

THERMOPHYSICAL PROPERTIES OF COMPOSITE METAL-FILLED COPOLYMERS OF POLYVINYLPIRROLIDONE

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Abstract. The effect of the presence of finely dispersed metal fillers of various natures (Zn, Co, Ni) on the thermophysical characteristics (Vick heat resistance, glass transition temperature) of polyvinylpyrrolidone block copolymers with 2-hydroxyethylmethacrylate was studied. It was found that the heat resistance of the obtained composites significantly exceeds the heat resistance of unfilled copolymers and is in the range of 360–395K, depending on the nature and content of the metal filler. The change in heat resistance correlates with the change in glass transition temperature, which was evaluated according to the results of thermomechanical and dynamic mechanical thermal analyses. The results of this work are an additional source to characterize the structure of metal-filled copolymers: they confirm the participation of metal filler particles in the formation of the nodes of the copolymer spatial network, and also prove the formation of a different polymer network structure in the interfacial layer on the surface of the metal particle and in the polymer volume.

Keywords: polyvinylpyrrolidone, 2-hydroxyethylmethacrylate, copolymers, metal-filled polymers, heat resistance, glass transition temperature.

1. Introduction

The processes of modifying polymer materials with metal fillers of various natures are the subject of numerous studies, the result of which is the creation of new materials with unique properties for various fields of science and practice.^{1–7} Obtaining metal-filled polymer composites with a wide range of technological and operational properties, their combination and predictable regulation become possible due to a number of factors. First of all, it is the presence of polymer matrices different in nature and, accordingly, in their characteristics (thermosets,^{8,9}

thermoplastics,^{3,10} elastomers,^{11,12} hydrogels^{13,14}) and metal fillers (metals,^{8,15} noble metals,^{16,17} ferromagnets,^{18,19} metal alloys,^{20,21} bimetals,²² and hybrids²³). The properties of the composite are significantly influenced by the choice of the modification method of the polymer matrix, which is determined by the method of obtaining metal-filler particles (chemical, physical, electrochemical)^{24–27} and the method of introducing the filler into the polymer matrix (synthesis of metal-filler particles in the polymer network,²⁸ synthesis of metal-filler particles during the formation of the polymer matrix,²⁹ mixing in the melt^{18,30} and solution,¹¹ polymerization of the monomer in the presence of the metal particles^{8,14}).

Nowadays, a new progressive class of polymer composite materials are metal-filled hydrophilic polymers and hydrogels based on them.^{1,14,28,29,31–35} Due to the porous structure and the presence of hydrophilic functional groups, polymer hydrogels are characterized by high sorption capacity for low molecular weight substances, and permeability to liquids and gases.^{36–40}

Modification of hydrogels by filling with metal particles provides them with new properties, for example, electrical, magnetic, catalytic, bactericidal, antifungal, fluorescent, optical, etc. Metal-filled hydrogels are already used in biotechnology and medicine, the production of packaging materials, microelectronics, optics and optoelectronics, chemical catalysis, sensor devices, and in other fields.^{41–45}

Due to their properties, polymer composite metal-filled hydrogels based on grafted copolymers of polyvinylpyrrolidone (PVP) with 2-hydroxyethylmethacrylate (PVP) (pHEMA-gr-PVP) are interesting and promising for science and practice.^{36,46} By the polymerization filling method, composite metal-filled copolymers of HEMA with PVP and hydrogels based on them were obtained, which were characterized by a wide range of physical, mechanical, electrical, magnetic, and chemical properties.^{14,47,48} Such polymers are characterized by a combination of their properties from both the polymer matrix (sufficient resilience, strength, elasticity, biocompatibility with the living organism, sorption capacity) and the metal filler (MF) (electrical conductivity, heat resistance, and magnetic properties).

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The combination of the properties of the hydrogel matrix and MF ensures the uniqueness of such materials and, accordingly, the need and perspective of their research in the direction of creating materials for the production of various sensors, catalysts, medical bandages, vascular prostheses, magnetic sorbents, *etc.*^{14,47-50}

At the same time, products based on metal-filled hydrogels, depending on their purpose, can be used in conditions of elevated temperatures, for example, medical films during sterilization, temperature sensors, and heating of materials due to energy dissipation during turning or cutting operations.

Thus, a need arises to study the temperature operation regimes of metal-filled pHEMA-gr-PVP copolymers, since the temperature intervals of the phase and physical states determine their mechanical properties and, accordingly, the fields of practical use. Therefore, the aim of the work was to investigate the effect of the presence of metal filler on the thermophysical characteristics of pHEMA-gr-PVP copolymers.

2. Experimental

2.1. Materials

The following substances were used: 2-hydroxyethylmethacrylate (Sigma Chemical Co, Saint Louis, MO, USA), which was purified and distilled in a vacuum (residual pressure = 130 N/m², T_B = 351 K); polyvinylpyrrolidone (AppliChem GmbH, Darmstadt, Germany) of high purity was dried at 338 K in a vacuum for 2–3 h before use; iron (II) sulfate was used of p.a. grade.

