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EFFECT OF THE LOW-MOLECULAR ADDITIVES NATURE ON THE ADHESIVE PROPERTIES OF BASED ON POLYVINYLPIROLIDONE COMPOSITIONS

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Abstract. The influence of low-molecular additives of different structure on the polyvinylpyrrolidone and hydroxyethyl compositions has been researched. The adhesive ability based on the contact angle compositions carried on linings of variable nature has been characterized. The effect of additives of different nature on the adhesive strength of the glue seam of polyvinylpyrrolidone containing compositions estimated by Dupre-Ung methodology has been studied.

Keywords: polyvinylpyrrolidone, hydroxyethyl, contact angle, adhesion ability, work of adhesion.

1. Introduction

As it is known, adhesion is the phenomenon of inter-phase interaction between the two surfaces of the different in its nature bodies put in contact. The adhesion causes the sticking of solids – substrates – by using gluing substance named called adhesive as well as bond of coating with basis [1, 2].

The scientific resources usually differentiate two types of adhesion: the first one is specific adhesion or adhesion itself, which is the strength of adhesion between the adhesive and the contacting surfaces, and the other one is mechanical adhesion defined as penetration of adhesive into the pores of material and the maintenance of cured adhesive due to mechanical jamming [3].

In review and analyses of the adhesion phenomena the thermodynamic approach of solving problems in two areas was widely used: the formation of adhesive contact and interaction between the contacting surfaces. Since these problems are closely related to the consideration of inter-phases processes, most attention has been paid to the evaluation of the phenomenon of wetting and spreading. Quantitative characteristic of the contact wetting is the contact angle q. The prerequisite adhesion strength is wetting of the surface lining. With the decrease in contact angle the adhesive strength has been enhanced [4].

Today for the majority of technologies based on the modified polymer materials the main role belongs to polymers with high surface activity, good water solubility, high ability to the complex formation, and high sorption characteristics. The polymers with the above mentioned features are polyvinylpyrrolidone (PVP) and its copolymers.

Study of the influence of low-molecular additives with different surface activity on the structure and activity of the adhesive polymer matrix will enable their controlled regulation, which is essential in the development of water-soluble adhesives of biomedical purposes.

2. Experimental

2.1. Initial Materials

Polyvinylpyrrolidone (PVP) was used with molecular weight of 28000. It is a white or white-yellowish powder with light specific smell, hygroscopic, easily soluble in water, alcohol, chloroform, and practically insoluble in ether. Its pH is ranged from 3.0 to 7.0. Before applying the PVP was dried under vacuum at 338 K for 2–3 h.

2-Hydroxyethylmethacrylate (r_{20} = 1079 kg/m^3, n = = 1.4520) was purified and distillated in vacuum (residual pressure of 14 N/m^2, boiling point 351 K).

Orthophosphoric acid (H_3PO_4) under normal conditions is a colorless hygroscopic crystal, completely soluble in water. In this work we have used 80 % aqueous solution of orthophosphoric acid – a colorless, odorless cheese-like liquid having a slight odor. It is completely soluble in ethanol, water and other solvents; density of the solution is 1.75 g/cm^3.

Isopropyl alcohol ($CH_3CH(OH)CH_3$, IPA) is a colorless transparent liquid with a typical pungent odor with T_m = 362.5 K, $T_{boil.}$ = 355.4 K and density 0.7851 g/cm^3 (at 293 K). Vapors are well mixed with air and easily form explosive mixtures. IPA is soluble in acetone, benzene and other solvents (water, organic) mixed in any proportions.

Lecithin – a general term for any group of yellow-brown fatty substances that are found in the tissues of animals and plants, egg yolks, and consists of phosphoric acid, choline, fatty acids, glycerin, fats, and phospholipids. Lecithin is a surface-active agent, works well at the surface of different substances.

Linings of the different nature, such as "organic glass", "glass silicate", "ceramics with glossy surface", "ceramics with untreated surface", "steel plate", "bone" were applied in the work.

