



ELSEVIER

Available online at www.sciencedirect.com

SCIENCE @ DIRECT®

Composites: Part B 34 (2003) 637–645

composites
Part B: engineering

www.elsevier.com/locate/compositesb

On polyethylene–polyaniline composites

M. Chipara^{a,*}, D. Hui^b, P.V. Notingher^c, M.D. Chipara^d, K.T. Lau^e, J. Sankar^f, D. Panaitescu^d

^aDepartment of Mechanical Engineering, University of New Orleans, Lakefront, New Orleans, LA 70148, USA

^bCyclotron Facility, Indiana University, 2401 Milo B Sampson Lane, Bloomington, IN 47408, USA

^cPOLITEHNICA University of Bucharest, Splaiul Independentei 313, Bucharest, Romania

^dCentral Institute of Chemistry, 204, Splaiul Independentei Av., Bucharest, Romania

^eDepartment of Mechanical Engineering, Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong, Peoples Republic of China

^fDepartment of Mechanical Engineering, North Carolina A and T State University, Greensboro, NC 27411, USA

Received 2 January 2003; accepted 24 March 2003

Abstract

Mechanical tests (elongation at break and tensile strength), DC electrical conductivity, and electron spin resonance (ESR) investigations on polyethylene–polyaniline blends are reported. While the concentration of the conducting polymer in the blend is raised, the DC electrical conductivity is increased, and the mechanical properties (tensile strength and elongation at break) are depressed. An universal expression for the dependence of mechanical and electrical properties on the concentration of conducting particles is empirically suggested and supported by experimental data. The ESR spectra are single lines, located close to the $g = 2.0$ value and assigned to the conduction electrons (with uncoupled electronic spins). The reduced asymmetry of the resonance supports the presence of mesoscopic conducting domains. The features of ESR spectra and the connection between ESR parameters and DC conductivity reflects the major role of polarons hopping in the electron transport and rules out the presence of both low and high spin bipolarons.

© 2003 Elsevier Ltd. All rights reserved.

Keywords: A. Polymer-matrix composites; B. Electrical properties; Mechanical properties; Magnetic properties

1. Introduction

Conducting polymers such as polyaniline and polypyrrole exhibit excellent electrical conductivities and outstanding thermal stability, while their chemical solubility and mechanical properties are poor leading to a reduced processability [1–8]. To overcome these difficulties most research efforts were focused on the chemical functionalization of such conducting polymers and on composites of conducting polymers with elastomers [1–9].

The conduction process in polyaniline and polypyrrole has been explained by the hopping of electrons along the polymeric chain [10–17], within the so-called Variable Range Hopping [10] description. Experimental studies on the temperature dependence of conductivity revealed that polyaniline is a one-dimensional conductor [12], characterized by a very weak probability of electronic jumps among

different polymeric chain in comparison to the jump probability along the chain. Polyaniline is a typical one-dimensional conductor. In extremely heavily doped polyaniline and polypyrrole, a tendency towards a two-dimensional conducting process has been noticed [12].

Electron spin resonance (ESR) is a very powerful method in the investigation of the fundamental mechanisms related to the electronic conduction polymers. The appearance of metallic islands at high concentration of dopants has been speculated by several authors [13–21]. ESR spectroscopy may be used to test for the presence of such metallic islands. If the size of the conducting island is larger or comparable to the skin depth, the electromagnetic wave will be distorted within the conducting particle, resulting in a typical resonance line shape, known as Dysonian [15,27]. Composites (blends) based on such conducting polymer exhibit a sudden drop in the electrical resistance as the fraction of the conducting phase is increased, accurately described by the percolation theory [22].

Various quasi-particles [16–21] such as excitons [17], solitons, polarons [16], and bipolarons [18] have been

* Corresponding author. Address: Cyclotron Facility, Indiana University, 2401 Milo B Sampson Lane, Bloomington, IN 47408, USA. Tel.: +1-812-855-6051; fax: +1-812-855-6645.

E-mail address: mchipara@iucf.indiana.edu (M. Chipara).

claimed to explain the physical properties of conducting polymers. ESR has been frequently used to investigate the nature of the quasi-particle responsible for the charge transport, the fine details of the electronic transport, and the interactions among electrons. ESR allows investigations on the nature and evolution of polarons and bipolarons in conducting polymers [18]. Polaronic quasi-particles [4–8] are responsible for a single resonance line located close to the $g = 2.00$ value, while the high spin bipolarons, carrying a $S = 1$ spins are responsible for a resonance line located at $g = 4.00$ [18,25–27]. The low spin bipolaron has $S = 0$ and hence presents no ESR spectrum [25–27]. The temperature dependence of ESR lines gives further details regarding the conduction mechanisms.

The present contribution aims at a better understanding of the mechanical and electrical features of polyethylene–polyaniline (PEPANI) composites, at both fundamental and empirical levels.

