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# Physical-mechanical Properties of Metal-filled Hydrogel Films, Obtained by Centrifugal Molding

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**Abstract:** Metal-filled hydrogel films based on polyvinylpyrrolidone with 2-hydroxyethyl methacrylate copolymers were obtained by centrifugal method. It is determined the influence of the content of metal powder filler, technological parameters of processing and formulation of initial polymer-monomer composition on the physical-mechanical properties of the obtained composition film materials. It was determined that obtained metal-filled films are characterized by the anisotropy of the physical-mechanical properties of surfaces.

**Keywords:** *centrifugal molding; hydrogel films; polyvinylpyrrolidone; metal containing hydrogels; physico-mechanical properties; anisotropy of properties.*

## 1. Introduction

Up to date there has been widespread interest, both in science and practice, among the metal-polymeric composites in new materials with specific characteristics – metal-containing polymeric hydrogels [1]. Polymeric hydrogels are materials with porous structure, which, in combination with the presence of hydrophilic functional groups, provides swelling of the polymer matrix in water and other polar solvents, that results in their high permeability for dissolved low-molecular substances [2]. Metal-containing hydrogels are distinguished from other metal-filled polymeric materials by the ability to change characteristics, obtained as a result of filling, depending on temperature, pH, humidity, content of low-molecular substances.

The special interest for obtaining a sorption-capable matrix cause the reactive polymer-monomeric compositions based on polyvinylpyrrolidone with 2-hydroxyethylmethacrylate (HEMA/PVP) [2]. They are interesting both in their polyfunctionality and in increased reactive ability due to the physical interaction of PVP with the metal surface. By the previous works [4] it was established regularities of the copolymerization of HEMA/PVP filled with the finely dispersed powders of metal compositions, which reflect the influence of the composition, nature and content of the filler metal, the reaction conditions on the process speed, yield of the polymer, structure and properties of the copolymers. The using as the initiating system of the complex PVP-Men+ [5] allowed the synthesis of copolymers with high speed (time of curing of compositions – from 10 s to 30 min.) at room temperature in air. High reactivity and workability of such compositions creates the preconditions for the use of film materials on the basis of the method of centrifugal forming [6].

Analysis of the process of the centrifugal formation showed the possibility of using this method for processing compositions of HEMA/PVP in the presence of ions of metals of variable oxidation and production of film composites based on them [6].



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In addition, this contributes to the high reactivity of metal-filled HEMA/PVP compositions and the ability to vary the residence time of the original composition in the liquid state [7, 8]. During the research, we have produced prototypes of metal-filled hydrogel films based on copolymers of HEMA with PVP, which are characterized by a set of unique characteristics – equal thickness, sorption capacity, improved physical and mechanical properties, anisotropic electrical conductivity of the surfaces, which provide a perspective of the studied materials. However, to obtain high-quality metal-filled films with predetermined characteristics and implementation of a fundamentally new method of their production, it is necessary to establish the influence of technological parameters of processing, the content and nature of the metal, the formula of the initial polymer-monomer composition on the properties of composite film materials.

## 2. Experimental Section

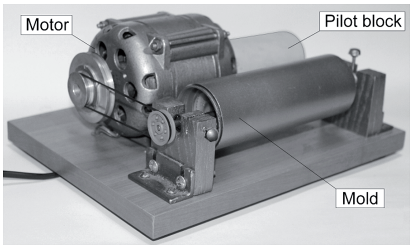
Using the results of previous researches [7, 8], for the synthesis of filled hydrogels selected polymerization in solvent compositions HEMA with PVP in the presence of 0,01% $FeSO_4$.

The composition selected experimentally based on the velocity of polymerization of PVP content and FeSO4, as well as the analysis of viscosity, based on the conditions of the filler particles sedimentation and the need for high performance process. For synthesis using 2-hydroxyethyl methacrylate ($\rho_{20}$=1079 kh/m$^3$, $n_D^{20}$=1,4520), purified and distilled under vacuum (residual pressure of 14 N/m$^2$, Boiling point = 351 K), the content of residual ethylene dimethacrylates not more than 0,15 %; PVP with MW 12 000 high purification before use dried under vacuum at 338K for 2-3 h.; zinc powder (the average size of particles 50 μm). The polymerization was carried out at 293K, outdoors, in daylight.

Metal-filled hydrogel films have been obtained using the designed laboratory device for centrifugal molding [6]. Constructed installation (Fig. 1.) contains a mold as hollow cylinder which is driven through a belt transmission by the electric motor.

Physico-mechanical properties (stress at break, strain at break, bursting strength and percentage elongation at bursting) have been investigated on universal tensile testing machine "Kimura Mashinery 050/RT-6010". The stress at break ($\sigma_{sb}$, MPa) and strain at break ($\varepsilon_{sb}$, %) were determined according to ISO 527-1, -2. The bursting strength ($\sigma_b$, MPa) and percentage elongation at bursting ($\varepsilon_b$, %) have been defined by film bursting with pin (Fig. 2.). The film was fixed in ring-shaped clamp of special device, assembled on tensile testing machine.