2.2. Analytical Methods

The wetting angle determination was carried out by the device, the primary node of which is the microscope (such as MBS -9) according to methodology [5].

The calculation of adhesion work to the work of cohesion ratio was conducted by the Dupre-Ung equation [6]:

$$W_a / W_k = \frac{(1+\cos q)}{2} \quad (1)$$

The adhesion strength of the obtained samples has been investigated according to the methodology [7]. To determine the adhesion strength of the glue seam the compositions were applied to the previously prepared metal plates and maintained at the temperature of 333 ± 5 K for 5 h. The value of adhesion strength s was calculated by the following formula:

$$s = P / S \quad (2)$$

where P – load which destroys the sample, N; S – adhesion area, cm^2.

3. Results and Discussion

The research of influence of concentration and nature of low-molecular additives on the adhesion properties of PVP-containing compositions has been conducted. In this work the additives of different physical, chemical, structural, and other properties have been used, namely orthophosphoric acid, isopropyl alcohol and lecithin in 0.3, 0.5 and 1 % concentrations, respectively.

Aqueous solutions with PVP content of 0.5, 1, 1.5 and 2 % have been prepared and additives of variable nature have been added applying the method of substitution. The PVP is subject to various transformations under acids influence whereas the nature of the reaction substantially depends on the nature of the acid and its concentration. The research was conducted applying the linings of different nature. The obtained results are selectively presented in Fig. 1.

It has been observed on the "steel plate" lining that with the orthophosphoric acid concentration increase, the contact angle decreases in comparison with pure PVP solution. At the concentration of PVP 2 %, a slight increase in the contact angle has been observed for all concentrations.

For "ceramics with glossy surface" and "organic glass" linings we observe the θ value increase for the H_3PO_4 content of 0.5 and 0.3 %, respectively. On the lining "ceramics with untreated surface" while increasing H_3PO_4 concentration to 1.5 %, the sharp decrease is observed in the values of the contact angle, however with the further increase of the concentration the value of θ increases for all compositions with H_3PO_4. At 0.3 % concentration of H_3PO_4 for the "silicate glass" lining there is a linear dependence of the curve on the PVP concentration increase. Generally, the contact angle θ decreases with PVP and H_3PO_4 concentration increase. At the maximum content of H_3PO_4 the rapid decrease of the contact angle value is occurred, however in the case of "organic glass" lining at the above mentioned concentration, the increase of adhesive ability takes place at the maximum concentration of PVP.

In the case of "bone" lining the H_3PO_4 content increase leads to an alternating character of curves and decrease in the θ value.

Similar researches were carried out for PVP aqueous solutions, where water was substituted by isopropyl alcohol at the same concentrations and the linings of different nature were used. The obtained results are selectively presented in Fig. 2.

With the increase of isopropyl alcohol concentration in PVP aqueous solution for "steel plate" lining a decrease in the value of the contact angle is observed with the increase of PVP concentration. For the "ceramics with glossy surface" lining the introduction of isopropyl alcohol into the aqueous solution of PVP has not significant influence on the θ value, however, for "ceramics with untreated surface" lining the increase of PVP and isopropyl alcohol concentrations leads to the contact angle gradual increase.

At the concentration of isopropyl alcohol of 0.3 % adhesion ability significantly decreases for the "organic glass" lining at 1 % PVP concentration. The following growth of the PVP content for other concentrations does not lead to significant changes in the contact angle values.