2. Experimental methods

Polyethylene (PE) is a polymer with excellent mechanical properties, high resistance to chemical agents, and good processability. Polyaniline (PANI) doped with about 10% HCl, was obtained chemically by oxidation [7]. The analysis of the temperature dependence of resistance indicated a one-dimensional electronic conduction in PANI [7]. While PE is an insulator, the pellets made from the same PANI powder used in this study had a conductivity of about 0.1 S m^{-1} , exhibiting a typical Variable Range Hopping like dependence of the DC conductivity on the sample temperature [7, 8,21]. Grains of low-density polyethylene with a degree of

crystallinity of about 60% and a melting temperature of about 110°C have been mixed with the submicron powder of doped polyaniline and milled together on a two-roller mixer at about 80°C , for about 60 min. The roller gap was 0.5 mm. Composites of polyethylene/polyaniline (PEPANI), containing 0, 5, 10, 15, 20 and 40% polyaniline (in weight) with a thickness of about $0.5 \pm 0.1 \text{ mm}$ have been obtained. Before milling the components were dried at 70°C , under vacuum, for 24 h.

The resulting PEPANI composites were homogeneous, presenting a good stability of electrical and mechanical properties. Sets of 10 samples, prepared in identical conditions, were subjected to mechanical, electrical, and ESR studies. The distribution of physical properties of samples, obeyed a Gaussian like shape with a standard error less than 5%, for all samples. The experimental results presented in the next sections represent the average over all 10 identical samples. The elongation at break and tensile strength of PEPANI dumbbells were measured by using a Monsanto T10 instrument, in air, at room temperature. The sample thickness was accurately measured and the DC conductivity data were corrected for the small differences in polymer thickness. DC conductivity measurements have been made at room temperature, by using a Keithley 6517 electrometer and a Keithley 8009 resistivity test fixture.

3. Experimental results

As noticed from Fig. 1A and B, the tensile strength, T , is reduced as the content of PANI (wt/wt) is increased. The elongation at break, ϵ decreases drastically as PANI is introduced in PE (Fig. 2A and B). Hence, the mechanical

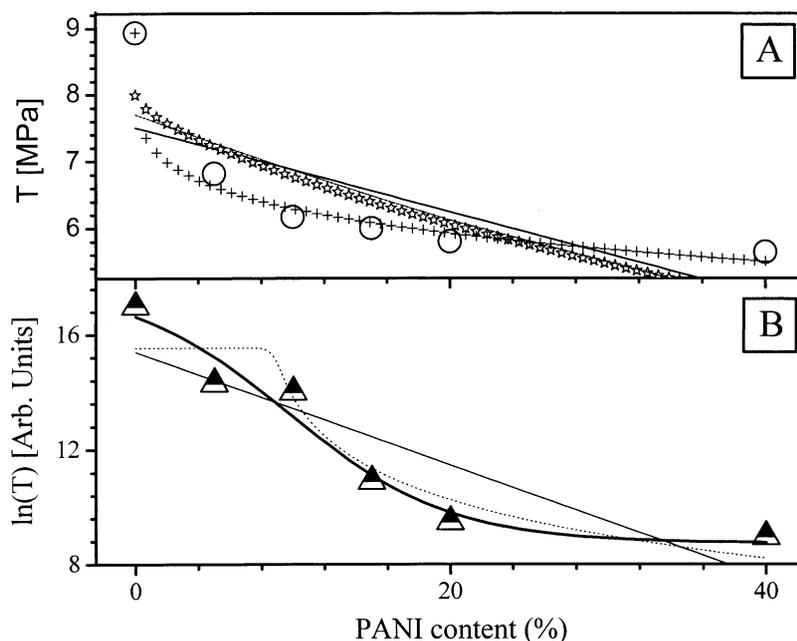


Fig. 1. (A) The dependence of the tensile strength on polyaniline content. (B) The dependence of the logarithm of tensile strength on polyaniline content.

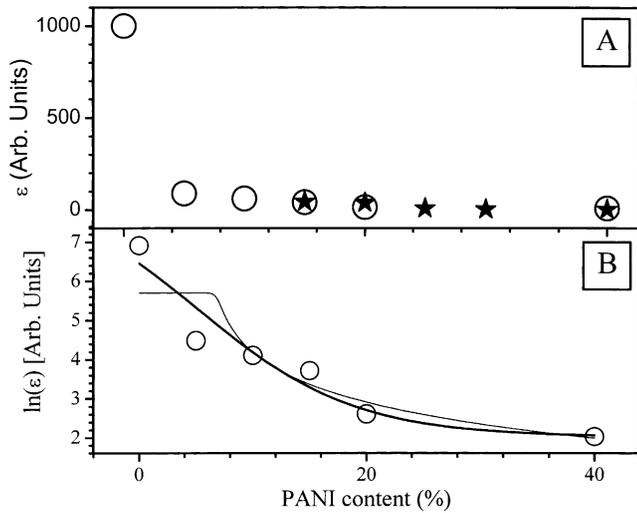


Fig. 2. (A) The dependence of the elongation at break (ϵ) on PANI concentration. Star points represents the dependence of the elongation at break on the back carbon content, as reported in Ref. [30]. (B) The dependence of the logarithm of the elongation at break (ϵ) on PANI concentration.

features of PEPANI composites become poorer as the PANI content is increased, as reported elsewhere [29,30]. The electrical resistance of PEPANI composites decreases rapidly as the fraction of polyaniline is increased (Fig. 3A and B). The sudden decrease is better seen in the dependence of the logarithm of the composite conductivity versus PANI content (Fig. 3B). The dependence reflects a typical percolation like process [23].

