PHYSICS AND CHEMISTRY
OF SOLID STATE
V.21, No.2 (2020) pp. 319-324

DOI: 10.15330/pcss.21.2.319-324

Vasyl Stefanyk Precarpathian
National University

ФІЗИКА І ХІМІЯ ТВЕРДОГО ТІЛА
Т. 21, № 2 (2020) С. 319-324

UDC 541.64 ISSN 1729-4428

G.V. Martynyuk[1], O.I. Aksimentyeva[2]

Features of Charge Transport in Polymer Composites Polymethylmethacrylate - Polyaniline

[1]*Rivne State Humanitarian University, Rivne, Ukraine, galmart@ulr.net*
[2]*Ivan Franko National University of Lviv, Lviv, Ukraine, aksimen@ukr.net*

The influence of polymer matrix of polymethyl methacrylate (PMMA) on the specific conductivity, percolation threshold, energy of activation of charge transport in polymer composites PMMA − polyaniline (PAN) is studied. Concentration dependence of the electrical conductivity of composites reveals percolation behavior with the low value of percolation threshold within 2 % content of polyaniline. It is found that in the polymer composites PMMA-PAN the specific conductivity increases by more than 8−9 orders of magnitude compared to the original matrix. On the base of temperature dependence of the specific conductivity of the obtained composites, it is concluded that PMMA polymer matrix does not change the semiconductor nature of PAN conductivity in the composite but effects on the activation parameters of the charge transport. From ESR spectra, it is found that the presence of a polymeric matrix causes significant delocalization of the charge along the macrochains of the dielectric polymeric matrix.

Key words: polymer composites, electrical conductivity, specific conductivity, polymer nanosystems, activation energy of charge transport, value of percolation.

Received 20 March 2020; Accepted 15 June 2020.

Introduction

Composite materials based on dielectric polymer matrices and conductive polymers are promising components of a new generation of electro-optical devices: organic LEDs, flexible displays, display boards, environmental monitoring sensors [1-3]. Along with the matrices of polyvinyl alcohol, polyvinyl chloride, polycarbonate, and others [4-6] used to produce such composite materials, a promising polymeric matrix is polymethyl methacrylate (PMMA) [7]. The choice of PMMA as a dielectric polymeric matrix is due to the high optical transparency of the films based on it, which enables optical and electro-optical applications, namely obtaining films with electrochromic properties (”smart windows”), elements of optical sensors, various boards, and flexible displays and conductive composites for anti-static screens [7-10].

An interesting electrochromic material that has the ability to change the color (and therefore the spectrum) under the action of applied voltage is polyaniline (PAN) [10, 11], as well as its derivatives [12-14] with their own electronic conductivity. Such polymers act in composites with PMMA or other matrices as conductive fillers. A necessary condition for the functioning of such composites is their ability to transfer charge (or electrical conductivity). The term “conductivity mechanism” refers to the mechanism of charge transfer from one particle of the filler to another [15]. Therefore, study the features of charge transport in conductive polymers are of the greatest interest for the production of functional polymer-polymer composites.

In many literary sources, fine crystalline PAN is regarded as a mesoscopic metal (“nano-metal”) [8, 11]: a metal core surrounded by a non-metallic (or semiconductor) shell. The diameter of such particles is 8 - 10 nm. According to X-ray diffraction data of PAN samples [14, 16], the sizes of crystalline PAN clusters are 2 - 3 nm, depending on the type and level of proton acid doping. The nanosize of particles of conducting polymers in composites obtained using the latest nanotechnologies (template or matrix synthesis, formation of polymer blends in a common solvent, in situ polymerization, etc.)

are preserved [17, 18].

The study of the influence of the polymeric matrix on the regularities of charge transport in nanosystems with conductive polymers presents an interesting scientific task and due to the possibility of practical application of such nanocomposites.

The aim of the work was to study the influence of the polymer matrix on the charge transport features in PMMA – PAN polymer nanocomposites obtained on the basis of polymer "blends" in a common organic solvent.

