

Oleh Suberlyak, Oleksandr Hrytsenko and Khrystyna Hishchak

SYNTHESIS OF NEW CONDUCTING MATERIALS ON THE BASIS OF POLYMER HYDROGELS

*Lviv Polytechnic National University,
12 Bandera str., 79013 Lviv, Ukraine
suberlyak@polynet.lviv.ua*

Received: March 11, 2008

Abstract. The new conducting polymer hydrogels on the basis of co-polymers of hydroxyethylenemethacrylate and polyvinylpyrrolidone with different nature non-organic fillers have been developed. The dependence of obtained materials electric characteristics on synthesis conditions, quantity and nature of powder filler, moisture content, ambient temperature and magnetic field action have been determined. The possibility of obtaining materials with anisotropic and unidirectional conductivity as well as the wide range of conductivity, which changes with moisture and ambient temperature, has been considered in this work.

Keywords: hydrogel, polyvinylpyrrolidone, polymer filling, conductivity.

1. Introduction

Polymer conducting composition materials are widely used at present for production of electro-heating elements, screening and antistatic covers, conducting glues, paints, pastes, air filter elements, and in medicine – for bony tissue growth stimulation as antithrombohenic implantants [1]. The increasing of electrical conductivity can be reached by introducing of composition material conducting fillers, such as metal powder, fibers, different types of technical coal, graphite, graphite fibers.

Phenol-formaldehyde, epoxy, furan and some other resins are mostly used as binders for these materials and form three-dimensional structures as a result of hardening. Some thermoplastics and rubbers are used as binders as well. But such polymer materials and their obtaining methods cannot always provide the uniformity of filling, the rate of composite production and its required properties. These methods are power-consuming, very expensive for implementation, long duration in time, and need expensive equipment. Quick-hardening compositions on the basis of (meth)acrylates and polyvinylpyrrolidone (PVP) are considered as perspective materials for the above-mentioned purposes. So, the aim of this work was the determination of conducting polymer hydrogels

obtained by polymer filling. The composition on the basis of 2-hydroxyethylenemethacrylate (HEMA) with PVP polymerized under the action of metal salts with varying oxidation degree has been used as the object of investigation. Such composition was synthesized at the Department of Plastic Materials Technology, Lviv Polytechnic National University [2, 3].

Using PVP-Meⁿ⁺ complex as initiating system the compositions were synthesized under room temperature on air with high velocity (the form is fixed after 10–30 min). The life time of such compositions can change in a wide range – from 5 sec to 30 min. The possibility of compositions preparation with different fillers nature on the basis of surface interaction between components was proved [4].

2. Experimental

Block polymerization of composition HEMA:PVP = 70:30 (mass parts) in 0.05 % FeSO₄ presence was chosen for synthesis of filled hydrogels on the basis of previous investigations [2, 3]. The formula of composition was selected experimentally on the basis of polymerization rate dependence on PVP and FeSO₄ contents and from viscosity analysis, considering the conditions of filler particles sedimentation and the necessity of providing high process productivity.

Purified and vacuum distilled HEMA (residual pressure 14 N/m², T_{boil.} = 351 K) with $\rho_{20} = 1079$ kg/m³, $n_D^{20} = 1.4520$ and ethyleneglycol dimethacrylate residual content no more than 0.15 %, as well as high purified and dried under vacuum (T = 338 K, time 2-3 h) PVP with MM = 28000, were used for polymerization.

The synthesis was carried out at room temperature on light in air oxygen presence. Inorganic conducting substances of different nature – non-metallic (graphite AUSS 5420-74), metallic (Fe, Co, alloy Fe-Co, Pb with particles size $\delta = 50$ nm), Cu (AUSS 4960-75) were used as fillers. The specific resistance was determined in accordance with procedure [5].

3. Results and Discussion

The results of specific resistance ρ_v and conductivity γ_v for compositions containing 50 % of filler are presented in Table 1. It is obvious from data obtained that unfilled polymer hydrogels, received by block method on the basis of co-polymers HEMA-PVP, have not electric conductivity. The introduction of conductive filler results in appearance of conductivity in these co-polymers. The conductivity significantly depends on filler nature. Graphite-filled hydrogels ($\rho_v = 29.5 \text{ Ohm}\cdot\text{m}$) are characterized by the lowest specific resistance and accordingly by the highest conductivity. Compositions containing finely dispersed copper, lead and Fe-Co alloy are characterized by comparatively identical conductivity that is approximately equal to $10^{-4} \text{ Ohm}^{-1}\cdot\text{m}^{-1}$. Compositions with cobalt have the lowest conductivity.