Pristine PE presents no ESR spectrum. The ESR spectra of PEPANI composites is a single narrow line (Fig. 4A), located

closed to $g = 2.0$ with a low asymmetry. The position and the shape of the resonance line is identical with the ESR spectrum of the polyaniline doped with HCl [21]. No resonance line located at $g \approx 4.0$ has been recorded. A typical Dysonian spectrum is represented in Fig. 4B. The dependence of ESR parameters on the concentration of polyaniline is shown in Fig. 5A–D. As it is exhibited in Fig. 5A, the peak-to-peak resonance line width, H_{PP} , decreases as the concentration of polyaniline is increased. The result is supported by the increase of the resonance line amplitude, I , as the polyaniline concentration is raised (Fig. 5B).

The double integral of the ESR spectrum, DI, has been calculated according to the relation

$$DI = K_S I H_{PP}^2 \tag{1}$$

where K_S is the shape factor, estimated using the slope method [25]. S is increased as the PANI concentration is increased (Fig. 5C), supporting the observed dependence of H_{PP} and I on PANI content. From Fig. 5D is observed that the resonance line asymmetry increases as the concentration of PANI is raised. The result at about 10% PANI may reflect a poor dispersion of PANI particles, which are concentrated in clusters.

4. Discussions

In the case of PEPANI composites, the polymeric phase consists of linear chains, with reduced branches. Due to the flexibility of PE macromolecular chain, the polymer is folded in closely packed crystalline domains.

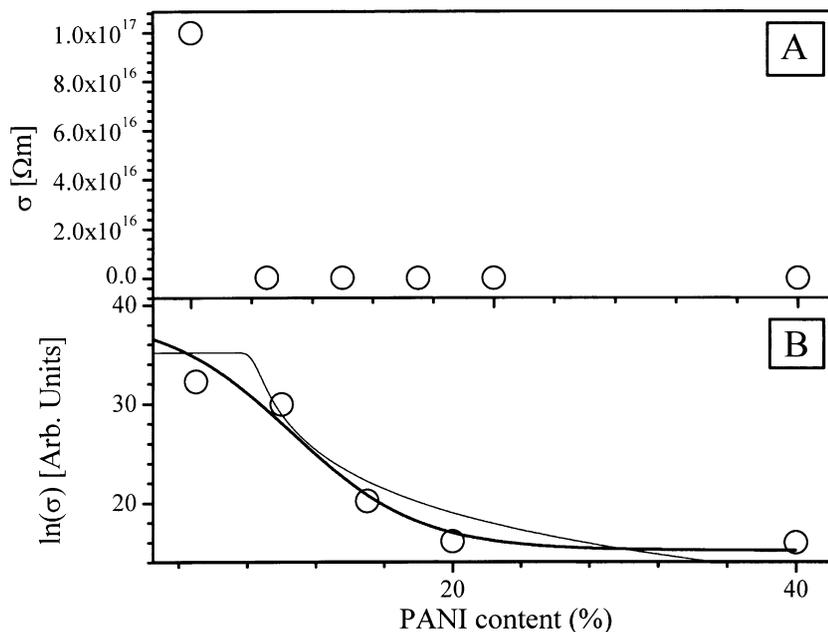


Fig. 3. The dependence of the electrical resistance (A) and of the logarithm of the electrical resistance (B) on PANI concentration.

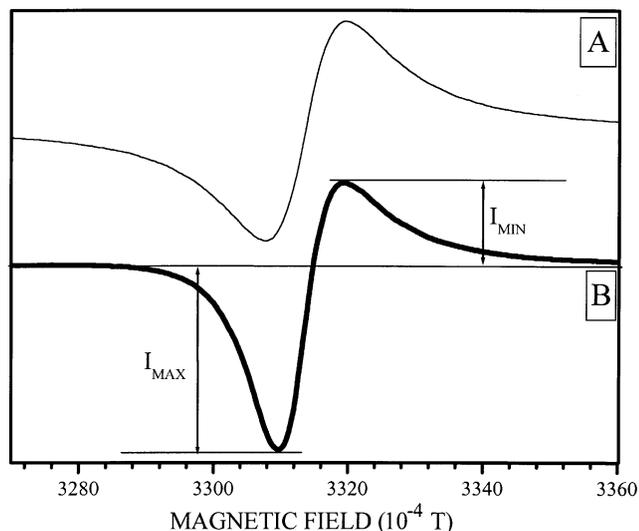


Fig. 4. (A) The ESR spectrum of PEPANI composites (actually is the resonance spectrum of the composite containing 25% PANI). (B) Typical Dysonian resonance line.

The macromolecular chain of PANI is shorter and has a reduced flexibility than PE chains. The low glass transition temperature of PE indicates that at room temperature, the segmental motions are activated and the amorphous domains will behave as a high viscosity fluid. This suggests a preferential location of PANI chains in PE crystalline domains, as shown in Fig. 6.

The empirical dependence of the tensile strength on polyaniline content is well described by an empirical exponential like decay

$$T = T_0 \exp(-Ax) \quad (2)$$

T_0 is the tensile strength of pure PE. The best fit of experimental data, is represented in Fig. 1A by the dotted line and corresponds to $A = 1.2 \pm 0.5$, and $T_0 = 7.5 \pm 0.5$ MPa. If PEPANI composites are homogeneous, the superposition principle will imply a stress distribution within the polymeric matrix and the conducting filler

$$T = T_{PE}(1 - x) + T_{PANI}x \quad (3)$$

where T_{PE} , and T_{PANI} represent the tensile strength for pristine polyethylene and polyaniline, respectively. The best fit is represented in Fig. 1A by a fine solid line and corresponds to $T_{PE} = 7.50 \pm 0.5$ MPa and $T_{PANI} = 1.2 \pm 0.2$. The estimated tensile strength for the pristine PE phase is lower than the measured value by about 30% (black line). The poor correlation between the experimental data and the predictions derived from such simplified models reflect the complex mechanical behavior of these composites.

