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Optical properties of silver-doped organic polymer films as solar control coating materials for advanced architectural glazing application

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Dedicated to Acad. Dimiter Ivanov on the occasion of his 120th birth anniversary

Metal-polymer nanocomposites possess a great potential for minimization of heat transfer losses and heat gains through the building envelope, finding application in the field of solar control coating materials. In the present paper we report the optical properties of a metal-polymer from Ag and polymethyl methacrylate (PMMA) nanocomposite fabricated by layer-by layer deposition technique. The X-ray diffraction pattern confirms the presence of silver particles in the thin films. The average size of silver particles was calculated by Debye-Scherrer formula. An absorbance band in the spectral range 350-550 nm due to the surface plasmon resonance of the silver nanoparticles was observed in transmittance spectra. The position of the absorbance band has been analyzed by the Bruggeman's model for the effective media. On the base of the obtained results the polymer-inorganic hybrid coatings were suggested for application as sun protective coatings.

Key words: nanocomposite films, silver, polymethyl methacrylate, Bruggeman's model

INTRODUCTION

Glazing elements are significant portion of the building envelope, although traditionally more attention is paid to the solid part of walls and roofs and they are one of the weakest thermal control points in building interiors. For example in a standard family residence, 10-20 % of all heat loss occurs through the windows [1]. Therefore in the glazing design, it is necessary to consider performance in terms of heat transfer, thermal comfort, light transmission, and appearance. To achieve good thermal insulation effect, the solar-protected glasses must be manufactured with a special coating that provides high transmittance of the visible light and reflected the IR beams. All coating must reflected the infrared beams in the spectral range 5-12 μm. In this region of the electromagnetic spectra the electrical appliances, heaters and the human body, i.e. internal heat sources for the building emit their thermal energy. Window glazing that reduces the entry of the infrared solar radiation (spectral range 0.8-2 μm) is most effective in summer and reduces the cooling demand. In contrast, in winter, this type of glazing increases the need for heating because it hinders the use of solar energy for passive heating. The development of glazing that reduces the quantity of solar radiation should not affect the possibility of seeing through windows, especially when a large amount of natural light is required, such as in office buildings. A reduction in natural daylight causes a corresponding increase in artificial light. This signifies higher energy costs as well as an increase in indoor temperature.

In [2] it is shown that the coatings which consist of alternating dielectric and metal (D/M/D) films on glass exhibit great energy saving effects by reflecting the IR radiation by the infrared reflective metal film and transmitting visible and near IR radiation. Film-plating glazing is treated with layers of another material to improve its thermal performance. The most common coatings are done with metals (Cr, Ti, Ag and stainless steel), metal nitrides (CrN, TiN, ZrN), or metal oxides (SnO_2, TiO_2, ZnO). The coating layers can be low-emissivity films, reflective films, tinted films or spectrally selective coating [1]. Many different polymers also can be incorporated in prototype solar energy control devices, e.g. poly- and monomeric pyrrole,viologens,4,40-diaminodiphenyl sulfone, poly(3-me-tylthiophene) or diclofenac, polyaniline (PANI) and poly(3,4-ethylene-dioxy-thiophene) (PEDOT) [3]. According to [2], the ideal

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film thickness is between 40 and 80 nm. Metal-polymer nanocomposites have an advantage over the oxide/noble metal multilayers in terms of ease of synthesis. There have been several co-evaporation and co-sputtering approaches to synthesize the nanocomposite structure [4]. They possess good adhesion to the organic polymer materials such as urethane-acrylate and poly-carbonate (PC) which are well known as a glazing material [2,5]. The special advantage of PC panels is that they can transmit to 90% from the visible light and they have good resistance to external conditions.

When nanoparticles embedded in a dielectric matrix are excited by light, the electric vector of the electromagnetic wave induces a charge density oscillation [6] corresponding to the plasmon frequency (ν_p) of metal particles, resulting in strong absorption of light at a particular wavelength ($\lambda_p = c/\nu_p$, where c is the velocity of light). Apart from the optical, applications as bandpass filters [7], there is a tremendous interest in achieving an optical absorber extending from the visible to the far-IR region [8] for a variety of applications. The broad absorption band in visible spectral range and increase of conductivity of metal-polymer films make them potential materials for applications in the field of solar absorbers.

