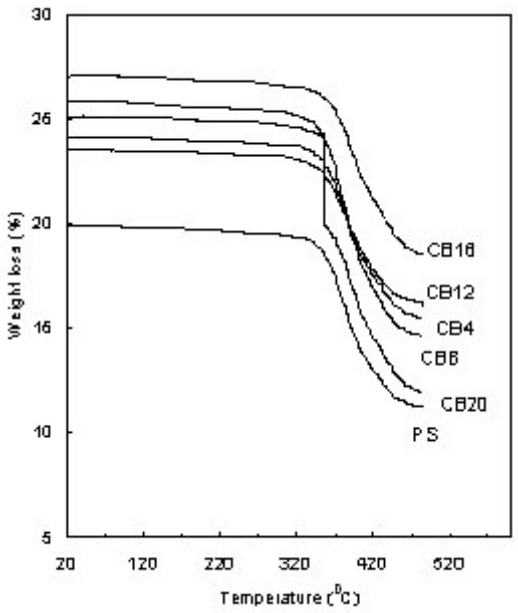

Fig. 6: TG curves of green PS and PS/CB composites

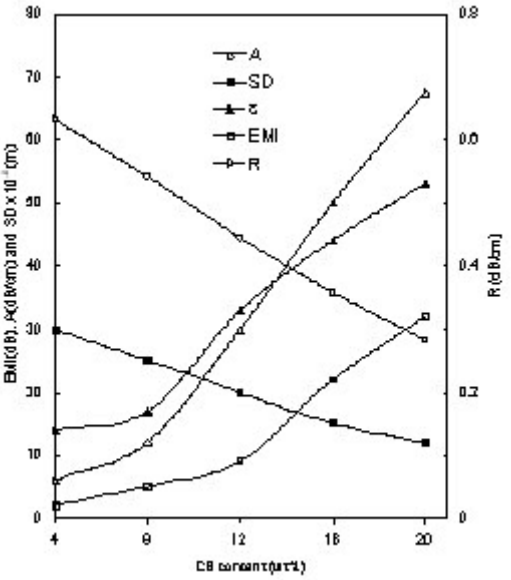

Fig. (8): EMI, dielectric constant (ε), skin depth (SD), reflection loss (R) and absorbance loss (A) as a function of CB content of composites

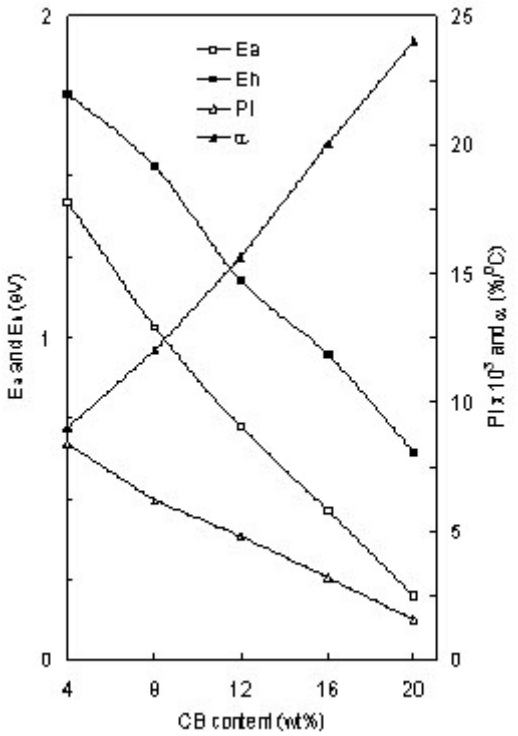

Fig. 7: E_a, E_h, PTCR intensity (PI) and temperature conductivity factor (α) as a function of CB content of composites

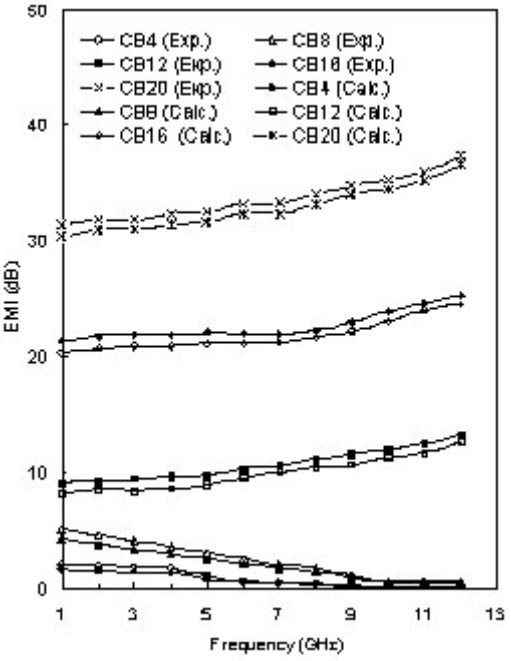

Fig. 9: Measured and calculated values of EMI of the composites in the frequency range of 1 GHz to 12 GHz.

