

INTERACTION OF COMPONENTS AND CONDUCTIVITY IN POLYANILINE – POLYMETHYLMETHACRYLATE NANOCOMPOSITES

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Received: December 20, 2009

Abstract. Polymer nanocomposites of poly(methyl methacrylate) (PMMA) with the conducting polymer – polyaniline (PANI) were prepared by blending polymer solutions in a mixed organic solvent. It is found that electrical conductivity of PMMA-PANI composites depends on the PANI volume content with an extremely low “percolation threshold” near the 1.0% of the PANI. In the concentration interval of 2-10 vol.% of PANI a specific conductivity exceeding one for acid doped PANI is observed in PMMA-PANI composites. Introducing a conducting polymer into a dielectric PMMA matrix slightly decreases the glass transition temperature, causing the flow temperature to rise significantly. It has been suggested that the increasing conductivity in PMMA-PANI composites is caused by an interaction of PANI nitrogen atoms with the functional groups of PMMA leading to additional doping of PANI.

1. INTRODUCTION

Polymer nanocomposites based on a conducting and insulating polymer matrix are a promising new generation of functional materials to be used in electrooptical and sensor devices – flexible displays, panels, organic light emitting diodes, sensitive films for environment monitoring [1,2]. In this aspect, active investigations are carried out for composites based on conducting polymers (polypyrrole, polythiophene, poly(phenylene vinylene), polyaniline) embedded in a dielectric matrix of polyvinyl alcohol, polyvinyl chloride, polycarbonate and others polymers [3-6].

Such conducting polymers as polyaniline (PANI) have received a great attention due to their simple synthesis, good environmental stability and electrical conductivity. The PANI may be considered as a

mesoscopic metal (a “nanometal”) with primary particle diameters in the range between 10 and 20 nm [4]. However, major problems relating to successful utilization of the PANI are poor mechanical property and low solubility in aqueous and organic solvents. Blending with such thermoplastic polymers as the polymethylmethacrylate (PMMA) is employed to improve the mechanical property and processability of the PANI [4,6]. The PMMA is chosen as dielectric matrix due to its high transparent ability in visible spectral range which is important for optoelectronics, sensors and “smart window” applications [7].

It is known that the nanosize of polymer particles is preserved in the polymer composites obtained by nanotechnology methods (template and matrix synthesis, polymer blending in a co-solvent,

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Table 1. Effect of the PANI content on the specific conductivity of PMMA-PANI nanocomposites.

PANI content, vol. %	0	1	2	4	10	20	100
σ_{293} , $\text{Ohm}^{-1}\cdot\text{m}^{-1}$	10^{-14}	$7.03\cdot 10^{-6}$	$8.12\cdot 10^{-5}$	$5.28\cdot 10^{-5}$	$2.76\cdot 10^{-5}$	$2.16\cdot 10^{-6}$	$3.6\cdot 10^{-7}$

Table 2. Microhardness and thermomechanic characteristics of PMMA-PANI nanocomposites.

PANI content, wt. %	Glass transition temperature, T_g , K	Flow temperature, T_f , K	Microhardness, $F_{\infty}\cdot 10^{-8}$, N/m^2
0	383	412	2.05 ± 0.10
1	381	414	1.87 ± 0.10
2	379	420	1.88 ± 0.10
4	382	425	1.81 ± 0.10
10	384	428	1.83 ± 0.10

self-assembling, "in situ" polymerization, etc) [3,8]. The mechanism of electron transport in such nanosystems is a topic of great interest [4-6].

We have studied the electrical, thermomechanical properties and molecular structure of polymer nanocomposites obtained by PANI and PMMA blending in their dilute solution in a mixed co-solvent.