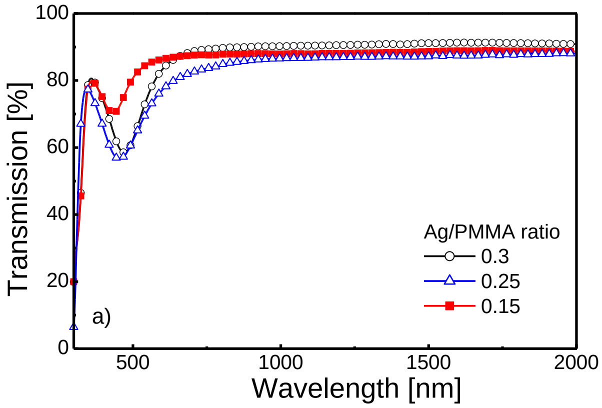
In the present work, we report the synthesis and optical properties of a metal–polymer (Ag-polymethyl methacrylate, hereafter referred to as Ag-PMMA) nanocomposite by layer-by layer deposition technique. The possibility of deposition of coatings for control of the spectrum of the transmitted true the window sunlight is discussed.

EXPERIMENTAL

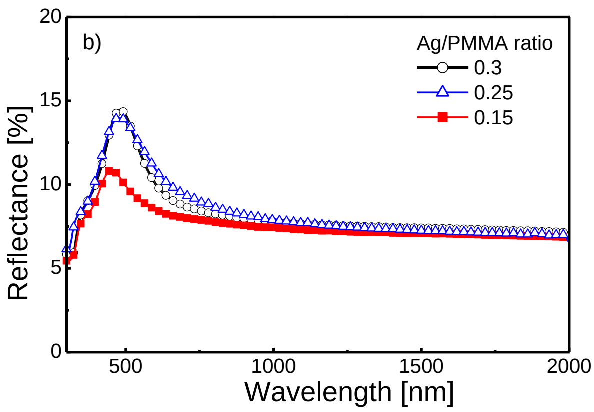
The coatings were formed in one cycle of thermal evaporation in high vacuum of 10^{-3} Pa from two sources - of silver and PMMA, respectively. The ratio between the evaporation rates of the two substances was controlled during the process. The films were deposited at 0.2 - 0.3 nm/s. To obtain thin films uniform in composition, the substrates were rotated continuously during the process of thermal evaporation. The substrate holder is a dome-shaped calotte that can be considered as a segment of a sphere. The evaporation sources are located approximately at the geometric centre of this sphere. The coatings consist of 6 alternating layers from silver and PMMA with three different thickness's ratio Ag/PMMM - 0.3, 0.13 and 0.25. The thickness of the silver layers was kept a constant ~ 5 nm. The phase structure of thin films was probed by X - ray diffraction (XRD). The substrate holder is a dome-shaped calotte that can be considered as a segment of a sphere. The evaporation sources are located approximately at the geometric centre of this sphere. Optical transmittance and reflectance measurements at normal incidence of light beam were carried out in the spectral range from 300 to 2000 nm using an UV–VIS–NIR spectrophotometer (Cary 05E, Australia).

RESULTS AND DISCUSSION

The transmittance and reflectance spectra of Ag-PMMA coatings in the spectral range 300-2000 nm are shown in Fig. 1.



(a)



(b)

Fig. 1. Transmittance (a) and reflectance (b) spectra of thin Ag-PMMA coatings with different Ag contain.