The conductivity of investigated composition materials depends on filler particles shape. So, the graphite has the developed surface and metallic particles have smooth round form. During polymerization filling the composition fills the free volume around filler particles. Metallic particles become separated one from another by the binder film that decreases the number of their contacts. So, it is necessary to introduce more filler into composition for conductivity increase. Due to porous and irregular shape of graphite particles the number of contacts is high and conductivity does not disappear.

The results of determination of filler amount influence on hydrogels specific resistance are presented in Fig.1. It is shown that increase of different nature fillers content acts on hydrogels specific resistance and on their conductivity as well. Thus the specific resistance of the composite is decreased in 184 times (from 29.5 Ohm·m to 0.16 Ohm·m) while graphite concentration increases from 50 % to 200 %.

Table 1

The effect of filler nature on hydrogels conductivity

Polymerization conditions: HEMA:PVP = 70:30 mass parts, $[\text{FeSO}_4] = 0.05 \%$; $T = 293 \text{ K}$,
filler content is 50 mass % from composition mass

No	Filler	$\rho_v, \text{ Ohm}\cdot\text{m}$	$\gamma_v, \text{ Ohm}^{-1}\cdot\text{m}^{-1}$
1.	-	$>10^9$	$<10^{-9}$
2.	Graphite	29.5	3.4
3.	Fe-Co	$13.7\cdot 10^2$	$7.3\cdot 10^{-4}$
4.	Cu	$18.6\cdot 10^2$	$5.4\cdot 10^{-4}$
5.	Pb	$91.5\cdot 10^2$	$1.1\cdot 10^{-4}$
6.	Co	$39.1\cdot 10^6$	$2.5\cdot 10^{-8}$

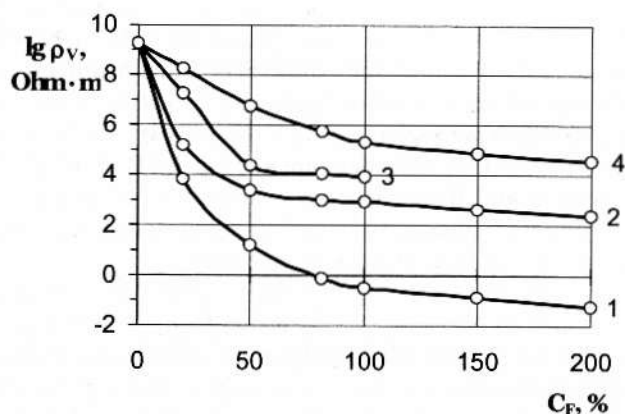


Fig. 1. Dependence of specific resistance on C_f filler content

HEMA:PVP = 70:30 mass parts; $[\text{FeSO}_4] = 0.05\%$; $T = 293 \text{ K}$;
filler: graphite (1), Cu (2), Pb (3) and Co (4)

The limiting content, under which composition is still fluid, exists for every filler. Under further filler adding the composition becomes non-technological. It is possible

to increase the filler content with initial composition fluidity conservation, using the possibility of HEMA-PVP co-polymers obtaining in solution and ability of obtained polymers to be in solid and swelling states.

So, if we obtain composition in block with C_1 filler content, we obtain the sample with conductivity γ_1 respectively. If we carry out the polymerization in solution (in water) with the same C_1 filler concentration and dry out the received sample to the constant weight, we obtain conductivity γ_2 .

It can be suggested that inequality $\gamma_1 < \gamma_2$ has to be right. For investigations we have used composition PVP:HEMA = 7:3 and graphite as a filler. The results are represented in Table 2. One can see from Table, the specific resistance of hydrogels obtained in solution (position 2) is in 24 times less than specific resistance of the same material but obtained in bulk (position 1). The conductivity of dry samples is significantly higher than that of swelled ones. The conductivity increases because of internal stresses which occur due to shrinkage and result in formation of additional contacts between particles.

Table 2

The effect of filler and solvent quantity on conductivity of hydrogels obtained in solutionPolymerization conditions: HEMA:PVP = 70:30, [FeSO₄] = 0.05 %, T = 293 K

№	Filler content, %	Solvent quantity (H ₂ O), m.p.	ρ_v , Ohm·m		γ_v , Ohm ⁻¹ ·m ⁻¹	
			in swelling state	in dry state	in swelling state	in dry state
1	50	-	-	29.49	-	0.04
2	50	50	3.72	1.23	0.3	0.8
3	50	100	1.00	0.48	1.0	2.1
4	300	150	0.11	0.03	9.4	33.3
5	500	200	0.08	0.05	12.6	20.0

The increasing of conductivity by means of filler content rising is not always technological. The sample mass increases (in the case of metallic filler), its strength characteristics, fluidity and moldability become deteriorated. The conductivity of polymer materials containing conducting fillers significantly depends on disposition of filler particles in relation to each other. The filler is distributed in polymer matrix with different structures formation: matrix (insular), statistic, orienting and laminated [1].