In polymeric composites, the debonding process has an important contribution in reduction the mechanical properties. Various factors as the shape of the conducting particles, their size, their concentration and the detailed interactions between conducting particles and polymeric matrix are responsible for debonding. The expecting dependence of

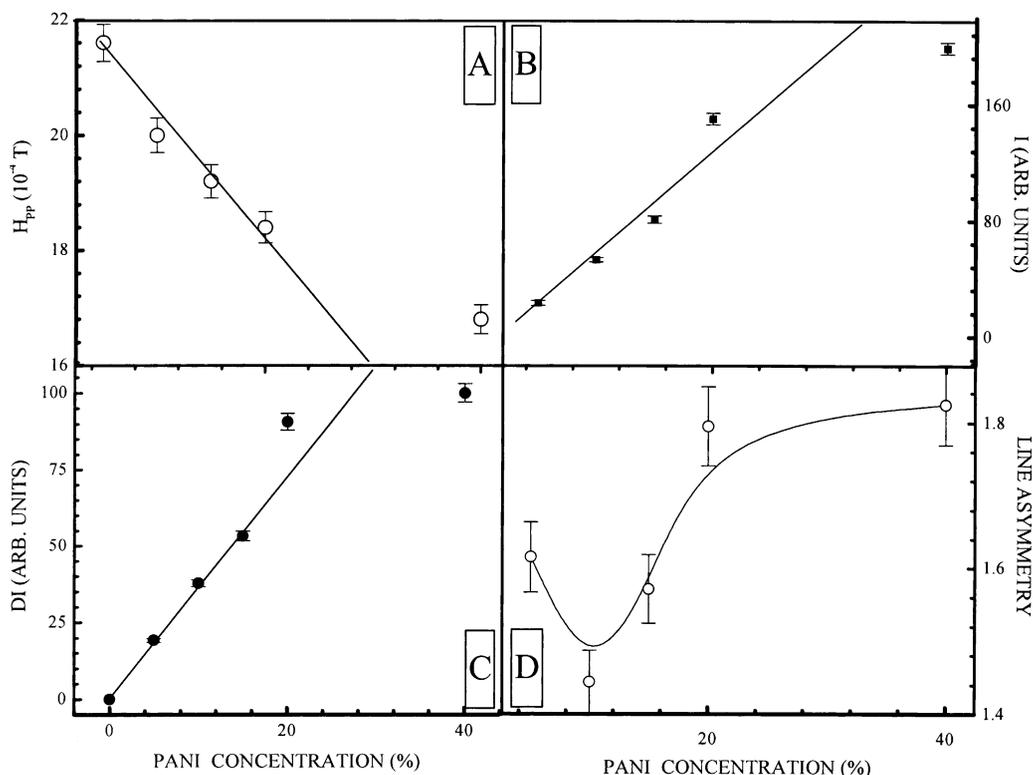


Fig. 5. (A) The dependence of H_{pp} on PANI content. The line reflects the predictions based on the superposition principle. (B) The dependence of I on PANI content. The line reflects the predictions based on the superposition principle. (C) The dependence of the parameter DI (that is proportional to the uncoupled spin concentration at a given constant temperature) on PANI content. The line reflects the predictions based on the superposition principle.

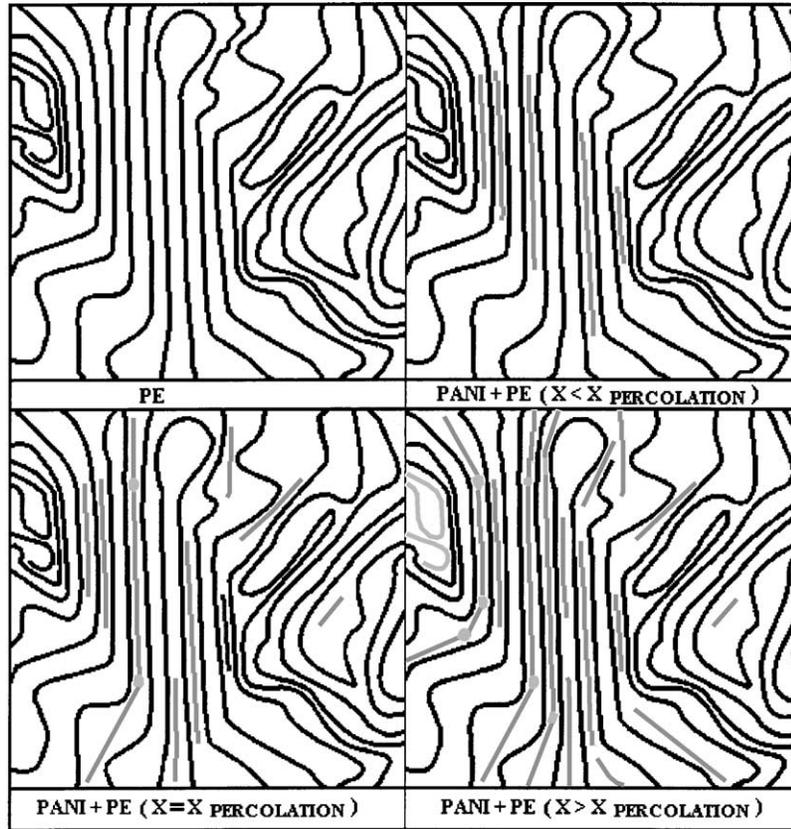


Fig. 6. (A) schematic representation of percolation in PEPANI composites.