The transmittance spectra showed that the Ag-PMMA coatings possess transmission higher than 80% in the infrared spectral range. All spectra demonstrate an absorption band situated in the 400-550 nm due to silver surface plasmon resonance. The plasmon peak in the spectra of the thin films indicates that the silver is included in the coatings in the form of small particles. According to [9] the increase of the particle's size leads to shift of the absorption band due to plasmon excitation at longer wavelengths and can explain the shift of the absorption band at higher Ag/PMMA ratios. The width and magnitude of the absorption band depend on the metal fraction in the nanocomposite, and therefore can be engineered. The spectra of the composite coatings show that the color appearance can be tailored, which presents a potential for applications in architectural windows and automotive glazing.

The X-ray diffraction pattern of the nanocomposite Ag-PMMA film at ratio 0.15 is shown in Fig. 2. Peaks due to the diffraction from the crystallographic planes (111) and (200) of silver are seen in the pattern. Two diffraction peaks at 32.8° and 35.6° indicate for the presence of Ag_2O in Ag-PMMA. The possible reason for the presence of Ag_2O in the thin films is the interaction of the silver with the oxygen atoms in the monomer building the polymer network of the PMMA.

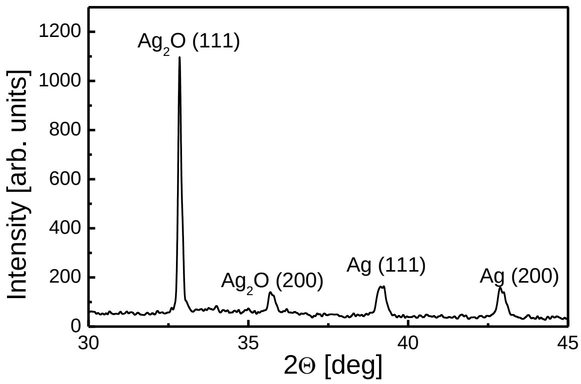


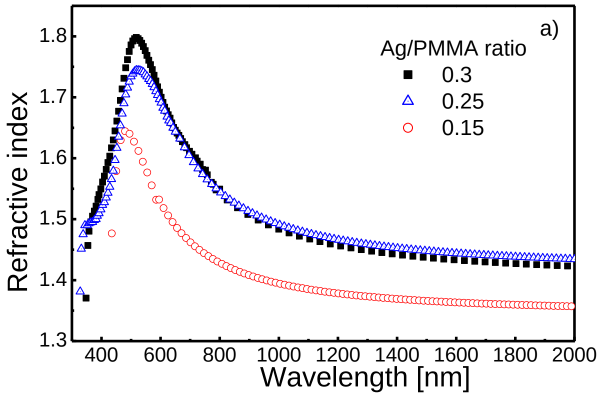
Fig. 2. X-ray diffraction pattern of thin Ag-PMMA film.

The Debye-Scherrer formula was applied for calculation of the average crystallite size:

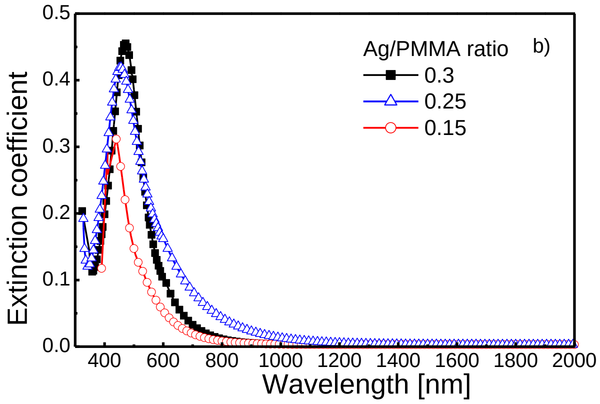
$$d_p = \frac{0.94\lambda}{\beta.\cos\Theta} \qquad (1)$$

where β is the peak width, λ is wavelength of the X-rays (in the present study Cu_α line was used and λ = 1.54056Å). Applying equation (1) for the diffraction peaks of the silver we found that the size of the crystallites is 25.9 nm.