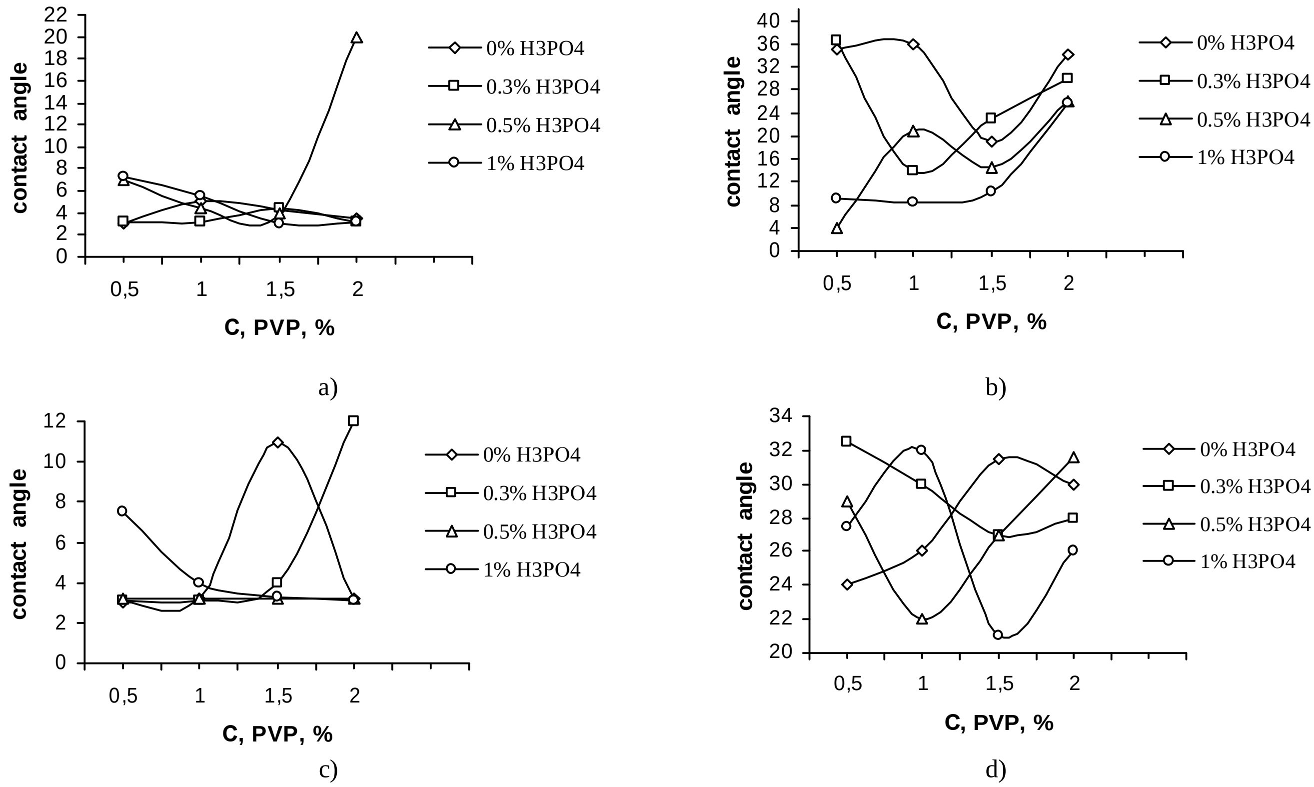


Fig. 1. Dependence of the contact angle θ on the concentration of H_3PO_4 in aqueous solution of PVP: ceramics with glossy surface (a); steel plate (b); organic glass (c) and bone (d)