the tensile strength on the fillers' concentration due to debonding is [28]

$$T = T_{PE}(1 - C_D x^n) \quad (4)$$

where C_D is a constant and n has a theoretical value of 0.666. Assuming that both T_{PE} , C_D and n are fitting parameters, the best fit results correspond to $T_{PE} = 8.9 \pm 0.2$ MPa, $C_D = 0.46 \pm 0.04$, and $n = 0.19 \pm 0.04$. It is remarkable the coincidence between the predicted and measured values of the tensile strength for PE (see the cross line in Fig. 1A). However, the theoretically expected value for n is 0.67 instead of 0.3. Forcing $n = 0.67$, the best fit results in $T_{PE} = 8.0 \pm 0.2$ MPa, and $C_D = 0.7 \pm 0.2$ (star line in Fig. 1A). These results reflect the importance of the adhesion between polyaniline particles and polyethylene. By inspecting Figs. 1A and 2B it is noticed that the tensile strength is more sensitive to the adhesion between the filler and the polymeric matrix than the elongation at break. The elongation at break is severely affected by the poor mechanical features of PANI. While the concentration of PANI is increased, the distance between PANI molecules is depressed. Due to the poor adhesion, the PE chains are able to slip along the PANI particle. This increases the stress exerted on PANI particles, which due to their extremely poor mechanical properties will generate microcracks and initiate the polymer fracture. Near the percolation threshold, we may imagine that the polymer has a continuous PANI

filament, as the reduced resistivity requires a contiguous pathway with no insulating (PE) barriers. A simple representation of the mechanical properties of the composite near the percolation threshold may be provided by the Voigt model, where the string is assigned to PE chains and a dashpot and a string with a very low elasticity represents PANI chains. The reduced elongation at break of PANI will trigger a rapid failure of the composite material. This suggests a formal analogy between the dependence of the DC conductivity on conducting particle concentration and the dependence of the elongation at break on PANI content, near the percolation concentration. To investigate in detail this possible connection, the dependence of the elongation at break on PANI content has been fitted by the expression

$$\epsilon_{COM} = \begin{cases} \epsilon^*, & x < x_0^\epsilon \\ \epsilon^*(1 - x_0^\epsilon/x)^a, & x > x_0^\epsilon \end{cases} \quad (5)$$

where ϵ^* is the elongation at break of tensile PE chains and x_0^ϵ is the concentration of PANI at which the rapid decay of ϵ is triggered. The best fit is represented by a fine line in Fig. 2B, and corresponds to $x_0^\epsilon = 5.7 \pm 0.5\%$, and $a = 1.1 \pm 0.1$. The star points in Fig. 2A represents the data from Ref. [30]. It is noticed that the dependence of the elongation at break is almost independent of the nature of filler particle. This result confirms that tensile strength is more sensitive to the adhesion between filler and polymeric matrix than the elongation at break.

A percolation like dependence of the tensile strength, T , has been considered (Eq. (6) and Fig. 1B)

$$T = \begin{cases} T^*, & x < x_0^\sigma \\ T^*(x - x_0^\sigma)^b, & x > x_0^\sigma \end{cases} \quad (6)$$

The best fit, represented by the fine line in Fig. 1B has been obtained for $x_0^\sigma = 7.6 \pm 1.5\%$, and $b = 2.1 \pm 0.1$.

The percolative decrease of the resistance or resistivity in blends of insulating polymers and conducting particles is represented mathematically by the relationship

$$\sigma = \begin{cases} \sigma^*, & x < x_0^\sigma \\ \sigma^*(x - x_0^\sigma)^c, & x > x_0^\sigma \end{cases} \quad (7)$$

where σ is the DC resistivity of the composite. The best fit is represented by the fine line in Fig. 3B and corresponds to $x_0^\sigma = 7.3 \pm 1.5\%$ and $c = 6.3 \pm 0.6$. The good agreement between experimental data and the predictions based on Eqs. (5) and (7) supports the hypothesis that the dependence of the elongation at break on polyaniline content is reminiscent to a percolation-like process [22].

From Fig. 3A it is observed that the percolation from insulator to conductor is broad. The gradual change in the physical properties of these composites as the filler content is increased is a general feature, noticed in Figs. 1–3. While such a behavior is not appropriate when large conductivities are required at relatively low content of conducting polymer, it is extremely important in applications where the electrical resistance of the composite has to be finely tuned. From the theoretical point of view the broad percolation would result in a poor correlation between theory and experiment and in significant errors, mainly in the estimation of the concentration of PANI at which the percolation occurs. To describe such a mild percolation and to estimate more accurately the percolation threshold, we fitted the dependence of the above-mentioned physical properties on PANI content by a Boltzmann equation (Eq. (8)). The best fit, represented in Figs. 1B, 2B and 3B by a bold line improves significantly the theoretical predictions, suggesting that close to the percolation threshold such a dependence is almost universal

$$\ln\left(\frac{P}{P_0}\right) = P_2 + \frac{P_1 - P_2}{1 + \exp\left(\frac{x - x_0^B}{d^B}\right)} \quad (8)$$

where P is the physical property, P_0 is the value of the physical property P for the pure polymer, P_1 and P_2 have been treated as fitting parameters, although for an ideal Boltzmann function they would represent the initial (0% filler) and final (100% filler) asymptotic values, x_0^B is the concentration at which is located the inflexion point, and d^B is the width of the Boltzmann sigmoid. The values of the parameters corresponding to the best fit are collected in Table 1.