In the next step we calculated the optical constants (refractive index, *n* and extinction coefficient, *k*) of the thin films. The calculation procedure is described in our previous papers [10,11]. It is seen that the refractive index of the thin films in the infrared spectral range (800-2000 nm) is 1.45-1.35. Abnormal dispersion is observed for wavelengths shorter than 550 nm.



(a)



(b)

Fig. 3. Dispersion of the refractive indices (a) and extinction coefficients (b) of Ag-PMMA films.

The real and imaginary parts of the complex permittivity, $\varepsilon = \varepsilon' + i\varepsilon''$ can be calculated from the refractive index and extinction coefficient by the following equations:

$$\varepsilon' = n^2 - k^2 \quad \text{and} \quad \varepsilon'' = 2nk \qquad (2)$$

We applied the Burgemman effective media theory to analyze the dispersion of the composite coatings. According to [12] the effective complex permittivity, ε is given by the equation 3, where ε_m and ε_d are the complex permittivity of the metal and dielectric material respectively, while f_1 and f_2 are their fractions, which satisfy the following condition - $\sum f_i = 1$.

The relation between the fractions f_1 and f_2 of the thin films in the multilayered coatings and their thickness is given in [13]. The period of the structure is $a = d_1 + d_2$, where d_1 and d_2 are the thicknesses of the metal and polymer thin films, respectively. The volume filling fractions f_1 and f_2 for the metal and polymer films are given by the following equations: $f_1 = d_1/a$ and $f_2 = d_2/a$.

$$\varepsilon = 1/4\{(3f_1 - 1)\varepsilon_m + (3f_2 - 1)\varepsilon_d \pm \sqrt{[(3f_1 - 1)\varepsilon_m + (3f_2 - 1)\varepsilon_d]^2 + 8\varepsilon_m\varepsilon_d}\} \qquad (3)$$

$$\varepsilon_m(\omega) = \varepsilon'(\omega) + i\varepsilon''(\omega) = \varepsilon_\infty - \frac{\omega_p^2}{\omega^2 + i\Gamma\omega} = \varepsilon_\infty - \frac{\omega_p^2}{\omega^2 + \Gamma^2} + i\frac{\omega_p^2\Gamma}{\omega(\omega^2 + \Gamma^2)} \qquad (4)$$

To describe the complex permittivity, ε(ω), of the silver as a function of the angular frequency we used the Drude-Sumerfield model, given by the equation 4, where ε_∞ is the relative dielectric constant (for the silver $\varepsilon_\infty = 9$ [12]).

$\omega_p = \sqrt{n_e e^2/\varepsilon_0 m}$ is the metal plasma frequency, where n_e is the number of free electrons, *e* and *m* are the electron's charge and mass, respectively. Γ is a damping parameter and is related with the electron mean free path, $l = 4.375\times10^{-8}\mathrm{m}^{-1}$ and the Fermi velocity $v_F = 1.4\times10^{6}$ m/s by:

$$\Gamma = \frac{v_F}{l} \qquad (5)$$

For the description of the dispersion of the PMMA we used the data for the Sellmeier's coefficients published in [14]. In Fig. 4 a comparison is given of the real and imaginary parts of the complex permittivity calculated by Eqs. 2 and simulated from Eq. 3. Good coincidence between both is seen. Deviation close to the resonance frequency suggests the use of the Drude-Sumerfield model along with a critical point model [15].

It is well known that the pure PMMA films transmits up to 92% of visible light and gives a reflection of about 4% from each of its surfaces [14]. It filters ultraviolet (UV) light at wavelengths below about 300 nm (similar to ordinary window glass). Some additives to PMMA can be used to improve absorption in the 300-400 nm range. In Fig. 5 the simulated transmittance and reflectance are presented for a coating consisting of 10 alternate films from PMMA and Ag-PMMA. It is seen that the transmission drops drastically in the UV spectral range for wavelengths shorter than 400 nm and such coatings can be used for protection from the UV beams in the spectral range 300-380 nm. The coating possesses good transmittance in the visible spectral range. The value of T increase from 25-70% in the spectral range 400-550 and the coating possesses higher than 70 % transmittance for the wavelengths longer than 550 nm. It is known that the PMMA transmits infrared light up to 2.8 μm and blocks longer wavelengths up to 25 μm [14] which would insure good heat-insulation performance.

