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Investigation of optical and morphological properties of metalized nanocomposites

Sandra Varnaitė-Žuravliova [a,c,*], Virginija Jankauskaitė [a], Asta Guobienė [b], Igoris Prosyčevas [a,b]

[a] Research Centre for Plastic and Leather Products, Faculty of Mechanical Engineering and Design, Kaunas University of Technology, Studentu str. 56, LT-51424 Kaunas, Lithuania
[b] Institute of Materials Science, Kaunas University of Technology, Savanoriu ave. 271, LT-31343 Kaunas, Lithuania
[c] Textile Institute of Center for Physical Sciences and Technology, Demokratų str. 53, LT-48485 Kaunas, Lithuania

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ABSTRACT

Nanoparticles play an important role in scientific and technological fields, because they significantly affect the polymer matrix and lead to new properties. A combination of PMMA (poly-methylmethacrylate) with metal nanoparticles can offer very wide application field in medicine, because metals may act on a broad range of microbial targets, and many mutations may occur for microorganisms to resist their antimicrobial activity. Usually metal and other nanoparticles are coated onto surfaces of substrates. Unfortunately, the durability of such nanocomposites normally is very poor, because coatings are quite sensitive to different damages. Therefore the main target of this research was to apply nanoparticles on the surface of PMMA substrate and to affect them with microwave heating that nanoparticles intervene into the polymer matrix and form permanent damage resistance metal nanolayer. It was determined that the application of the metal nanolayer on the PMMA and the partial insertion of nanoparticles into the polymer were successful. Although Cu nanoparticles mostly formed deep elements than Ag nanoparticles in the nanocomposites, they both molded grains on the surface of nanocomposites. The incorporation of metal nanoparticles into the PMMA allowed expanding the application field of nanocomposites with more durable metal nanolayers.

1. Introduction

In recent years metal nanoparticles have been intensively studied since they play an important role in many scientific and technological fields. Nanomaterials include spherical, cubic, and needle-like nanoscaled particles of approximately 5–100 nm size, and near-nanoscaled devices (up to micrometers) [1,2]. Nanoparticles significantly affect the polymer matrix due to their surface ratios, leading to new properties which are not present in either of the pure materials [1–4]. In particular non-linear optics response of nanoparticles is a significant one in comparison with its bulk form [5]. With respect to metallic nanoparticles, the biocidal effectiveness has been suggested due to their size and high surface to volume ratio. Such characteristics allow to closely interact with microbial membranes, rather than the effect being due to solely release of metal ions [3,6]. Metal and other nanoparticles are now being combined with polymers or coated onto surfaces which may have a variety of potential antimicrobial applications [7,8]. Thin polymer based nanocomposite coatings obtained by vacuum methods demonstrate unique properties enabling possibilities to solve different technical problems. Their properties depend on different structural factors such as concentration, size distribution of embedded metal or polymeric nanoparticles and molecular structure of polymeric matrix [9–12]. Generation of active gas phase by electron beam evaporation or dispersion of bulk polymers is perspective technology. This method is effective, especially for deposition of coatings with complex structure and composition. Electron beam impact on polymer surface and evaporation of low-molecular fragments lead to the forming of numerous active particles in gas flow [10,11]. The incorporation of metal nanoparticles with the polymer matrix modifies the refractive index of the structure due to the unique size dependent properties of metal particles at the nanoscale. The bulk conducting materials are opaque to a large range of electromagnetic spectrum due to damping of the impinging wave by conduction electrons inside the materials. Because of their small size absorption response is generally concentrated in

* Corresponding author. Tel.: +370 60498506.
E-mail addresses: varnaite@lti.lt, varnaites@gmail.com (S. Varnaitė-Žuravliova).

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a narrow peak at the surface plasmon frequency. This resonance depends not only on the type of metal particles but also on the shape, size and optical property of the surrounding medium [13]. Generally, noble metals are widely used for synthesis of plasmonic nanoparticles, because of their ability to support plasmon resonances at visible wavelengths [14].

With respect to nanoparticles, the antimicrobial properties of silver and copper receive the most attention. Both of these have been coated onto or incorporated into various materials, including PMMA [1]. Polymers are considered as good host materials for metal and semiconductor nanoparticles, which exhibit exceptional optical and electrical properties [15]. Among various polymers, PMMA is highly transparent plastic with good mechanical strength, high light transmittance, chemical resistance, good insulating properties and is used in various applications. Accordingly, PMMA is a candidate substrate for optical and medical applications [16–18] as bone cement, dialyser, scaffolds for tissue engineering and potential candidate to waveguide production [19]. Microwave is an energy source which has found its applications in many scientific research areas. Microwave radiation has shown its capability for fast preparation of size controlled metallic nanostructures on different substrates [20,21]. A nanoparticle dispersed in polymer is called polymer nanocomposite and it is considered as a single homogeneous material. These materials exhibit unique thermal, mechanical and biological properties when compared to conventional composites [22,23]. An inverse relationship between nanoparticle size and antimicrobial activity has been demonstrated, where nanoparticles in the size range of 1–10 nm have been shown to have the greatest biocidal activity against bacteria [6,24]. Also, it appears that bacteria are far less likely to acquire resistance against metal nanoparticles than other conventional and narrow-target antibiotics. This is thought to occur because metals may act on a broad range of microbial targets, and many mutations would have to occur for microorganisms to resist their antimicrobial activity, as shown with *Escherichia coli* [25]. Truncated triangular silver nanoplates with a (1 1 1) lattice plane as the basal plane showed the greatest biocidal activity compared with spherical and rod-shaped nanoparticles. The differences appear to be explained by the proportion of active different shapes facets presented in nanoparticles. Also, silver nanoparticles exhibit strong absorption of electromagnetic waves in the visible range due to surface plasmon resonance, which is caused by collective oscillations of the conduction electrons of nanoparticles upon irradiation with visible light [26–28].