All of above-mentioned structures, except matrix, are in real polymer materials. Matrix ones are used as models for theoretical calculations. The statistic distribution of particles occurs under mechanical filler

dispersion, so that the average distance between particles is significantly less than in the case of cubic lattice (matrix structure). It is necessary to approach filler particles to direct contact or to the distance in few angstroms if we want to increase conductivity of polymer compositions with conducting fillers significantly. In each case the current passing will be presented as uninterrupted chain of contacts or significantly close filler particles. The disposition of conductive particles by lines parallel to electric current direction is the most desirable. In connection with this fact the artificial obtaining of conductive metallic filler chain structures – its magnetic orientation is of great interest. The results of such investigations are presented in Table 3.

Table 3

The effect of magnetic field on the anisotropy of hydrogel materials conductivityPolymerization conditions: HEMA:PVP = 70:30, [FeSO₄] = 0.05 %, T = 293 K, H = 23 kA/m, filler content is 40 % from composition mass

№	Filler	ρ_v , Ohm·m		$\gamma_v \cdot 10^3$, Ohm ⁻¹ ·m ⁻¹	
		//	⊥	//	⊥
1	Fe-Co	*83/1370	> 10 ⁶	12/0,73	<10 ⁻⁶
2	Co	28·10 ⁵ /35·10 ⁶	> 10 ⁶	4·10 ⁻⁴ /3·10 ⁻⁵	<10 ⁻⁶

Notes: * in denominator – electric characteristics of hydrogels, obtained without magnetic field;

//, ⊥ - electric characteristics of hydrogels in direction parallel and perpendicular to magnetic field lines, accordingly.

The magnetic field that acts during hardening results in obtaining of samples with higher conductivity compared with samples obtained without it because under magnetic field action the filler orientation takes place and more metallic particles take part in conducting structure formation. It is evident from data obtained that different conductivity in interperpendicular directions is characteristic for samples obtained in the magnetic field. It is maximum in direction of magnetic field lines action, *i.e.* in direction of filler particles chains formation, and it is minimum or absent (depending on filler nature and concentration) in the perpendicular one.

It is interesting to investigate the filled conductive hydrogels behavior in wet medium for their complete characteristics and for determination of additional opportunities of their usage as well, since PVP-containing materials are characterized by high water absorption. The samples of identical thickness with fillers of different nature (graphite and cobalt) have been used for investigations. These samples were hydrated in distilled water. In definite intervals their water content and conductivity have been determined. The results of tests are presented in Table 4. The given results show hydrogels with different nature fillers have different character of conductivity change

lead particles, formed under temperature increasing. The insulation films are formed in the gap during their crosslinking with neighboring molecules by chemical bonds. The ρ_v increasing continues till material softening point ($T_v = 322$ K). The further specific resistance drastic decreasing is connected with internal movement growing under prolonged composition heating and probably with tunnel effect [1]. As electric contacts theory shows, the current passing is possible not only under direct contact of two conductors, but even if there is air layer or dielectric film between them. Most authors consider the tunnel effect to be the most probable mechanism of charge transfer in conducting compositions [1]. The tunnel resistance is the exponential function of gap thickness. We can see (Fig. 3) that value $\lg \rho_v$ is a linear function of polymer thermal expansion under temperature higher than T_v . So, there is the exponential dependence between ρ_v and polymer thermal expansion. If it is admitted that change of distance between Pb particles is directly proportional to linear polymer expansion, then ρ_v is exponential function of distance between particles. It is characteristic of tunnel mechanism for electrons transient through potential barrier. Thus, we can assume that in considered system the tunnel mechanism of electric conductivity agrees with temperatures $T > T_v$. The infringement of linear dependence under $T < T_v$ is probably connected with conductivity due to direct contacts between particles and to internal stresses rising in system as well.