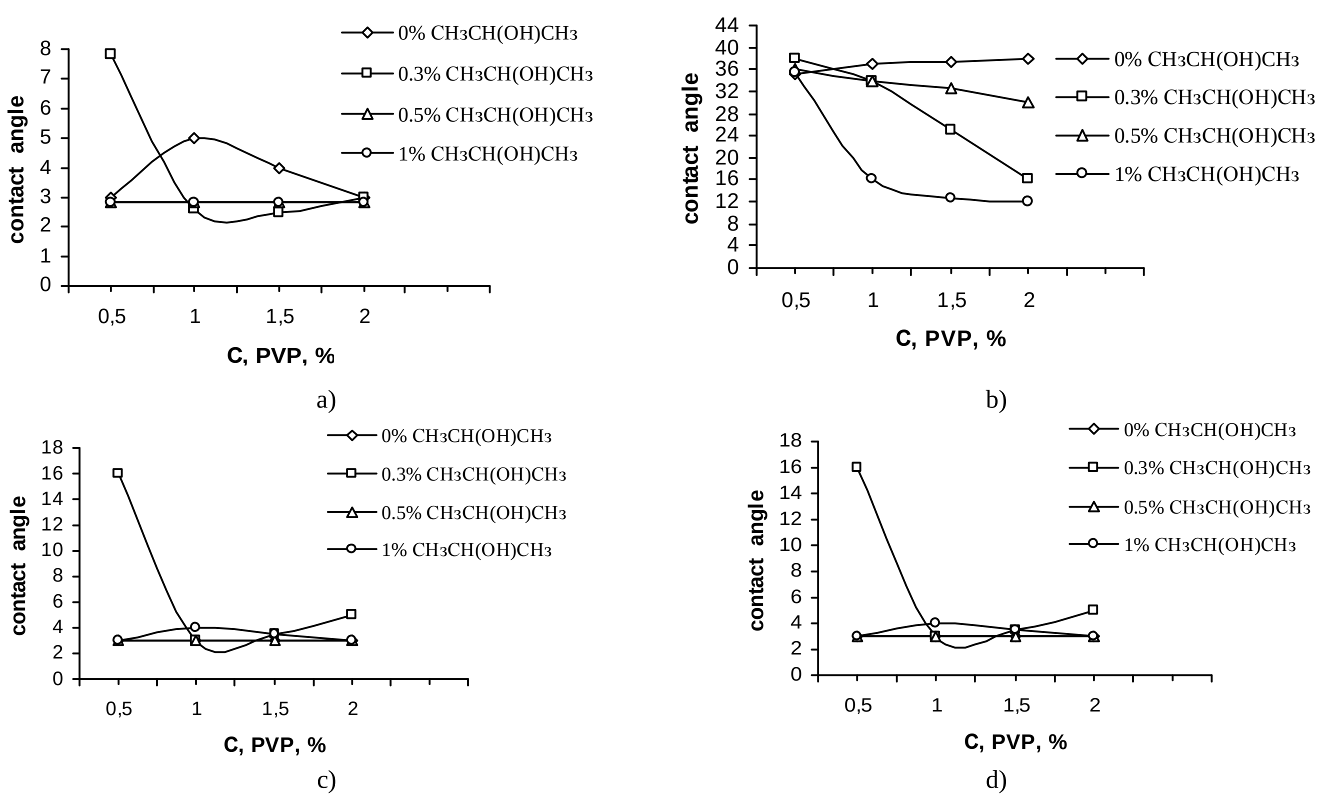


Fig. 2. Dependence of the contact angle θ on the concentration of $CH_3CH(OH)CH_3$ in aqueous solution of PVP: ceramics with glossy surface (a); steel plate (b); organic glass (c) and bone (d)

