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Formation and properties of films based on polyvinyl alcohol and doped with silver nanoparticles

A.L. Potapov[a,*], O.A. Daineko[a], N.A. Ivanova[a], V.E. Agabekov[a], Mohammed Bin-Hussain[b]

[a] Institute of Chemistry of New Materials of National Academy of Sciences (IChNM of NAS of Belarus), Belarus
[b] The King Abdulaziz City for Science and Technology (KACST, Saudi Arabia), Saudi Arabia

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ABSTRACT

Unlike traditional methods of introduction of prepared metal nanoparticles into polymer composition, in our method Ag nanoparticles (NPs) are formed in the course of drying of molding composition on the basis of polyvinyl alcohol (PVA) due to slow reduction of ions Ag by "soft" organic reducing agents – quaternary ammonium compounds. The sizes of Ag NPs are determined and character of their distribution on the surface of PVA film is established by means of spectrophotometry, atomic force microscopy (AFM), transmission (TEM) and scanning (SEM) electron microscopy. Correlation is found between the data on absorption spectra and micrographs done by means of optical microscopy, AFM, TEM and SEM. Variations of the sizes and features of Ag NPs distribution in the polymeric film are examined.

1. Introduction

Currently, scientists around the world are actively engaged in obtaining new composite materials, in particular polymers with precious metals in the form of nanoparticles (NPs), nanowires and nanofibers and studying their specific properties [1–12].

The laboratory of optical anisotropic films of IChNM of NASB is involved in creation of film polarizers and other optical films for different purposes based on polyvinyl alcohol (PVA), including films with Ag, Au NPs [13].

The purpose of this study is to develop the technology of producing polymeric films on the basis of PVA containing Ag NPs of defined size, to investigate properties and structure of PVA film with Ag NPs, the size and nature of Ag NPs distribution on the film surface depending on the components and method of preparation of PVA composition.

Also, the influence of external factors (e.g., exposure to UV irradiation, effect of direct current) on the film structure is investigated.

The essence of our method is growing the Ag NPs in the PVA matrix during the drying of the composition.

2. Materials and research methods

Traditional methods of producing polymer composites with metal nanoparticles, described in the literature [1,14–16] rely on the synthesis and stabilization of individual Ag NPs, which then are introduced into the polymer matrix. In contrast, the essence of the method developed by us is in doping of polymer film with Ag NPs, which have formed by drying of molding composition due to the slow reduction reaction of ions Ag by "soft" organic reducing agents.

10% solution of PVA "Mowiol 28-99" manufactured by Hoechst Akiengesllschaft (Germany) was used for obtaining of PVA films.

Prepared PVA composition contains dosed amounts of additives of "soft" reducing agents, stabilizer and plasticizers, and $AgNO_3$. After Ag nitrate introduction the composition is dispersed in ultrasonic bath.

The content of the main components of PVA composition was varied in the following limits:

- PVA varied in the range from 2.5 to 15 wt.%;
- Quaternary ammonium compounds (QAC, three-methyloctadetsilammonia) – from 0 to 0.5 wt.%;
- $AgNO_3$ – from 0.05 to 1 wt.%.

Watering solution was applied to degreased mirror glass with the help of smearing. PVA composition was dried in a furnace at a temperature of $35.0 \pm 2.0\,^{\circ}C$ during 36 h, till a residual moisture content of 7.0–10.0% [13].

The composition for preparation of films comprises an aqueous solution of PVA with gelling and plasticizing additives. Components of the composition, and further injected aqueous QAC, a cationic surface-active compound serve as Ag reducing ions. While the film is drying Ag NPs appear due to the reduction reaction of Ag ions.

* Corresponding author. Tel.: +375 298589959; fax: +375 172859299.
E-mail address: potapov555@tut.by (A.L. Potapov).

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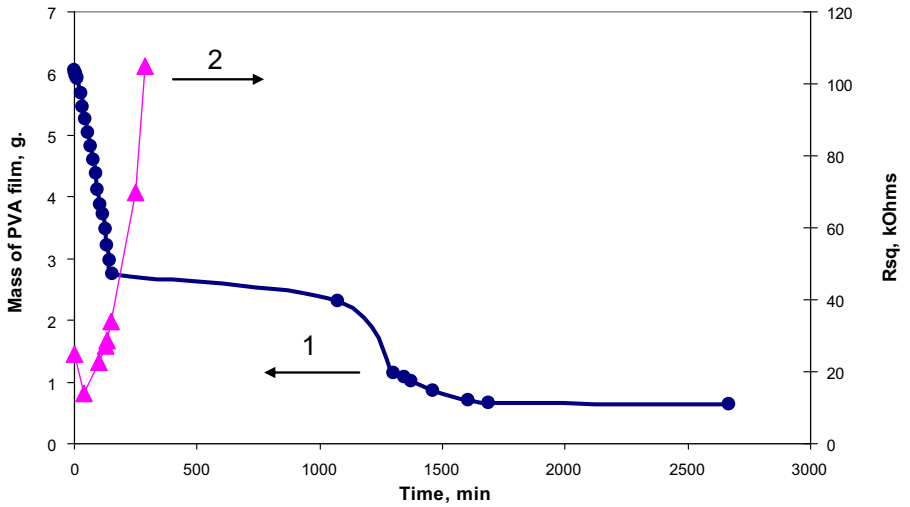