I. Experimental technique

PMMA with a molecular weight of $6x10^5$ and a destruction temperature T_d = 473 K was used to form the composites. As electrically conductive filler used PAN, doped with sulfuric acid. The synthesis of PAN was carried out by the oxidative polymerization of 0.2 M solution of aniline sulfate in 0.5 M solution of sulfate acid with an equimolar amount of a solution of ammonium peroxodisulfate $(NH_4)_2S_2O_8$ (oxidizer) at room temperature [19]. The polymerization process lasted 24 hours. As a result, a conjugated polymer was formed in the form of a fine crystalline dispersed precipitate of black color with a dark blue tint. The resulting product was filtered, washed with distilled water until complete removal of electrolyte residues, were neutralized with 5 % ammonia solution and dried under dynamic vacuum to constant weight at T = 353 K for 8 hours. The result was an undoped form of polyaniline - the emeraldine base. The doping was carried out with the exposure of a certain amount of emeraldine base in 0.5 M sulfuric acid solution for 24 hours. The resulting solution was filtered, dried under dynamic vacuum. Ultrasonic dispersion of sulfuric acid-doped PAN and PMMA solutions mixed in the desired proportion in a mixture of DMF-chloroform (1:1) was carried out for two hours. The composites were obtained after evaporation of the organic solvent in vacuo at temperatures of 343 - 363 K for several days [9]. The specific density of composite was 1.04 ± 0.01 g/cm^3.

The conductivity of PMMA – PAN composites was measured by the two-contact method at room temperature. Samples in the form of cylinders of size (d = 1.8 mm, h = 2 mm) were made by the method of thermal pressing at a pressure of 150 atm at T = 353 K. The temperature dependence of the resistivity of the obtained composites was studied in the temperature range T = 298 - 397 K as described in [12]. ESR spectra were obtained using an X-band ESR spectrometer at the Institute of Physics of the Polish Academy of Sciences (Warsaw) on powder samples in quartz ampoules in the temperature range of 4.2 - 300 K.

II. Results and Discussion

The electrical conductivity of polymer composites with conductive filler depends essentially on its content. In traditional composites with metal or carbon fillers, appreciable conductivity values are achieved with a filler content of 50 – 70 % [20, 21], and the conductivity mechanism is determined by the properties of the electrically conductive component only. The smallest concentration of filler at which a sharp jump in electrical conductivity is called the percolation threshold [22].

It is established that in the polymer composites PMMA − PAN specific conductivity may increase by more than 9 orders of magnitude compared to the original PMMA matrix with extremely low content of conductive polymer [23 - 25]. The concentration dependence of the electrical conductivity of the formed composite on the content of the filler (PAN) has a percolation character with a low "percolation threshold" within 2 vol. % content of PAN (Fig. 1). The appearance of this dependence is similar to the percolation behavior of polyvinyl chloride - polyaniline composite doped with camphorosulfonic acid [26] with a "percolation threshold" of 0.8 - 1.0 vol. %.