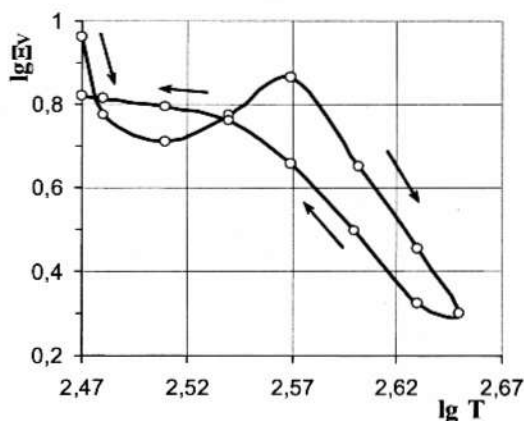


Fig. 3. The logarithmic dependence of filled hydrogel specific resistance on temperature
Polymerization conditions: HEMA:PVP = 70:30,
[FeSO₄] = 0.05 %; filler – Pb (50 % from composition mass)

The curve $\rho_v = f(t)$ for graphite-filled hydrogel differs from preliminarily considered one. In this case (Fig. 2b) the conductivity at the first stage drastically decreases (ρ_v increases). ρ_v slightly decreases at temperatures higher than T_v . The mentioned differences in conductivity may be connected with different mechanism of charges transfer. The dependence $\rho_v = f(t)$ for graphite-filled material is typical for materials in which the transfer of charges carriers performs along network of conductive filler particles contacting with each other. This filler is distributed in non-conductive matrix. Since the coefficient of thermal expansion of polymer medium is higher than the filler one in few orders, the thermal expansion of matrix under temperature rising results in reducing of contacts surface between graphite particles or even in breaking of uniform cluster sections into insulated clusters. It can be seen from significant composite conductivity decrease. The contact spots on graphite particles are covered by polymer film under heating that explain the misalignment of heating and cooling curves.

4. Conclusions

Thus as a result of investigations, the possibilities were determined as well as the methods of obtaining of moisture and temperature sensible filled conductive polymer hydrogels on the basis of hydroxy-ethylenemethacrylate with polyvinylpyrrolidone were proposed. It was determined that compositions containing non-metallic filler – graphite – are characterized by significantly higher conductivity than metal-containing hydrogels in proportional concentrations.

The quantity of absorbed moisture differently affects the hydrogels conductivity depending on filler nature. For graphite-filled materials, in particular, the resistance change has the extreme character – when moisture content is less than 8.6 %, the specific resistance increases to 1049 Ohm·m, after that it drastically decreases and under $W = 35$ % is 166 Ohm·m. For metal-filled materials ρ_v is within the range of 153–39·10⁶ Ohm·m with water content changing from 0 to 35 %. Dependence of ρ_v on W can be used for moisture gages production.

The conductivity of hydrogels filled with ferromagnetic powder significantly increases while their obtaining under the magnetic field action – the resistance decreases in few orders, obtained materials have conductivity anisotropy.

Dependence of conductivity change upon temperature has extreme character. The developed materials are characterized by the highest specific resistance within temperature range of 273–283 K.

References

- [1] Gul V. and Shenfil L.: Elektroprovodyashchiye polymernye kompozitsyi. Khimiya, Moskva 1984.
- [2] Suberlyak O., Skorokhoda V. and Hrytsenko O.: Voprosy khimii i khimicheskoy technologii, 2000, **1**, 236.
- [3] Hrytsenko O., Havlo I., Skorokhoda V. and Suberlyak O.: Visnyk NU "Lvivska Politehnika", "Khimiya, technologiiya rehovyn ta yih zastosuvannya", 2001, **426**, 68.
- [4] Hrytsenko O., Orlova A. and Skorokhoda V.: Visnyk NU "Lvivska Politehnika" "Khimiya, technologiiya rehovyn ta yih zastosuvannya", 2003, **488**, 300.
- [5] Lushcheykin G.: Metody issledovaniya elektricheskikh svoystv polymerov. Khimiya, Moskva 1988.

СИНТЕЗ НОВИХ ЕЛЕКТРОПРОВІДНИХ МАТЕРІАЛІВ НА ОСНОВІ ПОЛІМЕРНИХ ГІДРОГЕЛІВ

Анотація. Розроблені нові електропровідні полімерні гідрогелі на основі кополімерів гідроксіетилметакрилату з полівінілпіролідом з неорганічними наповнювачами різної природи. Встановлена залежність електричних характеристик одержаних матеріалів від умов синтезу, кількості та природи порошкового наповнювача, вмісту вологи та температури оточуючого середовища, дії магнітного поля. Показана можливість отримання матеріалів з широким інтервалом електропровідності, яка змінюється із зміною вологи та температури середовища, а також з анізотропною та однонаправленою електропровідністю.

Ключові слова: гідрогель, полівінілпіролідон, полімеризаційне наповнення, електропровідність.