Progress in Organic Coatings 81 (2015) 80–86

Contents lists available at ScienceDirect

Progress in Organic Coatings

journal homepage: www.elsevier.com/locate/porgcoat

Heat treatment impact on molecular structure of polymer-based silver containing coatings deposited from the active gas phase

A.A. Rogachev[a,b], M.A. Yarmolenko[a,b,*], Xiaohong Jiang[a], A.V. Rogachev[a,b], Ruiqi Shen[a], Zhou Yingjie[a]

[a] International Chinese-Belorussian Scientific Laboratory on Vacuum-Plasma Technology, College of Chemical Engineering, Nanjing University of Science and Technology, Nanjing 210094, China
[b] Francisk Skorina Gomel State University, 104 Sovetskaya Street, Gomel 246019, Belarus

ARTICLE INFO

Article history:
Received 1 September 2014
Received in revised form
29 December 2014
Accepted 30 December 2014
Available online 19 January 2015

Keywords:
Electron beam deposition
Silver nanoparticles
Molecular structure
Nanocomposite coatings
Surface plasmon absorption

ABSTRACT

The features of chemical composition and molecular structure of polymer silver containing coatings and their changes under the heating were studied. The coatings have been deposited from the gas phase formed by electron-beam dispersion of polymer and silver salt mixture. The impact of polymer matrix and silver salt nature on the parameters of surface plasmon effect occurrence, as well as on the molecular structure of the coatings has been established.

1. Introduction

The nanocomposite polymer-based thin layers have unique properties that cannot be generally obtained by their individual constituent elements. Particularly, are interesting thin-layer systems containing nanoparticles of noble metals, in particular, silver. They attract attention of researchers due to the surface plasmon resonance effect which has found wide application in surface-enhanced spectroscopies, biological and chemical sensing, catalysis and medicine [1–4].

Among the different ways to synthesize these nanocomposites, the vacuum solvent-free methods such as physical, chemical vapor deposition and hybrid plasma chemical techniques are advantageous and provide easy control not only of nanocluster growth but also of its size, shape and distribution into polymer matrix volume [4–7]. The advantages of vacuum-plasma chemical methods of nanocomposite systems synthesis can be the absence of limitations in the solubility of polymer matrix, for example, sparingly soluble polymers such as polytetrafluoroethylene (PTFE) and polyethylene (PE) [6–8].

These layers are formed under nonequilibrium condition because of the complex physical and chemical processes, that is why their structure and properties are usually unstable. In this regard, the search of technological ways aimed to increase the reproducibility of the structure and the properties of the deposited thin layer polymer systems is an urgent task. The most effective and technologically simple method to give the thin layers the desired structure and properties is the heat treatment [6,9,10]. The effect of annealing on the molecular structure of the one-component polymer coatings is predictable and well-studied [11]. With thermally decomposed salt present in the thin polymer layer, the processes of the metal particles formation and the rebuilding of the polymer component molecular structure occur simultaneously.

In this regard, the study of the processes occurring under different external influences, in particular under heating which improves the uniformity of the layers' chemical composition, their thermodynamic stability, is of the practical and scientific interest [6,11,12]. In [13] it is shown that the annealing of single-component polymer coatings formed during the electron beam dispersion of polymers is accompanied by changing order, branching, degree of macromolecules unsaturation. For nanocomposite layers, the structural and morphological features may occur because of the presence of high dispersed filler in the polymer coating; the nature of this

* Corresponding author at: International Chinese-Belorussian Scientific Laboratory on Vacuum-Plasma Technology, College of Chemical Engineering, Nanjing University of Science and Technology, Nanjing 210094, China.
Tel.: +375 232 578253; fax: +375 232 578253.
E-mail address: simmak79@mail.ru (M.A. Yarmolenko).

http://dx.doi.org/10.1016/j.porgcoat.2014.12.019
0300-9440/

filler has impact on the behavior and the kinetics of the processing changes [10,12,13].

The main purpose of this work is to determine the impact of heating regimes on chemical composition and molecular structure of polymer silver-containing coatings deposited from the active gas phase formed by electron beam dispersion of target components.

2. Experimental

Polymer composite coatings were deposited from the active gas phase generated by electron-beam dispersion of mechanical mixture of polyethylene (PE), polymethyl methacrylate (PMMA), polylactide (PLA) powders with either the powder of silver nitrate or the powder of silver chloride using the method given in [14]. Chemical structure of the polymer is shown in Fig. 1.

The weight ratio of the components in the mixture in all cases was 1:1. The electron-beam projection device was used as an electron source with directly heated cathode allowing to form beams with current density $J = 50–500\ A/m^2$ and energy of particles $E = 0.1–2.5$ keV. The electron-beam generator with filamentary cathode which allows to form beams with current density $j = 0.01–0.03\ A/cm^2$, energy $E = 0.8–1.6$ keV is used as the electron source. Such low-energy electron guns are used while obtained polymer-based coatings in vacuum [7,14,15]. These evaporators cannot be used for forming coatings on the basis of metal, oxides and other chemical compounds of metals, as they are notable to generate high temperature in the beamed area. The deposition process of coatings was produced at initial pressure of residualgases in the vacuum chamber $\approx 4 \times 10^{-3}$ Pa.