Table 1

The parameters corresponding to the best fit of physical properties, obtained by using a Boltzmann sigmoid (Eq. (8))

Physical property	P_1	P_2	x_0^B	d^B	Figure
Tensile strength	17.9	8.7	9.7	5.1	1
Elongation at break	7.2	1.9	9.9	6.4	2
Resistivity	39	15.2	10.6	3.76	3
ESR data	1.9	0.3	19.1	2.74	7

ESR consists in the resonant absorption of energy by a system of uncoupled electronic spins placed in external magnetic field from the magnetic component of a microwave field. The external magnetic field raises the degeneracy upon the quantum magnetic number, generating two energy levels (for a free electron spin) while the microwave field induces resonance transition among these Zeeman levels. The resonance line position is defined by the relationship [25–27]

$$h\nu = g\beta H\Delta M_S \quad (9)$$

where h is the Planck constant, ν is the microwave field frequency, β is the electronic Bohn magneton, H is the external magnetic field, and ΔM_S expresses the change in the orientation of the electronic spins (for a free electron with $S = 1/2$ this leads to $\frac{1}{2} - (-\frac{1}{2}) = 1$). For a free electron the theoretical value of the gyromagnetic ratio g (including relativistic corrections) is $g = 2.0023$ [26]. The g factor is sensitive to the interactions of the uncoupled electronic spins with local electric and magnetic fields and depends on the effective value of the spin [27]. The ESR spectra of PEPANI composites are located close to $g = 2.0$. This indicates that the resonance spectrum is due to an uncoupled electronic spin and that the interaction with the polymeric matrix is negligible (the angular momentum is quenched). The result is not trivial; in certain polymers the charge transport properties were related to bipolarons. A pair of electrons with parallel spins represents a high spin bipolaron. This quasi-particle has an effective spin $S = 1$. Hence, $\Delta M_S = 2$ and the equivalent g value would be about 4.0. No resonance line located at $g = 4.00$ has been observed. This rules out the presence of high spin bipolarons in PEPANI composites [22]. The low spin bipolaron consists of two electrons, with opposite spins. The effective spin of this bipolaron is zero and hence no ESR spectrum is recorded.

As it is shown in Fig. 4A, the ESR spectrum of PEPANI composites is a narrow line, almost symmetric. The reduced asymmetry is too small ($I_{MAX}/I_{MIN} < 2.7$ for all PANI concentrations, see Fig. 5D [27]) to consider the resonance line shape Dysonian. This indicates that the conducting islands have linear dimensions smaller than 10^{-5} m, supporting the mesoscopic picture of charge transport in conducting polymers.

The peak-to-peak resonance line width reflects the interaction of the electronic spins. Two main relaxations

are competing to the final line width [26,27], the spin–spin relaxation characterized by the relaxation time T_{SS} and the spin lattice relaxation, characterized by T_{SL} .

$$H_{PP} \propto \frac{1}{T_{SS}} + \frac{1}{T_{SL}} \quad (10)$$

The features of the resonance line suggest that the spin–spin interactions are dominant. The decrease of H_{PP} as PANI content is increased reflects the enhancement of exchange interactions, due to the decrease in the average distance between uncoupled electronic spins. The result indicates that the material has a very good homogeneity, at submicron scale. The dependence of H_{PP} on the PANI content obeys, up to 20% PANI, a simple superposition principle ($H_{PP} = C_0 + C_1x$; where C_0 and C_1 are constants).

The resonance line intensity is proportional to the number of electrons that experience a spin flip, due to the resonant absorption of energy. It is dependent on the number of electronic spins. As noticed from Fig. 5B the resonance line intensity is increased as PANI content is increased, supporting the dependence of H_{PP} on PANI content. From Fig. 5B is observed that at low concentration the prediction of the superposition principle are accurately obeyed. ($I = I_0 + I_1x$; where I_0 and I_1 are constants).

The concentration of free radicals, C , at a given temperature is proportional to the double integral of the resonance line, DI

$$C = K_M DI \quad (11)$$

where K_M is a constant at a given constant temperature. As it is inferred from Fig. 5C, the increase in the fraction of PANI dispersed into PE increases the value of DI. The relationship between DI and PANI content is almost linear up to about

40%, where saturation is reached. This relationship suggests that the dominant quasi-particle present in these composites is the polaron. The conclusion is also confirmed by the results depicted in Fig. 3A, which indicates that the increase in polyaniline leads to a monotonous increase of the conductivity.

In a tentative to search if the ESR data are also described by the empirical Boltzmann equation, the dependence of $\ln(100 - DI(\%))$ on PANI content has been studied. As is noticed in Fig. 7A, the ESR data are well described by a sigmoid like dependence although the inflection point is located at larger amount of filler (Table 1). The deep connection between DC conductivity and ESR data is shown in Fig. 7B. However, the correlation is not direct as the DC conductivity depends on the number of charge carriers (electrons in the case of polyaniline) while DI depends on the difference between the populations of the two Zeeman sublevels [27].