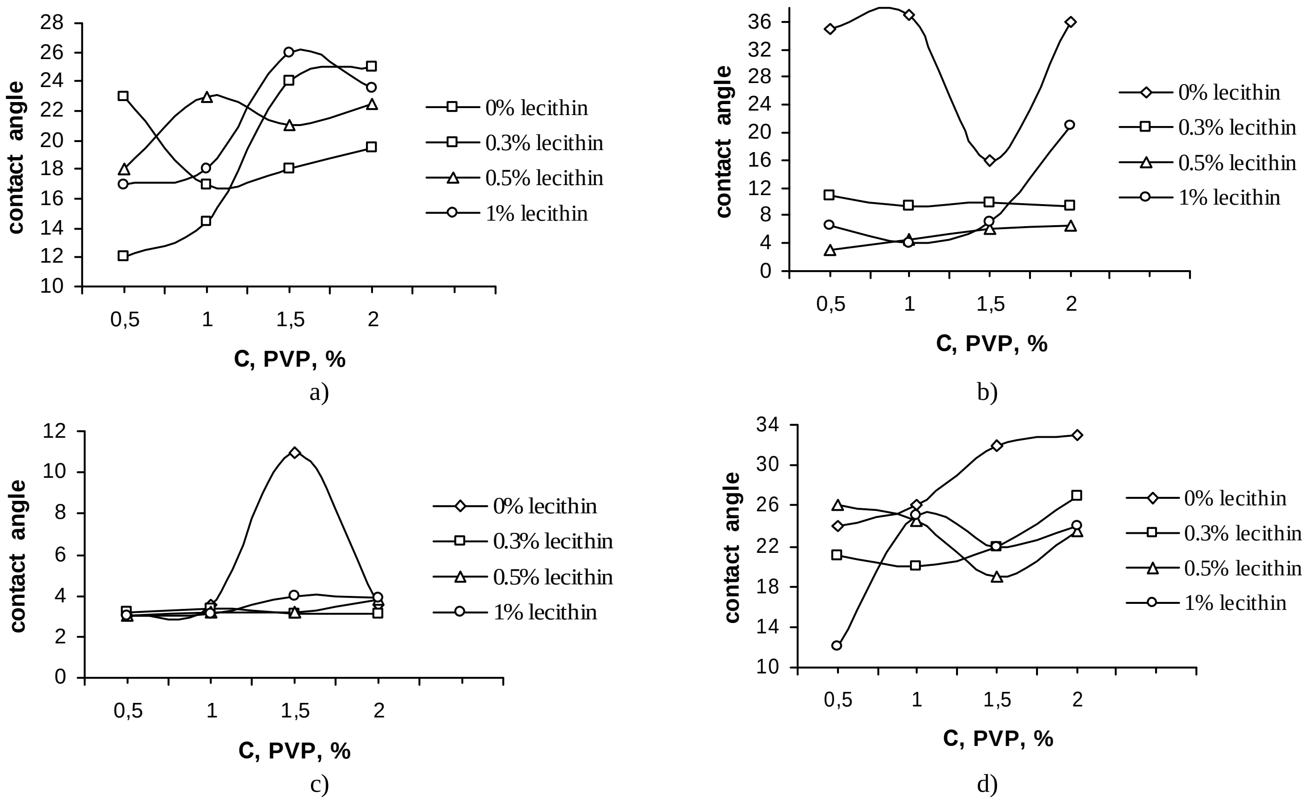


Fig. 3. Dependence of the contact angle θ on lecithin concentration in aqueous solution of PVP: ceramics with glossy surface (a); steel plate (b); organic glass (c) and bone (d)

The change of the isopropyl alcohol concentration in aqueous solution of PVP in the case of the "silicate glass" lining is not affected by the value of the contact angle in comparison with the original solution. For "bone", the most natural lining, 1 % aqueous solution of PVP is characterized by the increase in the contact angle at a minimum content of isopropyl alcohol. The further increase in PVP content decreases the adhesion ability.

Fig. 3 shows some investigations of PVP aqueous solutions with lecithin at the concentrations of 0.3, 0.5 and 1 %.

With the lecithin introduction in the PVP aqueous solution a decrease in the adhesion ability is observed in comparison with the original solution of PVP for almost all linings. Only for "ceramics with untreated surface" lining with the increase of PVP and lecithin concentration the value of contact angle θ increases.

The similar studies of PVP compositions were conducted under the established conditions and replacing water for 2- hydroxyethylmethacrylate (HEMA).

For this purpose compositions of polyvinylpyrrolidone of molecular weight 28000, with PVP content of 0.5, 1, 1.5, and 2 % have been prepared based on 2-hydroxyethylmethacrylate (HEMA) in the presence of benzoyl peroxide. In Fig. 4 the contact angle dependences for the PVP compositions in HEMA on "steel plate" and "ceramics with untreated surfaces" linings are selectively represented.