(a)




(b)

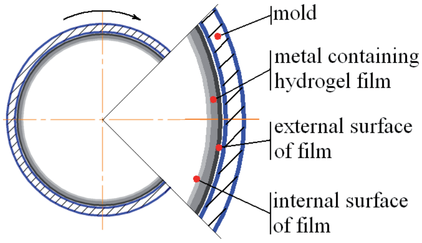



Fig. 1: *Installation for centrifugal molding of composite films of polymer hydrogels (a) and centrifugal mold with hydrogel specimen (b).*

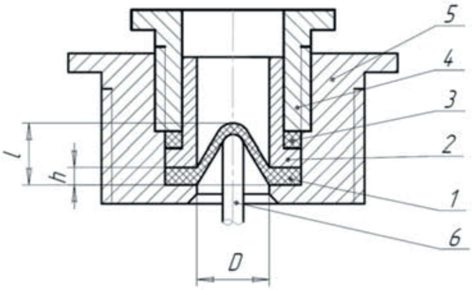



Fig. 2: *Scheme of device for film materials physical-mechanical characteristics determination by bursting: 1 – film; 2 – ring-shaped clamp; 3 – fluoroplastic seal; 4 – clamping nut; 5 – holder; 6 – pin.*

The bursting strength ($\sigma_b$, MPa) and percentage elongation at bursting ($\varepsilon_b$, %) for hydrated films have been calculated by following formulas:

$$\sigma_{br} = \frac{F}{D \cdot h} \cdot 10^{-6}, \varepsilon_{br} = 257 \cdot \frac{l}{D} - 25,$$

where F – stress, under what the sample is destroying, N; D – diameter of ring-shaped clamp hole, m; h – film thickness, m; l – pin transposition from moment of contact with sample till moment of bursting, m.

## 3. Results and Discussion

The centrifugal force that occurs during rotation of the heterogeneous composition leads to its stratification – segregation of components that occurs due to the difference of densities of components (Fig. 3.).

(a) (b)

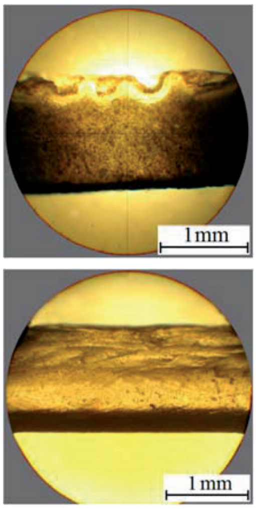



**Fig. 3:** *The influence of frequency of rotation of the cylindrical mold (ω, rev/min) on the filler segregation (HEMA:PVP:H2O=70:30:50 mass parts, [Zn]= 40 wt %.): (a) – 700, (b) – 2000.*

The phenomenon of segregation is a major factor during centrifugal molding of HEMA/PVP compositions filled with powders of metals, which will influence the anisotropy of properties of thin film materials. It is obvious that the filling material particles under the action of centrifugal force will migrate in viscous composition to the inner surface of the mold, i.e. in the outer layers of the film. The magnitude of centrifugal force depends mainly on the frequency of rotation of the cylindrical form, mold diameter and density of the composition [6]. In addition to these kinematic and physical factors on the structure and properties of the metal-filled film will affect the viscosity of the composition and the rate of polymerization, which depends on the composition and content of solvent.

First by interesting is research of the effect on the properties of composite films such factors as the composition of the polymer-monomer composition, filler content and solvent rotational speed of the form. The strength properties of the investigated films were characterized by stress at break ($\sigma_{sb}$, MPa), elastic – strain at break ($\varepsilon_{sb}$, %). The data obtained showed that with increasing the content of PVP in the composition is from 10 to 30 mass parts strength decreases significantly during break (Fig. 4.).

(a) (b)

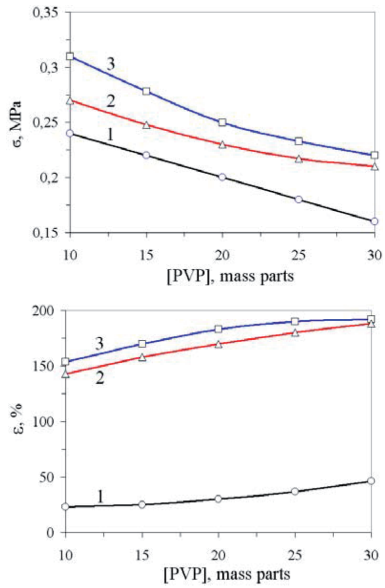



**Fig. 4:** *The effect of PVP content in the composition on the physical-mechanical properties of metal-filled hydrogel films at break and bursting (composition: solvent (water) = 2:1, [Zn] = 20 wt.%, [FeSO4] = 0,01 wt.%, ω = 700 rev/min): 1 – stress and strain at break; 2 – bursting strength and percentage elongation of external surface at bursting; 3 – bursting strength and percentage elongation of internal surface at bursting.*