2. EXPERIMENTAL

The dispersion of PANI doped by sulphuric acid was prepared by oxidative polymerization of aniline (Aldrich) with ammonium persulphate ("CP" grade) in a 0.5 M sulphuric acid solution according to [9]. The specific density of PANI doped with sulphuric acid was 1.224 g/cm^3 , the specific volume conductivity measured at room temperature $\sigma_{293} = 3.6\cdot 10^{-7} \text{ Ohm}^{-1}\cdot\text{m}^{-1}$. The dielectric PMMA matrix with a molecular mass of 600000 mol/g characterised by glass transition temperature $T_g = 383\text{K}$, temperature of destruction $T_D = 473\text{K}$. The PANI-PMMA composites were prepared by blending a PANI and PMMA solution in a mixed toluene – dimethyl sulphoxide - chloroform solvent under ultrasonic treatment for 24 hours. The solvent was evaporated in dynamic vacuum conditions at $T = 323\text{K}$ over 3 days.

The samples for conductivity investigations were prepared by pressing the PANI-PMMA composites in cylinder bulk samples ($d = 1.8 \text{ mm}$, $h = 2 \text{ mm}$) at the power of 150 atmospheres at $T = 353\text{K}$. The electrical conductivity of the PMMA-PANI composites was measured by the two-probe method at room

temperature in the air. The thermomechanical curves were obtained in the conditions of uniaxial compression of the cylinder samples ($d = 8 \text{ mm}$, $h = 8-11 \text{ mm}$) under simultaneous heating with the rate of 2 grad/min [10]. The microhardness of composites was measured by a Hepler consistometer as a limited point of fluidity (F_{∞} ; N/m^2) at the characteristic power [10]. The Raman spectra of composites were obtained on a T64000 spectrometer, (Ar laser 514.5 nm) at room temperature.

3. RESULTS AND DISCUSSION

It is believed that PANI-PMMA composites are a colloidal dispersion of polyaniline [6,8] inside a PMMA host matrix. It is found that the electrical conductivity in such polymer composites can be controlled in a wide range (more than 8-10 orders of magnitude) by a small amount of PANI (Table 1). The nature of the conductivity dependence on the PANI content is very similar to the percolation shape for blend polyvinyl chloride/polyaniline doped with camphorsulfonic acid [6] with an extremely low "percolation threshold" in the range of 0.8 – 1.0 vol.% of PANI. When the PANI content becomes higher than 2 vol.%, the σ values of PMMA-PANI composites decrease only slightly, while between 10 and 20 vol.% of PANI σ decreases by almost one order of magnitude (see Table 1). Such behavior of the conductivity may be explained by the decreasing mechanical strength of the composites, confirmed by their decreasing microhardness (Table 2).

We have suggested that an extremely low threshold of percolation for the PMMA-PANI com-

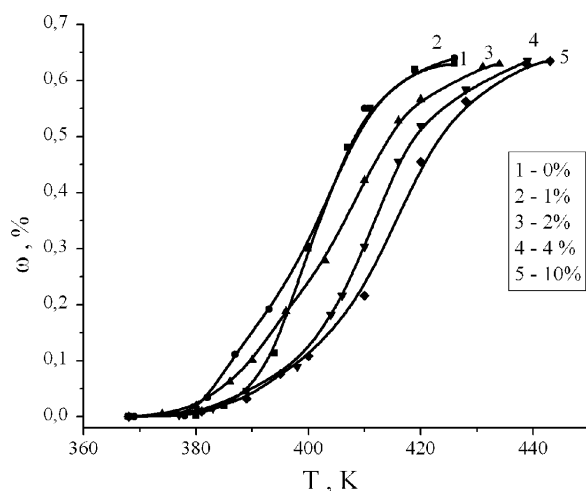


Fig. 1. Temperature dependence of relative deformation for PMMA-PANI composites at different PANI content.