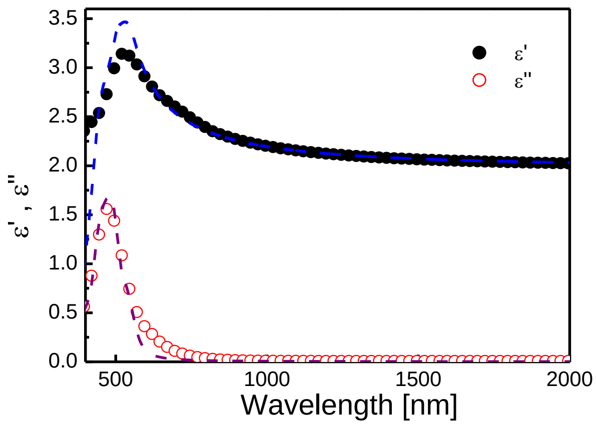


Fig. 4. Calculated (symbols) and simulated (dash lines) spectra of the complex permittivity, ε = ε' + *i*ε'' for a coating with Ag/PMMA ratio 0.15 (or $f_1 = 0.055$).

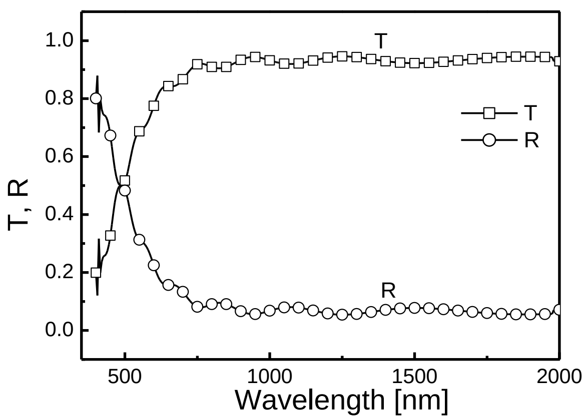


Fig. 5. Simulated transmittance and reflectance spectra of coating consisting from 10 alternated films from PMMA and Ag-PMMA with ratio 0.15.

CONCLUSION

The present paper reports the optical properties of nanocomposite materials from Ag and polymethyl methacrylate (PMMA) deposited though layer-by layer technique. The single Ag-PMMA coating demonstrates an absorption band in 350-550 nm range due to surface plasmon resonance in silver nanoparticles. The complex permittivity, ε was analyzed by the Bruggeman's model for the effective media. The optical properties of each individual layer were studied in order to consider the possibilities for optimization of the heat-insulation performance and the visible-light trans-mittance of the heat-insulating multilayers.

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ОПТИЧНИ СВОЙСТВА НА СРЕБРО-ОРГАНИЧНИ ПОЛИМЕРНИ ТЪНКИ СЛОЕВЕ КАТО СЛЪНЦЕЗАЩИТНИ ПОКРИТИЯ ЗА СЪВРЕМЕННИ ПРИЛОЖЕНИЯ В АРХИТЕКТУРАТА

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(Резюме)

В настоящата статия е представено изследване на оптичните свойства на нанокомпозит от слой от сребро и полиметилметакрилат (PMMA) получен чрез техника на послойно отлагане. Чрез рентгенова дифракция е потвърдено присъствието на сребърни частици в тънки слоеве. Средният размер на сребърни частици се изчислява чрез формулата на Дебай-Шерер. Абсорбционната ивица в спектралния диапазон 350-550 nm в спектрите на пропускане се дължи на повърхностен плазмонен резонанс на сребърни наночастици. Позицията на ивицата е анализирана чрез прилагане на модела на Бругеман за ефективната среда. На основата на получените резултати за оптичните свойства на полимерни-неорганични хибридни слоеве са направени изводи за приложение, като слънцезащитни покрития.