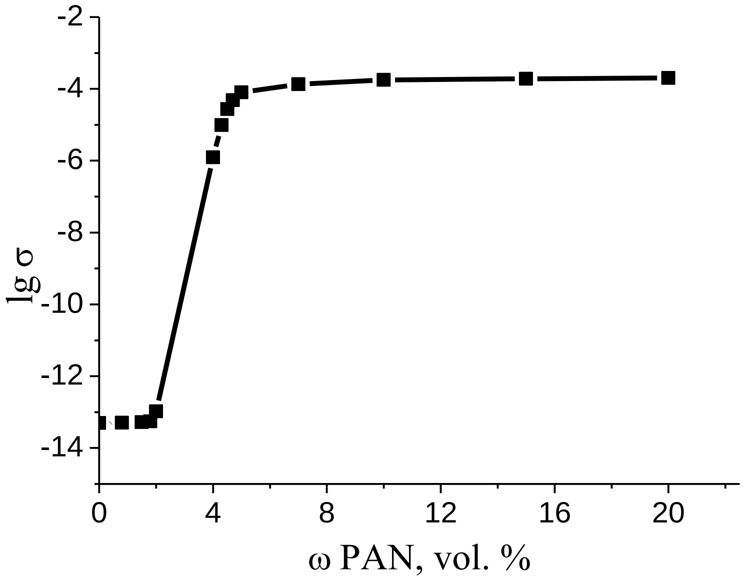
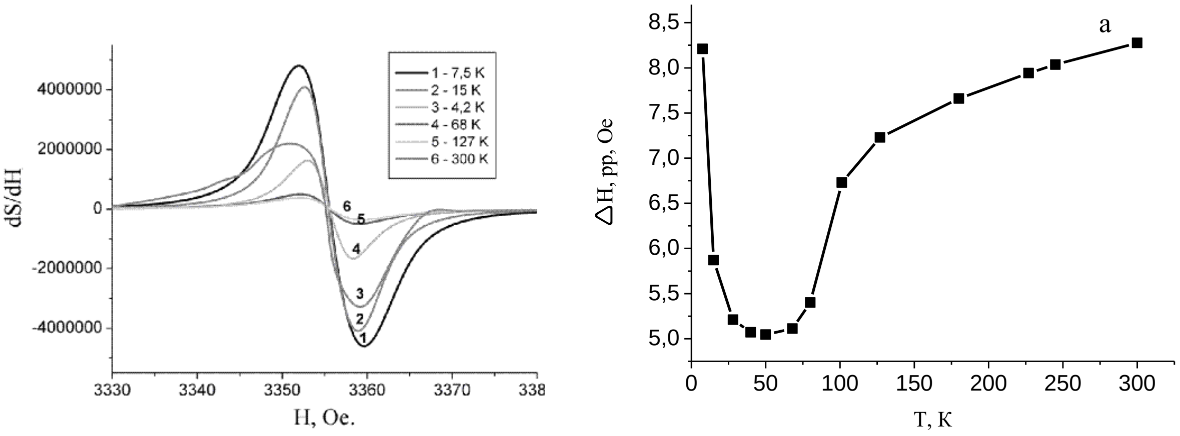


Fig. 1. The dependence of the logarithm of the specific conductivity of PMMA – PAN composites on the content of the polymeric filler.

Table 1

The dependence of the specific conductivity on the content of the polymeric filler for PMMA-PAN composites

ω, vol. % of PAN	0	1	2	4	10	20	100
σ_{298}, $S\cdot m^{-1}$	10^{-14}	$7.03\cdot10^{-6}$	$8.12\cdot10^{-5}$	$5.28\cdot10^{-5}$	$2.76\cdot10^{-5}$	$2.16\cdot10^{-6}$	$3.60\cdot10^{-6}$



a b

Fig. 2. (a) ESR spectra for PMMA −10 % PAN at different temperatures; (b) Dependence of signal width ΔHpp (distance between peaks) on temperature for composite PMMA – 10 % PAN.

If the content of PAN becomes higher than 2 vol. %, the conductivity value of the PMMA – PAN composite exceeds the conductivity of the PMMA polymeric matrix by 8 - 9 orders of magnitude, after which it remains almost constant. It is interesting that the conductivity of the PMMA – PAN composite with a filler content of 2 - 15 % slightly exceeds the conductivity of pure PAN (Table 1).

We assume that high values of the specific conductivity (σ) at exceeding the percolation threshold for PMMA – PAN composites are caused by the formation of their own conductive network inside the host polymer and thus forming a continuous electrically conductive phase, which is uniformly distributed over the entire volume of the polymer composite, that is, a continuous conductivity cluster is formed [22, 23].

As shown by B. Wessing and co-authors [8], the conductivity in thermally compressed PAN composites doped with d,l-camphorosulfonic acid with PMMA containing 40 % PAN may be higher than that of pure PAN. A probable cause of this phenomenon may be the additional doping of the polyaniline by PMMA functional groups near the melting point. On the other hand, the dielectric polymeric matrix can affect the degree of coupling of the conductive polymer structure by orienting the macrochains in one direction to form one-dimensional 1D structures [9]. The presence of structures of this type ensures the preservation of the physico-mechanical properties of high-polymer matrices without disrupting the semiconductor nature of the conductivity of the conjugated polymer, and sometimes even enhances charge transport, affecting its electronic structure, which leads to changes in the concentration of polaron charge carriers. Perhaps in this case, a structural matrix effect is manifested [24-26], which consists in the ability of the polymer matrix to influence the length and chemical structure of polyaminoarene chains, including their spatial structure.