The choice of coating material is conditioned by several factors. The PMMA is used as the material to form various photoelectron systems, in particular solar cells [16–19]. To increase the efficiency factor of solar cells, the silver nanoparticles are deposited on their surface. In this regard, the study of systems based on PMMA and silver nanoparticles is of scientific and practical interest. On the other hand, the silver nanoparticles are effective against pathogenic microorganisms resistant to antibacterial medicine. In medical practice, during creation of materials with sustained-release medicamental components are used biodegradable materials: polylactides, polyhydroxybutyrates [20]. These facts have predetermined the polylactide use in the work. The polyethylene has been chosen as the model polymer. It should be noted that this work does not pay attention to the structural features of the deposited organic layers, as these questions have been discussed in detail in a number of papers [14].

At present, the coatings containing antibacterial components and metal nanoparticles are the most effective against the pathogenic microorganisms. It is known that in the polymeric matrix the presence of polar groups determines the release rate of medicinal component in various environments, including biological one. The appearance of intensive molecular interaction between the polar groups of polymer and medicinal component will contribute to a slow release of the medicine. The different combination of polar (PMMA) and nonpolar (PE) polymers with a medicinal component allows programming the kinetics of medicine release. The use of biodegradable polymers allows predicting not only the release rate but also the release rate. The products of salt dispersion modify the structure of the deposited polymer layer. It can have a significant influence on the behavior of the interaction of the medicinal component and the polymer, as well as on the release rate. The article continues the research of already executed works, our interest was to study the coatings based namely on PE, PMMA and PLA [14].

The effective thickness of the formed coatings was 1 μm and during the deposition process its changes were controlled by the quartz crystal microbalance (QCM).

The heat treatment of the coatings was performed in air at the temperature up to 225 °C for 1 h followed by cooling to room temperature.

The substrates were quartz plates (for spectroscopic measurements in visible area), silicon (1 0 0) substrates (for microscopic measurements) and sodium chlorine (NaCl) plates (for IR spectroscopic measurements). The deposition of coatings was produced on the substrates with the surface temperature of 25 °C.

The coatings deposition was not accompanied by a noticeable change in the temperature of the substrates.

The study of the molecular structure of the formed polymer coatings was performed on Vertex-70 Bruker Fourier transform infrared (FTIR) spectrophotometer using a standard transmission unit. The ultraviolet–visible (UV–vis) spectra were obtained using a Cary-50 Varian spectrophotometer.

X-ray powder diffraction (XRD) patterns were recorded with a Bruker D8 Advanced X-ray diffractometer with Cu Kα radiation (λ = 1.54056 Å) at 40 kV and 40 mA.

Solver P47-PRO scanning probe microscope was used for studying the morphology of the coating with atomic force microscopy (AFM) method. The silicon cantilevers of NSG11S series were used as probes with typical force constant of 5.5 N/m and resonant frequency of 220 kHz.

JEM 2100 (Jeol) high resolution transmission electron microscope was used for determining the size and shape of the particles and their distribution in the volume of polymer matrix. Thin layers nanocomposite samples were deposited directly onto a carbon-coated copper grid.

3. Results and discussion

At the first stage of the study was determined the impact of heat treatment on the chemical composition of the coatings obtained by electron-beam evaporation of silver salt. It was established that the layers structure and its changing during the annealing depend on salt composition. Thus, in UV–vis spectrum of the coating formed by electron beam evaporation of silver chloride, immediately after deposition, the intensive plasmon absorption was fixed near 410 nm indicating the formation of silver nanoparticles in the layer [21]. When stored under normal conditions, a monotonic decrease was observed in optical density of the said absorption band and after 2 days of exposure, the absorption

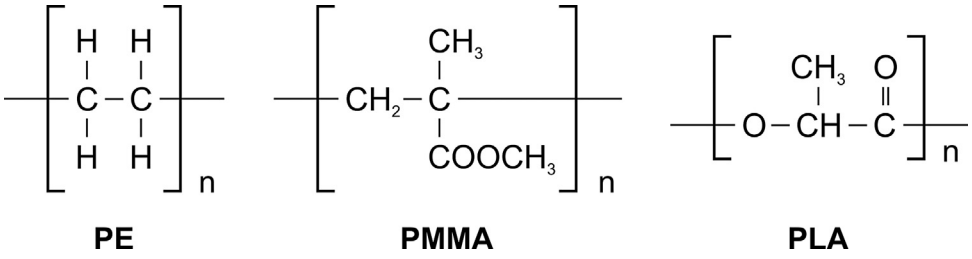

Fig. 1. Chemical structure of the polymer.