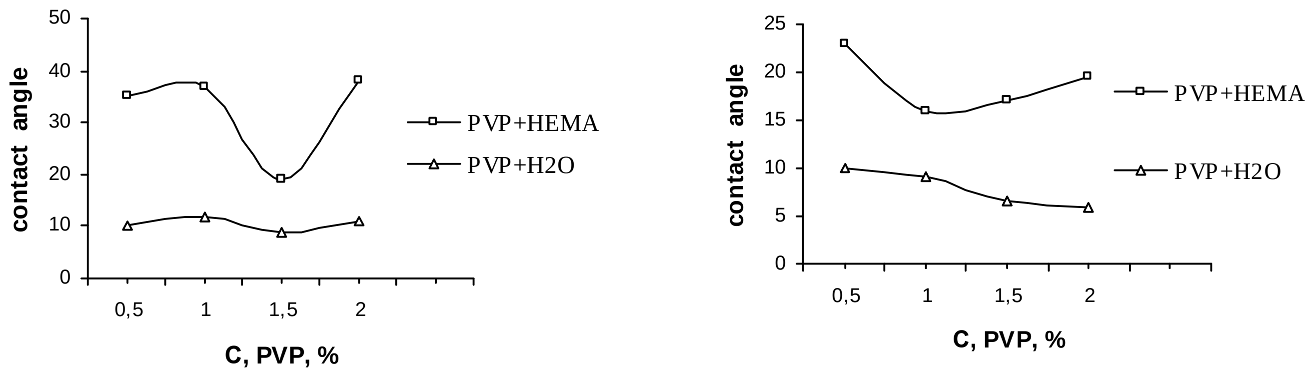
The introduction of HEMA as a solvent for PVP resulted in the stabilization of the compositions properties. The value of the contact angle decreases in comparison with PVP aqueous solutions, and thus adhesion properties of compositions for most linings are improved.

To improve surface wettability with PVP solution orthophosphoric acid (H_3PO_4) and isopropyl alcohol in concentrations of 0.3 and 1 % have been applied as low-molecular additives. The solutions of HEMA with 1 % PVP have been prepared for the studies. All these additives have been introduced by the substitution method and the obtained results are represented in Fig. 5.

The conducted research has shown that the greatest changes have occurred for the compositions on the "steel plate" lining. The solutions on the "bone" lining showed the best result. They have slightly smaller contact angle and therefore a good adhesive ability. Introduction of H_3PO_4 and isopropyl alcohol into the system have caused the completely mirror changes of the curves nature for "steel plate" and "ceramics with untreated surface" linings due to the different nature of the additives.

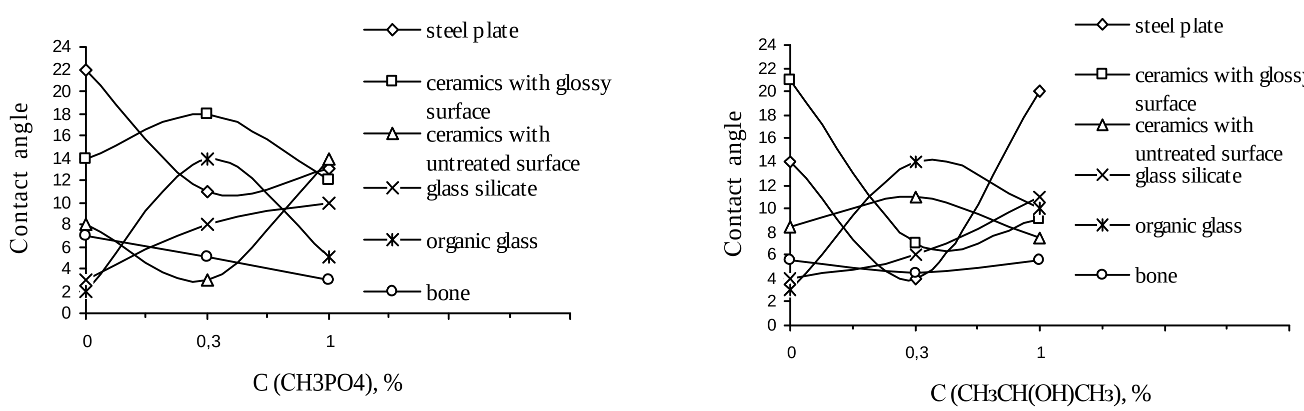
Using the contact angle the work of adhesion value can be calculated. The work of adhesion can be determined from Dupre equation [6]. In practice, a combination of Dupre equation and Ung law is applied. All above mentioned allows the indirect calculation of the work of adhesion through the surface tension of the liquid and the equilibrium contact angle of wetting of solid surface with liquid.

