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THERMAL STUDIES OF SILVER-POLY(METHYLMETHACRYLATE) NANOCOMPOSITES

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Abstract

The novel nanocomposite material based on surface-modified silver nanoparticles (Np) with average diameter of 6 nm and poly(methylmethacrylate) (PMMA) matrix was synthesized. The effect of silver loading on the thermal properties of PMMA was studied. The obtained transparent nanocomposites Ag/PMMA films were characterized by IR spectroscopy and thermal techniques (TGA, DSC). The chemical composition of the PMMA matrix is not changed in the presence of the metal nanoparticles, but the thermal stability of the nanocomposites was found to be better than thermal stability of the pure polymer. Also, Ag nanoparticles have pronounced effect on a glass transition temperature (T_g) of PMMA.

Introduction

Polymer composites containing metal Np have being investigated for a broad variety of applications such as microelectronics, optical filters, magnetic or optical data storage, etc. [1,2] Because of their high surface to bulk ratio, nanoparticles significantly affect the matrix leading to some new properties which are not present in either of the pure materials. These nanocomposite systems require particles with uniform size, controlled dimension and regular shape. A disturbing factor in such filled polymer system is non-uniformity of composite properties owing to poor dispersion of the nanoparticles. Surface modification of the filler with suitable coupling agent is often recommended to enhance filler dispersion, as well as aid in processing. Thermal properties of the nanocomposites are affected by the filler content, the chemical composition of the filler surface and different synthetic routes. As no evidence of the influences of silver Np on thermal properties of Ag/PMMA nanocomposite and glass transition temperature of PMMA were found in the literature, we were focused in the present paper to explain these effects.

Experimental

Silver hydrosols were prepared using $NaBH_4$ as a reducing agent, as described elsewhere [3]. Silver nanoparticles were transferred into chloroform using oleylamine as transfer agent. In order to prepare Ag/PMMA nanocomposites, silver nanoparticles (0.5-2 wt %) dispersed in chloroform were mixed in an appropriate ratio with PMMA (Diakon™ CMG 314V), dissolved in chloroform. After evaporation of the solvent in vacuum oven at room temperature, yellow coloured transparent films with thickness of about 25 μm were obtained.

IR measurements of pure PMMA and Ag/PMMA nanocomposites were carried out on a Bruker Vector 22 Spectrometer (Opus 2.2 Software). Thermogravimetric analyses (TGA) were carried out on a Perkin Elmer TGS-2 instrument either in air or under nitrogen atmosphere (flow rate 25 cm^3/min) with heating rate of 10 ^{0}C/min. Differential scanning calorimetry (DSC) measurements were performed using Perkin Elmer DSC-2 instrument in the temperature range from 50 to 170 ^{0}C under nitrogen atmosphere (heating rate was 20 ^{0}C/min).

Results and Discussion

According to the IR measurements, no difference between the IR spectra of the pure PMMA and Ag/PMMA nanocomposites were found, indicating that Ag/PMMA nanocomposites resemble solid solution with weak interaction between the polymer matrix and nanofiller particles. The thermal stability of the synthesized samples was examined by non isothermal thermogravimetry both in nitrogen and air atmosphere, Fig. 1. The obtained results showed, that the presence of the silver Np increased the thermal stability of polymer probably because of inhibiting effects of the Ag Np on some degradation stages of the thermal and thermo-oxidative degradation of PMMA. For example, the thermal degradation of the filled polymer with 2 wt% of the Ag Np is shifted towards higher temperature for about 26°C in the nitrogen and about 27°C in the air atmosphere.