Using ESR spectroscopy in the range *T* = 4.2 - 300 K it was established that PMMA−PAN composites give a clear EPR signal at room temperature with a g-factor value of 2.0025 ± 0.0002 (Fig. 2, a).

According to the analysis of the temperature dependence of the ESR, it can be assumed that in the synthesized nanocomposites there is a significant delocalization of charge carriers along the PMMA dielectric polymeric matrix, which causes increased values of the specific conductivity (Table 1). This is also evidenced by the change in the shape of the ESR signal, namely its significant extension − the distance between the peaks ΔHpp increases to 5.05 - 8.29 Oe for the PMMA – PAN composite (Fig. 2.b), as compared to the unfilled PAN (3.1 - 3.4 Oe) [9, 27, 28].

This increase in the ΔHpp value for the PMMA – PAN composite compared to the PAN confirms the delocalization of the electron density of the conductive filler in the PMMA matrix. In addition, the temperature dependence of ΔHpp for the PMMA – PAN composite is characterized by the presence of a minimum in the temperature range of 30 - 60 K, which may indicate the reorganization of the electronic structure and the manifestation of the effects of magnetic interactions [28, 29]. Close correlation between ESR parameters (line width, peak height ratio) suggests that both mobile and fixed spins exist in the electronic structure of the obtained composites. That is, at temperatures of 4.2 - 300 K, the electron density is uniformly distributed in the composite matrix, which causes an increase in the conductivity of PMMA – PAN composites compared to pure PAN.

Thus, the formation of PMMA – PAN composites exhibits specific effects that are related to the peculiarities of polymer nanostructures formation. Such effects are not observed in mechanical mixtures, but are inherent mainly in nanosystems. The results of Raman spectroscopy confirmed that PMMA macromolecules in the process of formation of PMMA – PAN composites enter into weak intermolecular interaction with PAN molecules due to coordination or donor-acceptor bonds [9, 23].

For acid-doped PAN, the temperature dependence of electrical conductivity is caused by two contributions: (a) purely metallic conductivity, which is limited by the quantum dimensions of the metal core and (b) the process of thermo-activated tunneling between the primary particles [14, 27, 29]. An important factor in influencing the dependence of electrical conductivity on temperature is the nature of the polymer, the type and concentration of the filler.

For all composites under study, as for most organic semiconductors, the resistivity of the samples in the initial region decreases by exponential law with increasing temperature. The linear nature of the dependence lg (ρ/ρ_{293}) $-1/T$ for this plot indicates the thermoactivation nature of the conductivity and allows one to calculate the value of the charge transport activation energy (ε_σ) in this temperature range depending on the PAN content (Fig. 3).

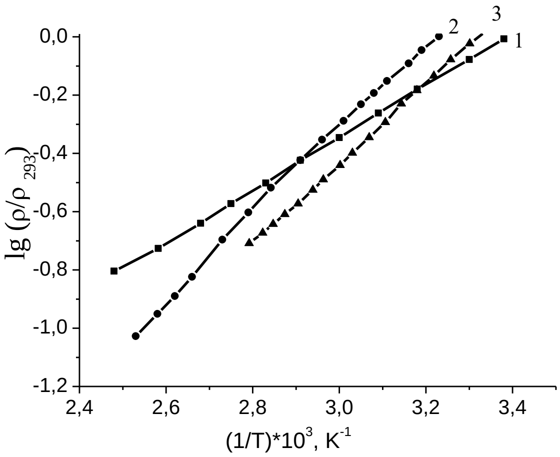


Fig. 3. Temperature dependence of normalized resistance of PMMA – PAN composites. PAN content: 1 – 100 %; 2 – 2 %; 3 – 10 %.

