5th International Workshop on Functional and Nanostructured Materials

31 August – 6 September, 2008, Ľviv, Ukraine



ABSTRACT BOOK

TITLE

5th International Workshop on Functional and Nanostructured Materials: Abstract Book

EDITOR

Jarosław Rybicki

TYPESETTING using T_{EX} BOP s.c., www.bop.com.pl

PRINTING

DP "Skhid Sontsya" TzOV "Splayn" 15 Dudaev Blvd., L'viv, Ukraine

TASK PUBLISHING 2008 GDANSK, POLAND ISBN 978-83-908112-5-3

5th International Workshop on Functional and Nanostructured Materials 31 August – 6 September, 2008, L'VIV, Ukraine

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Interaction of Components and Anomalous High Conductivity in Polyaniline-Polymethylmethacrylate Nanocomposites

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Conducting polymers such as polyaniline (PANI) have received great attention due to their simple synthesis, good environmental stability and electrical conductivity. However, major problems relating to successful utilization of PANI such as poor mechanical properties and solubility remain an unsolved problem [1]. To improve the mechanical properties and processability of PANI, blending with other polymers such as polymethylmethacrylate (PMMA) is employed. PANI may be considered as a mesoscopic metal (a "nanometal") with the primary particle diameters in the range between 10 and 20 nm [2]. A nanosize of polymer particles is preserved in the polymer composites obtained by nanotechnology methods (polymer blending in cosolvent, template and matrix synthesis, etc.). The mechanism of electron transport in such nanosystems is a topic of great interest. One of the reasons for the anomalous behavior of conductivity in polymer blends may be the interaction of components. To disclose this problem the structure and electrical properties of the nanocomposites obtained by disperse PANI blending in a PMMA dielectric matrix [3] have been studied.

It is found that electrical conductivity of polymer composites can be controlled in a wide range (more than 12 orders of magnitude) by a small amount of PANI. The conductivity dependence on the PANI concentration can be explained by a percolation model with an extremely low "percolation threshold" in the range of 0.8–2.6 vol. % of PANI. The temperature dependence of the specific conductivity for PMMA-PANI composites is characteristics for organic semiconductors. The effective activation energy for charge transport depends on the PANI content in the composite. An anomalously high specific conductivity in PMMA-PANI composites is observed at the PANI concentration exceeding the percolation threshold, in the interval of 5–10 vol. %. Its value exceeds the value of specific conductivity for acid doped PANI. To explain this phenomenon, the methods of IR Raman spectroscopy, electron spin resonance (ESR) and UV-vis. absorption spectroscopy have been employed. Raman spectra (Figure 1) show that significant changes occur in the bands corresponding to the nitrogen atom in the PANI macrochain $(2500-3500 \text{ cm}^{-1})$ and ester oxygen attributed to PMMA (1270–1200 cm⁻¹ and 2180 cm⁻¹) as the PANI content of composites increases.

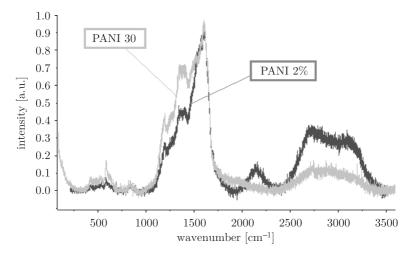


Figure 1: Raman spectra of PMMA-PANI composites

An ESR study of the spin dynamic in PANI-PMMA composites has been carried out in the temperature interval of 4.2–300 K. For polymer composites the line width, Δ Hpp, broadens from 3.5 Oe (PANI) to 8.3 Oe (PMMA-10%PANI), which is evidence of delocalization of the charge carriers in PANI affected by the PMMA dielectric polymer matrix [4]. The existence of a weak intermolecular interaction in the PMMA and PANI solutions at different ratios of polymers has been confirmed by the electron spectroscopy. The obtained results give a possibility to suggest that the anomalous high conductivity of the PMMA-PANI composites may be caused by "secondary doping" of PANI with a PMMA macrochain. Such additional doping leads to higher electrical conductivity in a composite as compared with unblended PANI.

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