This is due to a decrease in the number of chains of macromolecules in the unit volume of the swollen polymer, which resist destruction because with the increase of PVP in the original composition decreases the effectiveness of its grafting [9]. A significant increase (twice) the relative elongation during break with increasing PVP content up to 30 mass parts due to the simultaneous action of two factors:

*1) the influence of PVP on the composition and structure of the copolymer due to the injection due to the grafting with polyHEMA, macromolecules, PVP in the polymer forms a network with an increased size of the fragments of the chains between nodes of cross-linking [9]. Also, the part washed during the hydration of PVP, which did not participate in the reaction of grafting, improves the porosity of the polymer network.*

In the case of tensile forces long stretches of the chains between nodes of cross-linking capable to be straightened to a greater extent than short, and contributes to $\varepsilon_{sb}$ increasing.

*2) Effect of PVP content on the initial viscosity of the composition which depends on the intensity of segregation of the filler and the heterogeneity of the film thickness. With the increase of the homogeneity of the film material, increasing its strength and elasticity.*

However, research on stretching do not allow to account in full the impact strength of the films, the phenomenon of segregation of the filler and to detect the anisotropy of physical and mechanical properties. With this aim, additionally, investigated the stability of the films for a bursting, which is characterized by bursting strength ($\sigma_b$, MPa) and percentage elongation at bursting ($\varepsilon_b$, %). Research on bursting provide an opportunity to establish the strength and elastic characteristics of the hydrogel films depending on the surface of the force application. With this aim, we measured by applying a force to the outer surface and the inner and determined the bursting strength and percentage elongation at bursting, respectively, external $\left(\sigma_b^e, \varepsilon_b^e\right)$ and internal $\left(\sigma_b^i, \varepsilon_b^i\right)$ surfaces (Fig.1). As evidenced by the data indicated on Figure 4 the character of dependences of parameters $\sigma_b$, $\varepsilon_b$ for a bursting from the content in the molding compositions of PVP is the same change $\sigma_{sb}$, $\varepsilon_{sb}$ . However, as stipulated by the amount $\sigma_b$ and $\varepsilon_b$ affects the type of surface to which force is applied. It is determined that the parameters $\sigma_b^i, \varepsilon_b^i$ in their values are dominated by values $\sigma_b^e, \varepsilon_b^e$ (Fig. 4). This difference depends on the homogeneity of the material and the intensity of stratification of the filler on the film thickness.

The introduction into polymer powders of metals increases the surface hardness of filled with HEMA-PVP copolymers in the solid state [9]. However, in the case of swollen samples, the increase in the metal content of the initial composition leads to a decrease in strength and elongation of the material in relation to non-filled, during the bursting and during the break (Fig. 5).

The data obtained is an additional confirmation of physical interaction between metal surface and polymer. Therefore, particles of metals, and especially their agglomerates, which are formed in the outer layer of the film, playing the role of stress concentrators and are the centres of development of cracks during the application of load, the consequence of which is the destruction of the

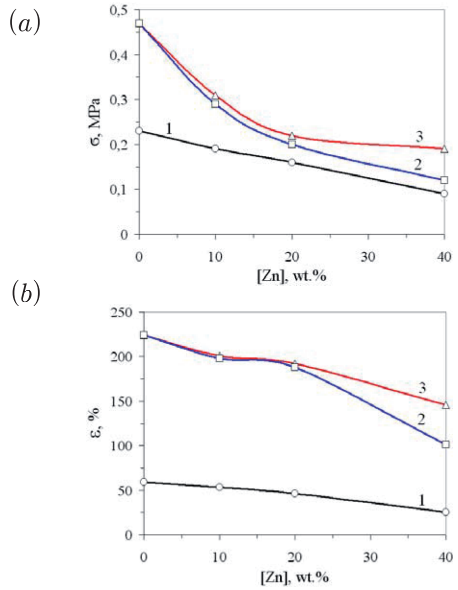



Fig. 5: *The dependence of physical-mechanical properties metal-filled hydrogel films at break and bursting content of metal (HEMA:PVP:H2O=70:30:50 mass parts, [FeSO4] = 0,01 wt.%, n = 700 rev/min): 1 – stress and strain at break; 2 – bursting strength and percentage elongation of external surface at bursting; 3 – bursting strength and percentage elongation of internal surface at bursting.*

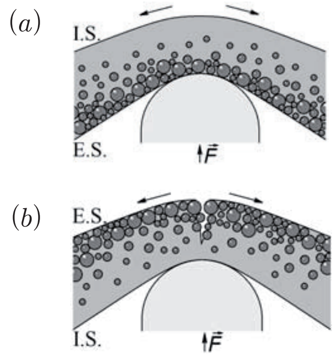



Fig. 6: *The behaviour of the composite film during the bursting the internal (a) and external (b) surfaces of (I.S. – internal surface, E.S. – external surface).*

sample (Fig. 6.).