The calculated data for PVP aqueous solutions with the addition of H_3PO_4 for all types of linings are shown in Table 1.



a) b)

Fig. 4. Dependence of the concentration effect of PVP (*M* = 28000) in solution of HEMA on the value of contact angle: steel plate (a) and ceramics with untreated surface (b)



a) b)

Fig. 5. Dependence of contact angle θ on H_3PO_4 (a) and $CH_3CH(OH)CH_3$ (b) concentrations in HEMA solution containing PVP

Table 1

The ratio of the calculated work of adhesion to the work of cohesion (W_a/W_c)

Material (lining)	W_a/W_c															
	PVP 0.5 %				PVP 1 %				PVP 1.5 %				PVP 2 %			
	initial	H_3PO_4, %			initial	H_3PO_4, %			initial	H_3PO_4, %			initial	H_3PO_4, %		
		0.3	0.5	1		0.3	0.5	1		0.3	0.5	1		0.3	0.5	1
Steel plate	0.92	0.92	0.99	0.99	0.91	0.98	0.97	0.99	0.98	0.96	0.98	0.99	0.92	0.94	0.96	0.96
Ceramics with glossy surface	1.00	-	0.99	0.99	0.99	1.00	1.00	-	1.00	0.99	1.00	1.00	1.00	1.00	0.97	1.00
Ceramics with untreated surface	0.97	0.95	0.98	0.96	0.98	0.98	0.98	0.98	0.98	0.98	0.98	0.98	0.98	0.98	0.98	0.97
Organic glass	-	1.00	1.00	0.99	-	1.00	-	-	0.99	1.00	1.00	1.00	1.00	0.99	1.00	1.00
Glass silicate	1.00	1.00	1.00	0.99	-	1.00	-	-	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Bone	0.96	0.94	0.95	0.95	0.96	0.95	0.97	0.94	0.94	0.96	0.95	0.97	0.94	0.95	0.94	0.96

Table 2

The ratio of calculated work of adhesion to the work of cohesion for PVP and HEMA compositions

Material (lining)	W_a/W_c			
	PVP 0.5 %	PVP 1 %	PVP 1.5 %	PVP 2 %
Steel plate	0.99	0.98	0.99	0.98
Ceramics with glossy surface	1.00	0.97	1.00	0.99
Ceramics with untreated surface	0.99	0.99	1.00	0.99
Organic glass	0.98	1.00	1.00	1.00
Glass silicate	0.99	1.00	0.99	0.99
Bone	0.99	1.00	0.99	1.00

Table 3

The ratio of calculated work of adhesion to the work of cohesion

Material (lining)	W_a/W_c			
	PVP 1 %			
	0.3 % H_3PO_4	1 % H_3PO_4	0.3 % isopropyl alcohol	1 % isopropyl alcohol
Steel plate	0.97	0.99	1.00	0.97
Ceramics with glossy surface	0.99	0.99	1.00	0.99
Ceramics with untreated surface	1.00	0.99	0.99	0.99
Organic glass	0.99	1.00	0.99	0.99
Glass silicate	0.99	0.99	1.00	0.99
Bone	1.00	1.00	1.00	1.00

As one can see, the introduction of low-molecular additives to the composition with the increase of its concentration increases W_a/W_k ratio. "Organic glass", "glass silicate" and "ceramics with glossy surface" linings prove the maximum value of adhesion in PVP aqueous solution. Similar studies have been carried out with isopropyl alcohol. With the increase of low-molecular additives and PVP concentrations in solution, the adhesion ability increases for all linings except "ceramics with untreated surface" and "bone" ones. Similarly, the ratio of the work of adhesion to the work of cohesion of PVP and lecithin aqueous solutions has been determined. When introducing the additives maximum wetting was observed for "organic glass", "glass silicate" and "ceramics with glossy surface" linings.