The physical properties of PEPANI composites decay after a storage period of 1 week, in air, at room temperature. Both the conductivity and the free radicals concentration are decreased with about 10%, indicating that a fraction of free electrons has been exhausted. Longer storage times, in air, at room temperature, do not further affect significantly the physical properties of the composite. The result reflects the thermo-mechanical generation of free radicals during mastication and the role of the conducting electrons in the protection of the polymeric chains; some of these free radicals recombine with free electrons, resulting in a decrease of free electrons concentration and of the conductivity. Due to the high concentration of PANI, it was not possible to record these free radicals by using ESR. The ageing of electrical conductivity in composites based

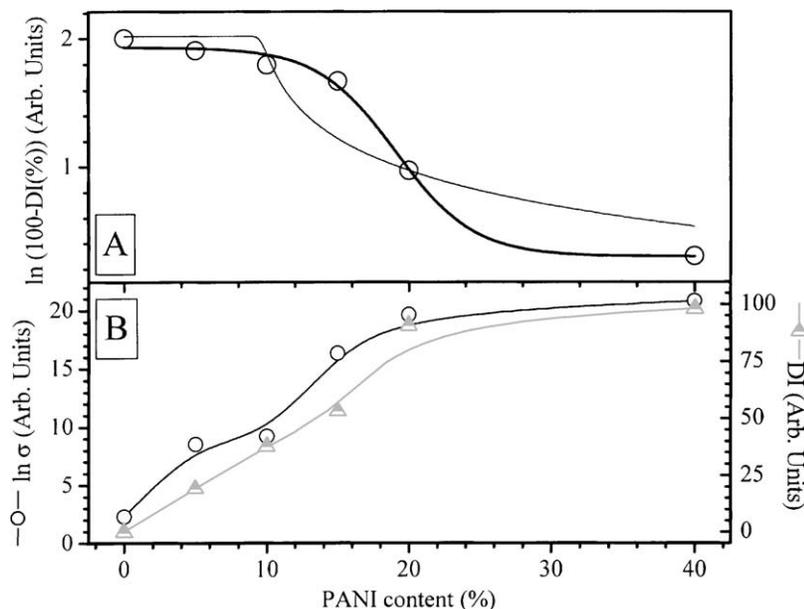


Fig. 7. (A) The dependence of $\ln(100 - DI(\%))$, where DI has been estimated in percents (the 100% value has been replaced by 99% to avoid negative values). (B) The dependence of the logarithm of the DC conductivity (in arbitrary units) and of DI on polyaniline content.

on conducting polymers has been studied by many authors [23,24].

5. Conclusions

The dependence of the tensile strength on the PANI concentration is governed by the poor adhesion between the PANI particles and the polymeric matrix. The elongation at break is controlled by the percolative generation of a unidimensional phase with poor mechanical features, consisting of interconnected PANI particles. It is proved that the dependence of the elongation at break and of tensile strength on the PANI content obeys a percolation like dependence. It is suggested that Boltzmann sigmoid may provide an empirical universal law for the dependence of physical properties, near the percolation threshold. It is observed the coincidence between x_0^σ , x_0^e , and x_0^R , which supports the idea of an universal behavior of electric and mechanic properties in conducting composites, close to the percolation threshold. This result is self-consistent as the percolation threshold for ESR data is occurring at a double concentration of black carbon that in the case of mechanical and electrical properties. The ESR data are controlled by the superposition principle rather than by a percolative process. The studies on PEPANI composites revealed that the conduction is due to electrons and that the polarons hopping is responsible for the charge transport. The resonance line shape indicates the mesoscopic structure of conducting regions. The absence of the resonance line located at $g = 4.00$ suggests that in such composites the contribution of high spin bipolarons is negligible. The increase of DI, in conjecture with the decrease of resonance line width and of the DC resistance indicates that low spin bipolarons, if present, have a small contribution to the charge transport. The percolation of the DC conductivity is broad, and at 40% polyaniline, the composite has a higher resistance than polyaniline. This result reflects the usual difficulties related with the mixing of the components by mechanical methods. The weak decay of the resonance line intensity and DC conductivity during a storage period of about week reflects the protecting (antioxidant) character of polyaniline and the price paid for the enhanced stability of the composite. The process is amplified by the fact that during the mechanical mixing of components a high concentration of free radicals is produced. To conclude, the process may be used to obtain composites with modest conducting feature which requires a proper control of the DC resistance. The healing/antioxidant character PANI particles is proved.

Acknowledgements

This work has been possible due to the support of the University of New Orleans Graduate Enhancement Fund

and of the Hong Kong Polytechnic University Grant (G-T 684).