With increasing of rotation frequency of centrifugal mold increases the intensity of migration of the filler to the outer surface of the film (Fig. 3). With the increase in filler content in the outer layers increases the number of stress concentrators, increasing the size of agglomerates and decreases between the thickness of the contact, resulting in reduced strength and elastic

(a)

(b)

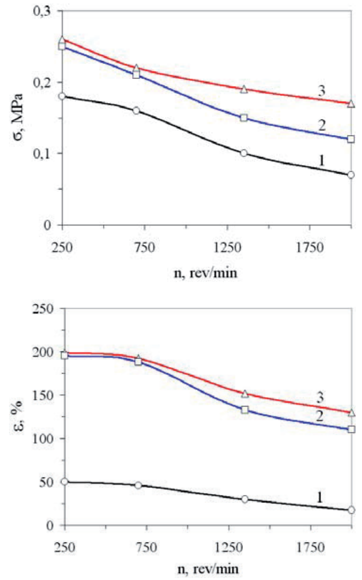



Fig. 7: *The dependence of physical-mechanical properties metal-filled hydrogel films at break and bursting of the rotational frequency of the form (HEMA:PVP:H2O=70:30:50 mass parts, [Zn]= 20 wt.%, [FeSO4] = 0,01 wt.%): 1 – stress and strain at break; 2 – bursting strength and percentage elongation of external surface at bursting; 3 – bursting strength and percentage elongation of internal surface at bursting.*

(a)

(b)

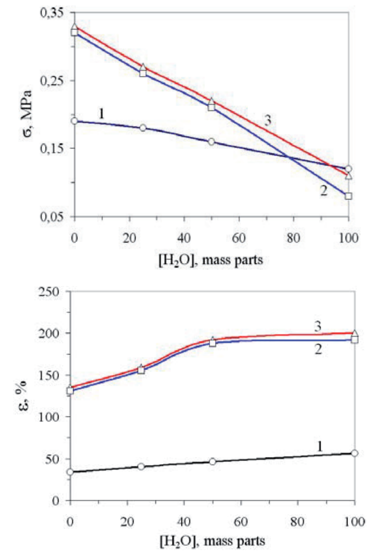



Fig. 8: *The dependence of physical-mechanical properties metal-filled hydrogel films at break and bursting the content of the solvent (HEMA:PVP=70:30 mass parts, [Zn]=20 wt.%, [FeSO4] = 0,01wt.%, n =700 rev/min): 1 – stress and strain at break; 2 – bursting strength and percentage elongation of external surface at bursting; 3 – bursting strength and percentage elongation of internal surface at bursting.*

properties of the composite films and enhanced anisotropy of their properties (Fig. 7).

The mechanism of reduction of strength characteristics of composite film materials due to segregation of the filler due to loss of film strength (decreasing as $\sigma_{sb}$ and $\sigma_b^e$ with $\sigma_b^i$) due to dilution of the composition with a solvent (Fig. 8).

At the same time there is an increase in elasticity of films. $\varepsilon_{sb}$ growth is due to increase elasticity of hydrogel matrix due to a significant decrease of efficiency of grafting PVP and the reduction of crosslinking density of polymer network [9]. Confirmation of the contribution of the characteristics of the matrix on the properties of films the results of the study $\sigma_b^e, \varepsilon_b^e$ and $\sigma_b^i, \varepsilon_b^i$.
As evidenced by the data in Figure 8, if the internal layer of the film prevails over strength and elasticity properties external. This factor is a consequence of the influence on the total elasticity of the film, which is characterized by the parameter of elongation at bursting.

## 4. Conclusions

Physical-mechanical properties of metal-filled hydrogel films based on HEMA-PVP copolymers, which were obtained by centrifugal molding, were investigated. It was determined that obtained metal-filled films are characterized by the anisotropy of the physical-mechanical properties. The difference in the properties of surfaces is a consequence of the segregation of the filler.

Investigation of bursting strength and percentage elongation at bursting of metal-filled films in different directions has shown that films strength and elastic properties during the applying force to their outer surface (relative to centrifugal mold) dominate by the characteristics of the films' properties during the applying force to the inner surface, although the nature of the property change is identical. Increasing the PVP content and solvent in the reaction composition, as well as increasing the revolution rate of the centrifugal mold causes a bursting strength decrease. At the same time, the increase of PVP content in the composition causes an increase of the composites elasticity.

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