The calculations of adhesion ability for the HEMA compositions are shown in Table 2.

One can see that the maximum value of adhesion strength is expectedly peculiar to organic glass, although in the case of natural bone the adhesive strength is high enough.

The results of the work of adhesion and the work of cohesion ratio when introducing low-molecular additives are shown in Table 3.

The results which are summarized in Table 3 show that the nature of additives improves adhesive ability of the compositions.

Good wetting of the surface lining is a prerequisite for adhesion strength. With the decrease in contact angle value, *i.e.* wetting increase, the adhesion strength is amplified. This is due to the increase of the contact area on surfaces which are well wetted.

The value of the glue line strength depending on the nature and quantity of low-molecular additive are shown in Fig. 6.

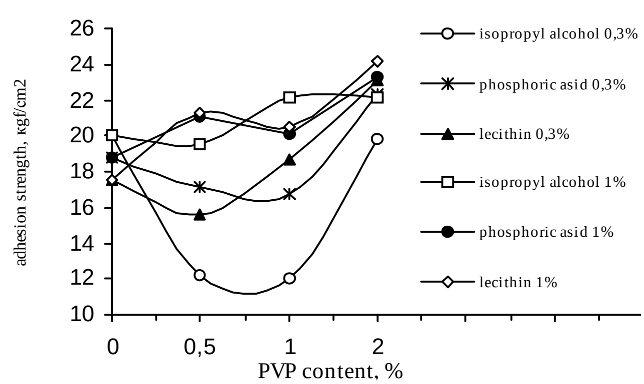


Fig. 6. Influence of the additive nature and PVP concentration on adhesive strength of the HEMA compositions

As can be seen, for the compositions with 0.5 % of PVP in HEMA the adhesive strength has unstable character with the increase of concentration regardless of the additive nature. The increase of PVP content in HEMA leads to increased adhesion strength for all additives. In case of the composition without additives, the increase in PVP concentration decreases the adhesive strength.

4. Conclusions

The influence of additives of different structure on adhesive strength of the glue line of the compositions based on polyvinylpyrrolidone has been studied. The increase of PVP content in HEMA leads to adhesion strength increase for all additives.

Based on the values of the contact angle on linings of different nature it has been found that low-molecular additives introduction improves the adhesion ability of PVP and 2-hydroxyethylmethacrylate compositions.

When introducing lecithin into PVP aqueous solution the improvement in adhesion ability in comparison with the original solution of PVP has been observed.

It has been found that isopropyl alcohol introduction into PVP aqueous solution leads to the adhesion ability improvement only for "steel plate" and "organic glass" linings.

It has been discovered that in the case of orthophosphoric acid introduction with the increase of its concentration and increase of PVP concentration in general, the value of the contact angle θ decreases.

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ВПЛИВ ПРИРОДИ НИЗЬКОМОЛЕКУЛЯРНИХ ДОДАТКІВ НА АДГЕЗІЙНІ ВЛАСТИВОСТІ КОМПОЗИЦІЙ НА ОСНОВІ ПОЛІВІНІЛПІРОЛІДОНУ

Анотація. *Досліджено вплив низькомолекулярних додатків різної будови на композиції полівінілпіролідону з гідроксиетилметакрилатом. Охарактеризована адгезійна здатність на основі кута змочування композицій на підкладках різної природи. Вивчено вплив додатків різної природи на адгезійну міцність клейового шва композицій на основі полівінілпіролідону, оцінену за методом Дюпре-Юнга.*

Ключові слова: *полівінілпіролідон, гідроксиетилметакрилат, кут змочування, адгезійна здатність, робота адгезії.*