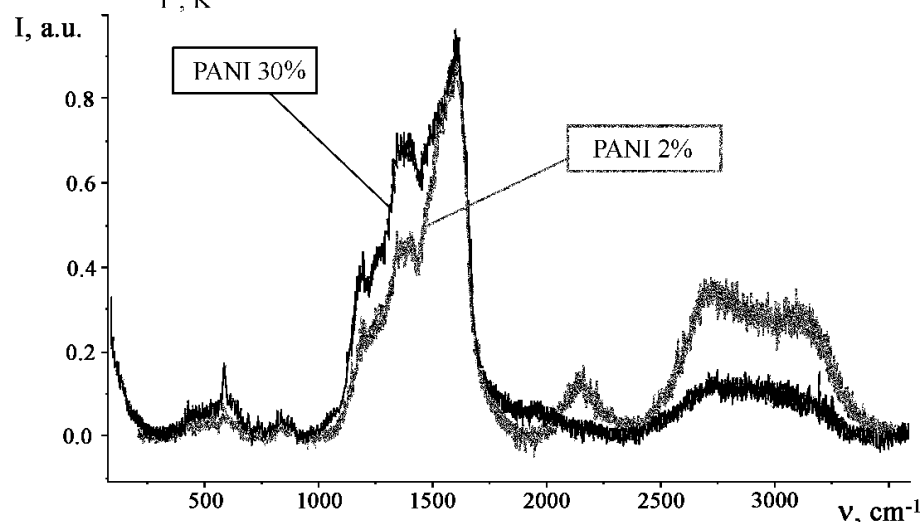


Fig. 2. Raman spectra of PMMA-PANI nanocomposites.

posites is due to the formation of a conducting network in the dielectric matrix inside the host polymer [9]. On the other hand, a dielectric polymer matrix may affect the conjugated polymer's electron structure and change the population of unpaired spins corresponding to the concentration of polaron carriers [5]. When the PANI concentration is higher than 2 vol.% the value of specific conductivity in PMMA-PANI composites exceeds one for acid doped PANI without a PMMA matrix (Table 1).

As shown by B. Wessing and collaborators [4] the conductivity in thermo-pressed composites of PANI doped by *d,l*-camphor sulfonic acid (CSA) with PMMA containing 40% PANI(CSA), may be higher in comparison with unblended PANI(CSA). As suggested, a probable reason for such a phenomenon may be additional doping of PANI by functional groups of PMMA near the melting temperature.

The effect of conducting polymer nanoparticles on the properties of a dielectric polymer matrix,

especially on its thermomechanical characteristics has not been studied extensively. It is the effect of inorganic fillers (nanogly, nanotubes, colloidal silica) on the glass transition temperature (T_g) of polymer nanocomposites that has been most often described in the recent literature [8]. Taking into account the low "percolation threshold" in the obtained PMMA-PANI composites their mechanical and thermomechanical properties have been studied at the PANI content of 1-10 vol.%.

A glass transition of a polymer will be affected by its environment when the chain is within several nanometers of another phase [8]. As can be seen in Fig. 1, an overall shape of the thermomechanical curves for PMMA and composites at different PANI content is similar.

The effect of PANI nanoparticles on the PMMA matrix consists in a decrease of the glass transition temperature (T_g) from 1 to 4K at a low PANI content (Table 2) and an increase at higher content.

Both the increases and decreases in T_g have been caused by an interaction between the matrix and the particles [8,11]. As a result of such interaction some decrease in the microhardness of composites (F_∞ changes from $2.05 \cdot 10^8$ to $1.83 \cdot 10^8$ N/m²) is observed (Table 2). Such changes are in good correlation with the concentration dependence of the glass transition temperature for PMMA-PANI composites (Table 2).

The flow temperature for PMMA-PANI composites arises significantly with the increasing PANI content compared to the free PMMA matrix (Fig. 1, Table 2). The PANI in the studied composites acts probably as an "active" filler interacting with PMMA macrochains at ambient temperature which leads to a higher flow temperature of composites in comparison with unblended PMMA.

The Raman spectra of composites obtained at a different PANI content are presented in Fig. 2. It has been shown that significant changes are observed in the bands corresponding to the nitrogen atom in the PANI macrochain ($2500\text{-}3500$ cm⁻¹) and ester oxygen attributed to PMMA ($1270\text{-}1200$ cm⁻¹ and 2180 cm⁻¹) as the PANI content in composites increases. Hence, these data confirm that the interaction between functional groups of conducting and insulating polymers proceeds in PMMA-PANI composites. Such interaction may be the reason for additional doping of PANI.