Fig. 1. The weight loss of PVA film by drying in air (1) and variation of electrical resistance Rsq of PVA film with Ag (2) over time.

The part of samples of PVA film with Ag was irradiated with a lamp "artificial sun" for full reduction of Ag^+ and activation of drying (Osram 300 W Ultra-Vitalux, mixed radiation of quartz burner and a tungsten filament, UVA – 13.6 W, UVB – 3.0 W).

Treatment time of PVA composition in ultrasonic bath is 1 h at temperature of 50 °C

2.1. The advantage of the method of synthesis of Ag NPs

There are several basic methods for the synthesis of Ag NPs.

- Citrate method (Turkevich method, reduction of Ag^+ by Na citrate while boiling in aqueous solution).
- Borane method (replenishment of cooled solution $AgNO_3$ with excess of $NaBH_4$ with intensive stirring).
- Method of synthesis of Ag NPs in two-phase aqueous-organic systems is based on the method of Brust–Schifrin. The idea of synthesis in two-phase systems is to obtain the NPs from reagents which are spatially separated in two immiscible phases. Toluene is usually used as the nonpolar medium and tetra-n-octylammonium is used as a phase transfer. A notable drawback of the method is the difficulty of simultaneously controlling growth of AgBr particles and metallic Ag. Thus, it can be assumed that the final size of Ag NPs will depend on the particle size of bromide and its coefficient of distribution between the phases [17].

Such methods as "Creighton method" or "Lee and Meisel method" are frequently used in scientific publications. In both methods, the NPs form in solution rather than in a composite. These methods are similar or identical to Turkevich method and borane method.

It should be noted that Ag NPs possess a combination of rare and important properties what makes them very successfully used in many fields of science and technology. Unique optical properties of Ag NPs, due to surface plasmon resonance (SPR), make it possible to produce optical films with new properties.

Unstabilized Ag NPs undergo rapid oxidation, and easily aggregate in solutions. It is known that the disadvantage of most of traditional and new methods for the synthesis of Ag NPs in aqueous media is the inability to achieve their highest concentrations in the final solutions, as well as the complexity of the implementation and the use of aggressive chemicals [1]. Furthermore, many methods require careful and time consuming cleaning of the resulting product.

We propose to synthesize Ag NPs directly in a water-soluble polymer matrix, which can be used for creation of optical films. PVA was used as a polymer matrix because it forms highly viscous aqueous solutions, which, like the films obtained therefrom have a high optical transparency and they stabilized Ag NPs [18]. This synthesis is easy to fulfill, not costly and environmentally clean [13].

The advantage of our method

- Polymer film based on PVA which is a stabilizer of Ag NPs in the liquid state and after drying, unlike liquid solutions with Ag NPs, prevents further deposition of Ag.
- *The ability of achievement of high concentrations of Ag NPs* due to the use of PVA matrix and the addition of a stabilizer, which after drying does not allow NPs to form fractals.

3. Study of the properties of PVA films with Ag NPs

3.1. Dynamics of drying of PVA film

Important parameters characterizing the formed PVA film are the time during which the film loses will excess moisture, weight loss and residual moisture.

Fig. 1(1) shows the dynamics of drying PVA composition in air.

The aqueous PVA composition contains: PVA – 9.45 wt.%, quaternary ammonium salt – 0.05 wt.%, silver nitrate – 0.5 wt.%, other ingredients and distilled water. Temperature of drying – 18 °C, relative humidity – 38%, the thickness of the resulting PVA film – 90 ± 10 μm.

The total weight loss was 89.6%. Drying of PVA film takes place in two stages. First, an intensive evaporation of solvents from the upper layers of PVA film with the mass loss of ~55% takes 2.5 h (water vapor passes freely through the liquid PVA).

Then, the process slows down harshly. After ~20 h, occurs gradual drying of film (on the surface of PVA film is formed which prevents the free evaporation). Already after 30 h the film loses all excess moisture.

It was established that the dried PVA film contains up to 90 wt.% PVA and others non-volatile substances, 5–7% of water (residual moisture), ~3–5 wt.% of nano- and submicron Ag particles.

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