As can be seen from Fig. 3, the semiconductor character of the electrical conductivity is not disturbed in the composites, but the influence of the polymer matrix on the activation parameters of charge transfer is traced. It is found that the effective activation energy of the composite conductivity (ε_σ) depends on the content of PAN and is in the range of (0.26 - 2.16) ± 0.04 eV depending on the content of the conductive filler (Fig. 4). As the PAN content increases, the value of the conductivity activation energy decreases significantly. The obtained results confirm the presence in the PMMA-PAN composites of a continuous self-conducting polymeric grid, which possibly provides higher values of the specific conductivity compared to the fine crystal filler. This suggests that as the content of PAN in the composite increases the number of percolation bridges, which creates additional channels for charge transfer, increase too. This causes a decrease in the activation energy of the conductivity and increase the length of free path of charge carriers [23].

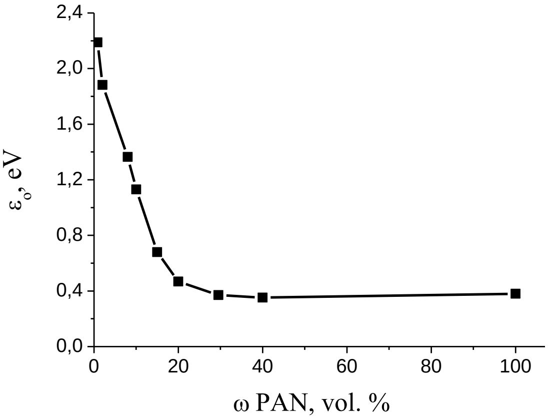


Fig. 4. Dependence of the activation energy of charge transport for PMMA – PAN composites on the content of electrically conductive filler (PAN).

Analyzing the results obtained, we can assume that the investigated composites behave as typical organic semiconductors after reaching the percolation threshold.

Conclusions

Therefore, based on the results of experimental studies, it is established that there is a strong interaction between the PMMA polymer matrix and the PAN filler, which is manifested in the low percolation threshold values for these composites, which is explained by the formation of a spatial conductive network. On the other hand, the dielectric polymeric matrix can affect the structure of the conjugated polymer, and therefore the number of unpaired spins corresponding to the charge carrier concentration. Confirmation of this assumption is the results of ESR spectroscopy according to which, when forming PMMA – PAN composite, the electronic structure of the material undergoes significant changes, which may indicate the formation of a composite with a molecular degree of dispersion, in other words, a nanocomposite [18, 23].

Martynyuk G.V. - Ph.D., associate professor; Department of Ecology, Geography and Tourism.

Aksimentyeva O.I. - Doctor of Chemical Science, Professor; Chief Researcher, Professor of the Department of Physical and Colloidal Chemistry.

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Г.В. Мартинюк[1], О.І. Аксіментьєва[2]

Особливості транспорту заряду в полімерних композитах поліметилметакрилат - поліанілін

[1]Рівненський державний гуманітарний університет, Рівне, Україна, galmart@ukr.net
[2]Львівский національний університет імені Івана Франка, Львів, Україна, aksimen@ukr.net

Вивчено вплив полімерної матриці поліметилметакрилату (ПММА) на питому електропровідність, поріг перколяції, енергію активації транспорту заряду в полімерних композитах ПММА - поліанілін (ПАН). Встановлено, що в композитах ПММА–ПАН за наявності електропровідного полімеру питома провідність зростає більше ніж на 8 - 9 порядків порівняно з вихідною матрицею ПММА, при цьому концентраційна залежність електропровідності виявляє перколяційну поведінку із низьким значенням порогу перколяції в межах 2 % вмісту ПАН. На основі температурної залежності питомого опору встановлено, що полімерна матриця ПММА не змінює напівпровідникового характеру провідності ПАН в композиті. але чинить вплив на активаційні параметри перенесення заряду. З даних ЕПР спектроскопії встановлено, що наявність полімерної матриці зумовлює значну делокалізацію заряду вздовж макроланцюгів діелектричної полімерної матриці.

Ключові слова: полімерні композити, питома провідність, енергія активації провідності, поріг перколяції.