It is known that polyaniline achieves a high conductivity mainly in case of strong proton acids used as doping agents [11]. In this polymer positive polarons (cation-radicals) are considered as probable charge carriers. The unpaired spins are localized on the nitrogen atoms and the positive charge is delocalized along a conjugated pi- electron system of a polymer backbone [12]. It has been found in the ESR investigation [5,9] that a PMMA matrix has a significant influence on the linewidth (ΔH_{pp}) of the ESR signal: it broadens from 3.5 Oe (PANI) to 8.3 Oe (PMMA-10%PANI). This confirms stronger delocalization of the charge carriers in PANI affected by the PMMA dielectric polymer matrix of which may be one of the probable reasons for increasing the composites' conductivity.

On the other hand, the increase in the conductivity in PMMA-PANI composites may be caused by "secondary doping" of primary acid doped PANI [12]. Such doping leads to a change in the macrochain conformation of PANI from a "compact coil" to an "extended coil" as it proceeds under the influence some solvents (m-cresol, *N,N*-methyl pyrrolidone) in PANI (CSA) [12]. It is believed that "secondary" doping conductivity in PMMA—PANI

blends causing the PANI coil conformation straightening would have such an effect.

4. CONCLUSION

The obtained results make it possible to suggest that an interaction of components proceeds in the process of formation of composites and becomes significant at ambient temperature in polymer composites based on a PMMA dielectric matrix and a PANI conducting polymer. A strong interaction of PANI nanoparticles with PMMA macrochains results in increasing the composite flow temperature from 412 to 428K. This effect is probably connected with some additional doping of the PANI imine nitrogen by the PMMA ester functional group. Such doping leads to higher electrical conductivity in the composite as compared with unblended PANI. According to the results of thermomechanical measurements the obtained composites are conductive and suitable for thermoplastic processing that may be used for producing antistatic screens, elements for electronics, etc.

REFERENCES

- [1] D. Mecerreyes, R. Marcilla and E. Ochoteco // *Electrochim. Acta.* **49** (2004) 3555.
- [2] M. Matsuguchi, A. Okamoto and Y. Sakai // *Sensors and Actuators B* **94** (2003) 46.
- [3] T. Liu, B. Christian and B. Chu // *Prog. Polym. Sci.* **28** (2003) 5.
- [4] D. Srinivasan, T.S. Natarajan, G. Rangarajan, S.V. Bhat and B. Wessing // *Solid State Comm.* **110** (1999) 503.
- [5] O. I. Aksimentyeva, O. I. Konopelnyk, V. V. Yurkiv, G. V. Martyniuk and V. A. Shapovalov // *Molec. Cryst. & Liq. Cryst.* **468** (2007) 309.
- [6] H. Namazi, R. Kabiri and A. Entezami // *Eur. Polym. J.* **38** (2002) 771.
- [7] F. Carpi and D. De. Rossi // *Optics & Laser Technology.* **38** (2006) 292.
- [8] D.R. Paul and L.M. Robeson // *Polymer.* **49** (2008) 3187.
- [9] O. I. Aksimentyeva, B. R. Tsizh, O. I. Konopelnyk, A.M. Ukrainets, V. A. Shapovalov, *Nanosystems and Nanotechnology* **5** (2007) 269.
- [10] A.M. Ukrainets, O.I. Aksimentyeva, O.I. Konopelnyk, G.V. Martyniuk and O.M. Yevchuk // *Voprosi Khimii i Khim. Technol.* **3** (2004) 132.
- [11] A. MacDiarmid // *Curr. Appl Phys.* **1** (2001) 269.
- [12] A.G. MacDiarmid and A.J. Epshtein // *Synth. Metals* **69** (1995) 85.