References

- [1] Planes J, Wolter A, Cheguettine Y, Pron A, Genoud F, Nectschein M. Transport properties of polyaniline cellulose acetate blends. *Phys Rev B* 1998;58(12):7774–85.
- [2] Ragunathan A, Kahol PK, Ho JC, Chen YY, Dao YD, Lin YS. Low temperature heat capacities of polyaniline and polyaniline poly-methylmethacrylate blends. *Phys Rev B* 1998;58(18):15955–8.
- [3] Sanjai B, Ragunathan A, Natarajan TS, Rangarajan G. Charge transport and magnetic properties in polyaniline doped with methane sulphonic acid and polyaniline polyurethane blend. *Phys Rev B* 1997; 55(16):10734–44.
- [4] Kahol PK. Magnetic susceptibility and electron spin resonance investigations of polyaniline and polyaniline poly(methylmethacrylate) blend. *Solid State Commun* 2001;117:37–9.
- [5] Srinivasan D, Natarajan TS, Rangarajan G, Bhat SV, Wessling B. Electron spin resonance absorption in organic metal polyaniline and its blend with PMMA. *Solid State Commun* 1999;110:503–8.
- [6] Han MG, Bun SV, Im SS. Thermal stability study of conducting polyaniline/polyimide blend films on their conductivity and ESR measurements. *Polym Adv Technol* 2002;13:320–8.
- [7] Notingher P, Panaitescu D, Chipara M, Toacsen M, Chipara MD. The physical properties of PVC/black carbon blends. International Conference on Dielectrics and Insulators, Budapest, September, 1997.
- [8] Chipara M, Goovaerts E, Chipara MD, Munteanu I. ESR investigations on polyaniline–polyvinylchloride blend. *Mater Res Soc Symp Proc* 2001;665:C8.8.1–C8.8.6.
- [9] Sixou B, Travers JP, Barthelet C, Guglielmi M. Electronic conduction in polyaniline–polyethylene oxide and polyaniline–Nafion blends: relation to morphology and protonation level. *Phys Rev B* 1997;56(8): 4604–4613.
- [10] Mott NF, Davies EA. *Electronic processes in non-crystalline materials*. Oxford: Clarendon Press; 1979.
- [11] Choi J, Chipara M, Xu B, Yang CS, Doudin B, Dowben PA. Comparison of the π conjugated ring orientation in polyaniline and polypyrrole. *Phys Chem Lett* 2001;343:193–200.
- [12] Wang ZH, Scherr EM, MacDiarmid AG, Epstein AJ. Transport and EPR studies on polyaniline; A quasi one-dimensional conductor with three-dimensional metallic states. *Phys Rev B* 1992;45(1): 4190–202.
- [13] Pinto NJ, Kahol PK, McCormick BJ, Dalal NS, Wan H. Charge transport and electron localization in polyaniline derivatives. *Phys Rev B* 1994;49(9):13983–6.
- [14] Farchioni R, Vignolo P, Grosso G. Transport properties of emeraldine salts: the nature of the metallic state. *Phys Rev B* 1999;60(23): 15705–13.
- [15] Pelster R, Nimtz G, Wessling B. Fully protonated polyaniline: hopping transport on a mesoscopic scale. *Phys Rev B* 1994;49(18): 12718–23.
- [16] Pratt PL, Blundell SJ, Hayes W, Nagamine K, Ishida K, Monkman AP. Anisotropic polaron motion in polyaniline studied by muon spin relaxation. *Phys Rev Lett* 1997;79(15):2855–9.
- [17] Salafsky JS. Exciton dissociation, charge transport, and recombination in ultra-thin conjugated polymer TiO₂ nanocrystal intermixed composites. *Phys Rev B* 1999;59(16):10885–94.
- [18] Chakrabarti S, Das B, Banerji P, Banerjee D, Bhattacharaya R. Bipolarons saturation in polypyrrole. *Phys Rev B* 1999;60(11): 7691–4.
- [19] Kohlman RS, Zibold A, Tanner DB, Ihas GG, Ishiguro T, Min YG, MacDiarmid AG, Epstein AJ. Limits for metallic conductivity in conducting polymers. *Phys Rev Lett* 1997;78(20):3915–8.

- [20] Joo J, Long SM, Pouget JP, Oh EJ, MacDiarmid AG, Epstein AJ. Charge transport of the mesoscopic metallic state in partially crystalline polyanilines. *Phys Rev B* 1998;57(16): 9567–80.
- [21] Galatanu A, Chipara MI, Chipara MD, Toacsen M. Structural properties of conducting and semiconducting polymers. *Physica B* 1997;234–236:242–4.
- [22] Stauffer D, Aharony A. Introduction of percolation theory. London: Taylor & Francis; 1992.
- [23] Sixou B, Mermilliod N, Travers JP. Aging effects on the transport properties in conducting polypyrrole. *Phys Rev B* 1996;53(8): 4509–21.
- [24] Wolter A, Rannopu P, Travers JP, Gilles B, Djurando D. Model for aging in HCl-protonated polyaniline: structure, conductivity, and composition studies. *Phys Rev B* 1998;58(12):7637–47.
- [25] Ranby B, Rabek JF. ESR spectroscopy in polymer research. Berlin: Springer; 1977.
- [26] Abragam A, Bleaney B. Electron paramagnetic resonance of transition ions. Oxford: Clarendon Press; 1970.
- [27] Poole CP, Farach HA. Theory of magnetic resonance, 2nd ed. New York: Wiley; 1987.
- [28] Yang J, Zhang I, Zhang I. Tensile deformation and fracture mechanism of highly field high density polyethylene/Al(OH)₃ composites. *J Appl Polym Sci* 2002;85:1207–18.
- [29] Chodak I, Omastova M, Pionteck J. Relation between electrical and mechanical properties of conducting polymer composites. *J Appl Polym Sci* 2001;82:1903–5.
- [30] Yi XS, Wu G, Ma D. Property balancing for polyethylene-based carbon black-filled conductive composites. *J Appl Polym Sci* 1998;67: 131–8.