The interest in copper nanoparticles arises from such useful properties of this metal as the good thermal, electrical conductivity and good antimicrobial properties at a cost much lesser than that of silver [29]. It has been reported that Cu nanoparticles have better bactericidal effects in comparison to Ag nanoparticles in single strains of *E. coli* and *Bacillus subtilis* [30].

The aim of the research was to metalize the surface of PMMA with Ag and Cu nanoparticles using electron beam evaporation method and partially insert them into the generated nanocomposites; to analyze optical and morphological properties of such nanocomposites and theoretically predict the size of nanoparticles used.

2. Experimental

Substrates of PMMA (poly-methylmethacrylate, "Plexiglas", 100 μm thickness) were metalized with silver (Ag) or copper (Cu) nanoparticles (purity 99.99%, Sigma Aldrich, UK) to a film thickness of 5 and 10 nm using electron beam evaporation ($T_{substrate}$ = 20 °C, residual gas pressure 10^{-4} Pa, deposition rate v = 1–2 nm/s). The film thickness during deposition was monitored with a quartz balance technique. The temperature of the substrates during deposition was controlled to a precision of ± 0.5 °C.

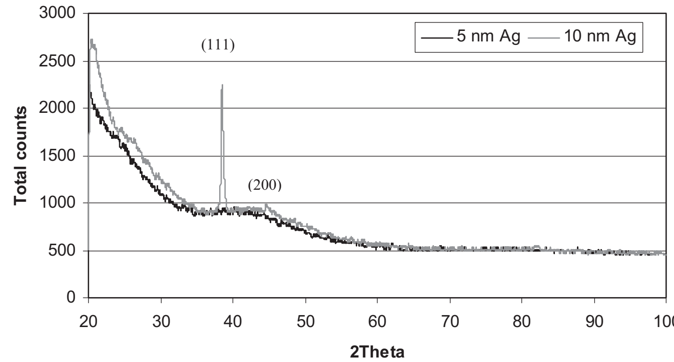

Fig. 1. XRD pattern of PMMA nanocomposites with Ag films of different thickness.

The nature and the size of crystal particles in generated composites were defined with X-ray difractometer DRON-3.0 using Ni-filtered CuK_α radiation, operating at 30 kV and 30 mA in a step scan mode with a step size of 0.02° for 2Theta and registration time of 20 s per step. The average crystal size was calculated form X-ray spectrum according to Scherrer equation [29]:

$$D = \frac{0.9\lambda}{FWHM \times \cos\theta} \quad (1)$$

where λ – wave length of X-ray, nm; *FWHM* – full width at half maximum, rad; θ – the diffraction angle, rad.

The interplanar spacing between the atoms was calculated using Bragg's Law [31]:

$$2d\sin\theta = n\lambda \quad (2)$$

from here

$$d = \frac{\lambda}{2\sin\theta}, \quad \text{when}\,(n = 1) \quad (3)$$

The UV–vis light spectrophotometer Avantes 2048 was used for determination of metal nanoparticles formation by measuring the absorbance spectrum. This spectrophotometer was composed of deuterium halogen light source (AvaLight DHc) and spectrometer (Avaspec-2048) with a detection system of 2048 pixel charge coupled device (CCD). The spectrometer was used in the region from 300 to 800 nm with the resolution of 1.4 nm.

The theoretical calculation of metal nanoparticles size using experimental data received by the UV–vis light spectrophotometer was done with MiePlot software [32]. Whereas metal particles were dispersed in PMMA matrix, the refractive indexes for surrounding media (PMMA) were taken from [33]. The complex refractive indexes of bulk silver were used for nanoparticles in calculations

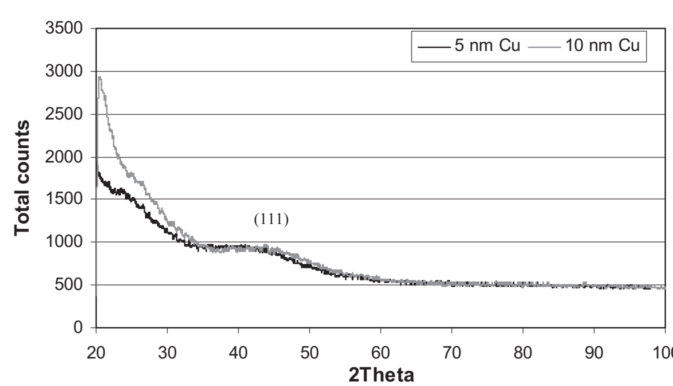

Fig. 2. XRD pattern of PMMA nanocomposites with Cu films of different thickness.