matrix increases, leading to the increase of the interparticle distance among conductive sites. Therefore the transport of charge carriers decreases leading to decrease in electrical conductivity[1-5]. Second, some of conductive paths were rupturing at percolation temperature, thereat the conductivity decrease into composites[6,7]. It is interesting to note that the percolation temperature shifts to a higher temperature with increasing CB content into composites. This is a strong clue that the inclusion of CB into PS matrix enhances the thermal stability and network structure of composites. To confirm this facts thermo-gravimetric (TG) analysis was carried out to see the thermal stability of the PS/CB nanocomposite. TG curves of green PS and PS/CB composites are depicted in Fig. (6). The TG results show that weight loss is due to water molecules (50 - 100 °C). Thus all the samples undergo two steps degradation. First step is corresponding to the loss of water followed by a weight loss due to the CB attached to the PS backbone and finally decomposition of PS backbone. The degradation temperature of the composites increases with increasing CB content, which indicates that there was an intermolecular interaction between CB and PS chains. This implies that CB particle is comparatively tightly bounded with PS chains.

However, the activation energy is associated with the height of the potential-energy barrier restricting the motion of charge carriers. The activation energy of composites is given by the following equation [1,10]:

$$\sigma = \sigma_0 \ \exp\left(-E_a / KT\right) \qquad ...(4)$$

The hopping energy is given by the following equation:

$$\sigma \sqrt{T} = \sigma_1 \ \exp\left(E_h / KT\right) \qquad ...(5)$$

where σ_0,σ_1 are the pre-exponential factor, K is the Boltzmann constant and T is the absolute temperature.

The estimated values of E_a and E_h as functions of CB content are plotted in Fig. (7). It is clear that the values of E_a and $E_h$decrease with increasing CB content into composites.

This indicates that the transport of charge carriers increases with increasing CB content leads to an increase of conductivity. It is interesting to note that both values of and are not similar. This values indicate thar the charge carriers transport into composites is controlled by tunneling conduction mechanism [1,12]. The PTCR intensity is defined as the ratio of the peak conductivity in the conductivity-temperature curve to room conductivity. The conductivity temperature factor α is given by the following equation:

$$\alpha = 2.303 \times \frac{\log\left(\frac{\sigma_2}{\sigma_1}\right)}{T_2 - T_1} \qquad (\%/^0 C) \qquad ...(6)$$

where σ_2 and σ_1 are the conductivity corresponding to the temperatures T_2 and T_1 respectively.

(E_h) The computed values of PI and α as functions of CB content are plotted in Fig. (5). It is seen that the PTCR intensity decreases while the conductivity temperature factor increases with increasing CB concentration, which means the PTCR effect becomes obvious with the increase of CB content. This is ascribed to the CB nanoparticles enhancement of the molecular structural of PS matrix and thermal stability of composites. These results mentioned above suggest the possibility for the environmental friendly use of the new PS/CB nanocomposites PTCR thermistors with good quality and stability for the industrial utilization in near future.

Electromagnetic interference shielding effectiveness (EMI)

EMI is the protection of the propagation of electric and magnetic fields from one region to another by using electrically conducting and magnetic materials [1,13]. EMI is defined as [15]:
where $P_1(E_1)$ and $PT(E_T)$ are the power (electric field) of incident and transmitted electromagnetic wave, respectively.

$$EMI = \log \frac{P_I}{P_T} = 20 \log \frac{E_I}{E_T} \quad dB \qquad ...(7)$$

The attenuation offered by a shield may depend on three mechanisms. The first is usually the reflection of the wave from the shield. The second is the absorption of the wave as it passes through the shield. The third is due to the re-reflections, i.e. the multiple reflections of the waves at various surfaces or interfaces within the shield. The reflection loss is a function of the ratio (σ_r / μ_r), whereas the absorption loss is a function of the product ($\sigma_r \mu_r$), where (σ_r) is the electrical conductivity of the shield relative to copper and (μ_r) is the magnetic permeability of the shield relative to free space. The multiple reflections, however, require the presence of large surface areas (e.g. a porous or foam material) or interface areas (e.g. a composite material containing fillers that have large surface area) in the shield. The loss connected with multiple reflections can be neglected when the distance between the reflecting surfaces or interfaces large enough is compared to the skin depth (SD) which in meters is defined [1,15]:

$$SD = \frac{1}{\sqrt{\pi f \mu_p \sigma}} \qquad ...(8)$$

where f is the frequency (in Hz), μ_p is the magnetic permeability by $\mu_p \mu_0 = 4\pi \times 10^{-17}$ H/m is the absolute permeability of free space (air), $\mu_r = 1$ for non magnetic material and σ is the electrical conductivity.

The shielding effectiveness *(EMI)* for a conductive material can be expressed by the following equation [2,15]:

$$EMI = R + A + M \qquad ...(9)$$

where R is the reflection loss of the electromagnetic wave, A is the absorption loss of the energy of the electromagnetic wave and M is the multi-reflection loss of electromagnetic wave.