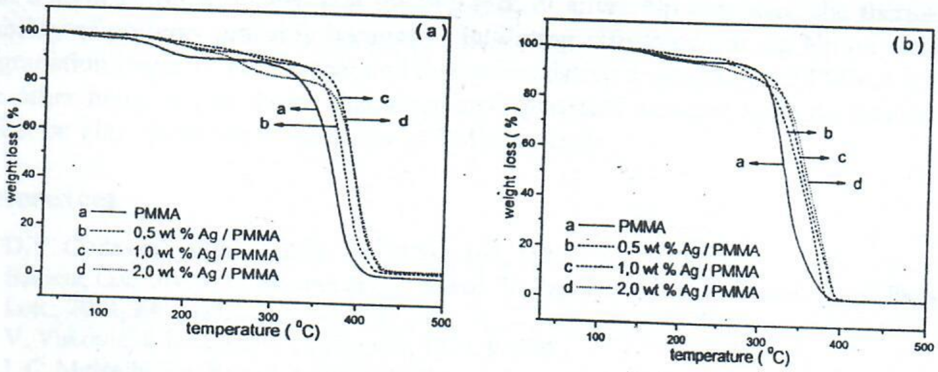

Fig. 1 TG curves of pure PMMA and Ag/PMMA nanocomposites with different content of the Ag Np obtained in nitrogen (a) and air (b).

It is generally considered that PMMA thermally degrade through depolymerisation [4]. The improvement of the thermal stability in PMMA nanocomposites may be associated with reactivity of metal with polymeric radicals and the different thermal stability of the resulting complexes or coordinates [5]. In the presents of oxygen, PMMA decomposition was explained by the dual function of oxygen. At lower temperatures, oxygen inhibits PMMA decomposition by reacting with a polymeric radical and forming a more stabile peroxy radical which degrades at higher temperature and releases a more reactive radical, resulting in the acceleration of

PMMA decomposition [6]. The inhibiting effects of the Ag Np on thermo-oxidative degradation of PMMA could be explained by the reaction of Ag Np with oxygen, which led to the slower degradation of the PMMA matrix [7].

Table 1. Glass transition temperature (T_g) of Ag/PMMA nanocomposites

content of Ag Np (wt %) in Ag/PMMA nanocomposites	0	0.5	1.0	2.0
T_g, (^{0}C)	97	96	92	91

The influence of silver nanoparticles on the glass transition behavior of polymer matrix was studied with DSC technique and the results are listed in Table 1. It can be seen the tendency of slight decrease of T_g values by increasing silver content for Ag/PMMA nanocomposites. Ash et al. [8] explained the decrease of T_g values in terms of thin film model. When the inter-particles distance is small enough, then the polymer between two particles can be considered as a thin film. Assuming that little or no interfacial interaction between the filler and matrix exists, the T_g decreases as the film thickness, i.e. inter-particles distance decreases.

Conclusions

The obtained results showed that the presence of silver Np increased the thermal stability of polymer probably because of inhibiting effects of the Ag Np on some degradation stages of the thermal and thermo-oxidative degradation of PMMA. On the other hand, it was shown that small inter-particles distance have pronounced effect on glass transition temperature of PMMA matrix.

References

[1] D.Y. Godovski, Advan. Polym. Sci., 2000, **165**, 153.
[2] Biswas, O.C. Aktas, U. Schurmann, U. Saeed, V. Zaporjtchenko, F. Faupel, Appl. Phys. Lett., 2004, **84,** 2655.
[3] V. Vuković, J. Nedeljković, Langmuir, 1993, **9**, 980.
[4] I. C. McNeill, Eur. Polym. J., 1968, **4**, 21.
[5] H. Wang, P. Xu, W. Zhong, L. Shen, Q. Du, Polym. Degrad. Stabil., 2005, **87**, 319.
[6] D. J. Peterson, S.Vyazovkin, A. C. Wight, J. Phys. Chem. B, 1999, **103**, 8087.
[7] Z. Kai, F. Qiang, F. Jinghui, Z. Dehui, Matter. Lett., 2005, **59**, 3682.
[8] B.J. Ash, L.S. Schadler, R.W. Siegel, Mater. Lett., 2002, **55**, 83.