Properties of Solutions and Films of Blends of Water-Soluble Cellulose Ethers with Poviargol

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Abstract—Rheological properties of moderately concentrated aqueous solutions of blends of methyl cellulose and carboxymethyl cellulose with Poviargol antiseptic (nanodispersed silver stabilized with polyvinylpyrrolidone) were studied. Composite films were prepared from solutions of the polymer blends, and the physicomechanical and thermomechanical properties of the films were examined. The region of thermodynamic compatibility of cellulose ethers with Poviargol was determined by the method based on sorption of solvent vapor.

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Polymer systems containing metal nanoparticles are being actively studied today [1]. In this context, a topical problem is preparation of medical materials based on blends of cellulose and its derivatives with polymeric antiseptics (Poviargol) containing nanoparticles of biogenic elements, in particular, silver. Dressing materials exhibiting high antimicrobial activity with prolonged effect were prepared by incorporation of silver nanoparticles into a matrix of bacterial cellulose (BC) and microcrystalline cellulose (MC) [2–5].

Poviargol (PVAG) is a polymeric composite of metallic silver nanoparticles stabilized with polyvinylpyrrolidone (PVP) [6]. It exhibits a wide spectrum of antimicrobial action, suppressing the growth of the majority of bacteria (staphylococci, streptococci, Escherichia coli, salmonellas, etc.). Furthermore, it exhibits anti-inflammatory, reparative, and immunostimulating activity [7].

Therefore, it seems promising to develop dressing and film materials based on cellulose ethers and Poviargol for treatment and prevention of wound infections. Incorporation of PVAG in cellulose derivative matrices can give rise to new physicochemical properties of the resulting materials, compared to films of supporting polymers. Therefore, it becomes appropriate to study the strength properties of composite films based on various cellulose derivatives in relation to the formulation, because the deformation and strength properties are important characteristics of dressing film materials.

In this study we examined the rheological properties of concentrated aqueous solutions of MC and NaCMC with PVAG, the deformation and strength characteristics of films prepared from the solutions, and the thermodynamic compatibility of the polymeric blend components in the solid state.

EXPERIMENTAL

Experiments were performed with commercial MC samples with the degree of substitution (DS) of 1.7 and degree of polymerization (DP_η) of 780, NaCMC with DS 0.73 and DP_η 450, and PVAG (Tekhnolog Special Construction-Technological Bureau, Russia) containing 8 wt % silver (relative to PVP). For comparative evaluation of mechanical characteristics, we also prepared blends from solutions of MC with DS 1.62 and DP_η 830.

To remove water-insoluble low-substituted microfragments of natural fibers, samples of cellulose derivatives were preliminarily dissolved in distilled water, and the solutions were filtered under pressure and freeze-dried.

Aqueous solutions of MC–PVAG and NaCMC–PVAG blends were prepared by mixing 2 wt % solutions at various component ratios. The rheological properties of moderately concentrated solutions were studied with
The properties of solutions and films of blends of cellulose ethers were studied. Experiments were conducted using a Rheotest-2 rheoviscometer in the range of shear rates $\tau = 3$–600 Pa at $T = 20$–50°C.

The compatibility of the polymers in the solid state was studied in relation to the blend composition by the method based on sorption of solvent vapors [8]. Films were formed from 2 wt% solutions by the dry method using a laboratory slot die with an adjustable gap, dried over phosphoric anhydride to constant weight, placed in a closed vessel with water, and kept at 20°C in an atmosphere of saturated water vapor to attain the equilibrium. After that, the samples were weighed, the degree of swelling was determined, and the polymer–solvent ($\chi_1$) and polymer–polymer ($\chi_{23}$) interaction parameters were calculated. Films for mechanical tests were formed from 8% aqueous solutions of polymer blends and dried to constant weight.

The physicomechanical characteristics of films were determined at room temperature in the uniaxial extension mode with a UTS universal installation for mechanical tests (UTStestsysteme, Germany). Specimens were extended at a rate of 20 mm min$^{-1}$ (100% of initial sample length in 1 min). In the course of the tests, the strain diagram was recorded, and the elastic modulus $E$, plastic limit $\sigma_p$, ultimate tensile strength $\sigma_u$, and breaking elongation $\varepsilon_b$ were determined. The relaxation transition temperatures were determined by the thermomechanical method with a UMIV-3 installation in the course of specimen heating at a rate of 5 deg min$^{-1}$ and a constant extension load of 0.5 MPa.

Figures 1 and 2 show the flow curves of 2% solutions of blends of MC and NaCMC with PVAG. The flow curves of MC and NaCMC are incomplete flow curves of non-Newtonian fluids. The viscosity of a PVAG solution does not appreciably change in the examined range of shear stresses, which is due to low molecular weight of polyvinylpyrrolidone. Heating of aqueous MC solutions leads to the formation of physical thermally reversible gels and to an increase in the viscosity (Fig. 3). Gelation is also observed in MC–PVAG blends containing up to 30% PVAG. At higher PVAG concentrations, no increase in the viscosity is observed in the examined temperature range. With a decrease in the MC fraction in blends, the gelation onset temperature increases and becomes higher than 50°C [9]. In solutions of NaCMC–PVAG blends, only a decrease in the viscosity with increasing temperature is observed (Fig. 4).

From the temperature dependences of the viscosity...