The calculated value of EMI shielding is given by the following equation:

$$EMI = 20 \log\left(\frac{120\pi\delta\sigma}{2.83}\right) + 8.69\left(\frac{h}{\delta}\right) \qquad ...(10)$$

Fig. (8) depicts the EMI, dielectric constant and skin depth as a function of CB content of composites. It is evident that the shielding efficiency increases with the CB loading level of the composites. As expected the increasing conductivity leads to corresponding decrease in skin depth which may be helpful in designing thinner EMI shields. A moderate increase in dielectric constant is observed when the CB content is low. As the CB content approaches a value corresponding to the transition region, a large change in dielectric constant is observed. The increase in the dielectric constant with CB content is a direct consequence of the interfacial Maxwell-Wagner polarization effect between the PS matrix and the high dielectric constant of CB nanoparticles[1,2]. Reflection and absorbance loss with CB content of PS/CB composites is shown in Fig. 8. The coefficient of reflection from the external surface is about 0.28 and coefficient of attenuation is about 67.6 dB /cm. The absorption loss exhibits rapid enhancement from 4.2 to 67.6 dB with the increased CB loading. This may be explained in terms of increase in conductivity as well as capacitive coupling effects [15].

EMI

Fig. (9) depicts the measured and calculated values of EMI of the composites in the frequency range of 1 GHz to 12 GHz. It is seen that at low CB content less than 8 wt% the EMI decreases with increasing frequency. On the other hand with increasing CB content more than 8 wt% the EMI increases with increasing frequency. The EMI of the sample CB20 reached a 33 dB, which make the above composites suitable for microwave shielding applications. It is interesting to note that the EMI measured agree well with theoretical models. It is worthily to note that the absorption dominated the total shielding effectiveness of the nanocomposites. This gives a real opportunity for application of these materials as electromagnetic wave shielding up to 12 GHz.

CONCLUSIONS

The salient features of the present

investigations are described as follows:

1. The inclusion of CB nanoparticles enhances both the interfacial adhesion between CB particles and PS matrix and crystallinity of composites.
2. The mechanical properties like hardness and tensile strength improve with increasing CB loading level. Thermo-gravimetric (TG) results indicate that the inclusion of CB nanoparticles enhances the thermal stability of the PS/CB composites.
3. The PS/CB nanoconducting composites based thermistors show typical PTCR effect. The conduction mechanism of conductivity is controlled by a tunneling mechanism.
4. The EMI shielding effectiveness of composites increases with increasing CB content from 3 dB to 33 dB in the frequency range of 1 to 12 GHz.
5. The absorption dominated total shielding effectiveness in range of 5 to 67 dB, indicates that these nanocomposites could be utilized effectively for microwave absorbance.

REFERENCES

1. F. El-Tantawy, *Journal of Applied Polymer Science*, **104**: 697-709 (2007).
2. F. El-Tantawy, *Journal of Applied Polymer Science*, **97**: 1125-1138 (2005).
3. F. El-Tantawy, Sung, Y. K., *Macromolecular Research*, **10**: 345-358 (2002).
4. F. El-Tantawy, K. Kamada, H. Ohnabe, *Materials Letters*, **57**: 242–251 (2002).
5. F. El-Tantawy, K. Kamada, H.Ohnabe, *Polymer International*, **51**: 635-645 (2002).
6. Q. Li, A. Siddaramaiah, N. H. Kim, G-H. Yoo, J. H. Lee, Composites: Part B (2008), doi: 10.1016/j. compositesb.2008.11.002.
7. V. Panwar, V. K. Sachdev, R. M. Mehra, *European Polymer Journal*, **43**: 573–585 (2007).
8. T. Thanpitcha, A. Sirivat, A. M. Jamieson, R. Rujiravanit, *Carbohydrate Polymers*, **64**: 560-568 (2006).
9. Z. Dang, L. Fan, S. Zhao, C. Nan, *Materials Research Bulletin*, **38**: 499-507 (2003).
10. I. M. Afanasov, V.A. Morozov, A.V. Kepman, S.G. Ionov, A.N. Seleznev, G. Van Tendeloo, V.V. Avdeev, *Carbon,* **63**: 263-270 (2009).
11. X. Peng, X. Min, G. Kecheng, *Polymer*, **42**: 4813-4816 (2001).
12. Y. K. Hong, C. Y. Lee, C. K. Jeong, D. E. Lee, K. Kim, J. Joo, *Review of Scientific Instruments*, **74**: 1098-1102 (2003).
13. K. Lakshmi, H. John, K.T. Mathew, R. Joseph, K. E. George, *Acta Materialia*, **57**: 371-375 (2009).
14. Z. Chun-Sheng, N. Qing-Qing, F. Shao-Yun, K. Kurashiki, *Composites Science and Technology*, **67**: 2973-2980 (2007).
15. F. El-Tantawy, K. M. Abdel-Kader, F. Kaneko, Y. K. Sung, *European Polymer Journal,* **40**: 415-430 (2004).