For the preparation of the reaction composition, considering its processability, HEMA in the amount of 60 ÷ 90 mass parts and PVP in the amount of 10 ÷ 40 mass parts were used. The lower limit of the PVP content is due to the fact that its lower content significantly increases the hardening time of the compositions, especially metal-filled ones, which are hardened without additional polymerization initiators. The upper limit is due to technological complications: a higher PVP content increases the duration of its dissolution in HEMA, and increases the viscosity of the composition, which complicates its dosing.

Fine powders of metals – Ni (metal content 99.9%; average particle size – 10-15 μm; China), Co (metal content 99.4%; average particle size – 1.3-1.5 μm; China), Zn (metal content 98.1%; average particle size – 5-8 μm; Germany) were used as MF for research.

2.2. Methods

2.2.1. Synthesis technique of pHEMA-gr-PVP copolymers and MF-filled composites based on them

We introduced finely divided metal powders in the composition of copolymers by polymerization filling. By

mixing the required amounts of HEMA with PVP for polymerization, a polymer-monomer composition (PMC) was obtained, to which the required amount of filler powder was added.^{14,47} The resulting PMC with the filler was periodically stirred for a time $\tau < \tau_{p.l.}$ ($\tau_{p.l.}$ is the pot life time of the composition – the time during which the reaction composition retains fluidity), and then dosed into a polymerization mold. The polymerization was carried out at room temperature for 0.3-1 h (depending on the composition formulation, nature and amount of MF).

2.2.2. Thermophysical properties

Heat resistance of copolymers was determined in accordance with ISO 306:2013 “Plastics – Thermoplastic materials – Determination of Vicat softening temperature”, which consists of determining the temperature at which a standard indenter with a flat bottom surface (\varnothing 1.128 ± 0.008 mm) is pressed under load to a depth of 1 mm into a test sample that is heated at a constant rate. Studies were performed by using a Höppler consistometer.⁴⁷

Thermomechanical studies were performed according to ISO 11359-1:1999 “Plastics. Thermomechanical analysis (TMA). Part 1. General principles”. The essence of this method is the determination of polymer sample deformation under the action of a permanent load, which is registered as a function of temperature in the form of thermomechanical curves (TMC).⁴⁷ TMC was obtained on a Höppler consistometer by recording the deformation of the sample (4 mm thick tablets) due to the action on the rod (area 23.7 mm²) of a load of 5.0 kg. The initial temperature of the study was 293 K. Subsequent deformation measurements were carried out after increasing the temperature every 3 K. The heating rate was set to \approx 1 K/min. The deformation of the samples (ε) was determined by the formula:

$$\varepsilon = \frac{\Delta l}{h} \cdot 100 \% = \frac{l - l_0}{h} \cdot 100 \% \quad (1)$$

where l_0 is load-free indicator readings (before lowering the rod), mm; l is indicator readings after 10 s of exposure under load, mm; h is tablet height, mm.

Dynamic mechanical characteristics, the tangent of an angle of mechanical losses $\text{tg } \delta$, was studied by dynamic mechanical thermal analysis (DMTA) with the help of a rheometer – Rheometric ARES (Advanced Rheometric Expansion System) (Rheometric Scientific, Inc., Piscataway, N.J., USA), using resilient oscillating deformation with a frequency of 1 Hz in the temperature range of 298...473 K and a heating rate of 3 K/min.⁴⁷

3. Results and Discussion

Previous works proved the formation of a spatially crosslinked structure of copolymers based on pHEMA-gr-PVP.^{36,46} It was found that during polymerization, co-

polymers with different crosslinking densities can be formed. There are no sharp boundaries between linear, branched, and spatially crosslinked macromolecules; in the synthesis process they are sometimes formed simultaneously. Depending on the crosslinking density, which can be characterized by the number of nodes per volume unit or the average distance between neighboring nodes, macro- and micro-network (lightly crosslinked) polymers are distinguished. In the case of metal-filled copolymers, MF particles act as additional crosslinking nodes.⁴⁷ It was found that the presence of MF particles affects the formation of the structure and properties of composites. Since the filler contributes to the formation of a polymer network with a higher crosslinking frequency, this effect will naturally be manifested in the thermal and physical characteristics of the resulting composites.

The heat resistance of materials in this work was evaluated by the Vick softening temperature, and the phase transitions of the polymers were evaluated using thermomechanical curves (TMC) and DMTA. Fig. 1a shows the temperature dependence of the deformation and heat resistance of the pHEMA-gr-PVP copolymer and copolymers filled with metals of various natures.

The initial section of TMC corresponds to the temperature region of the glassy state, where the energy of thermal motion of macromolecules is insufficient for the manifestation of deformation under load. Accordingly, at low temperatures (up to the glass transition temperature T_g), only small reverse deformations are observed for polymers in the glassy state. The region of the curve characterized by a sharp increase in deformation in a narrow temperature range corresponds to the structural transition of the system from a glassy state to a highly elastic one. The addition of MF to the copolymer in every case (Fig. 1a, curves 2-5) helps to shift the glass transition temperature to higher values compared to the unfilled pHEMA-gr-PVP copolymer (Fig. 1a, curve 1). The presence of metal particles is the reason for the formation of copolymers with a higher de-

gree of crosslinking, which indicates the formation of an additional spatial network due to the formation of physical nodes, the elements of which can be metal particles.⁴⁷ The introduction of finely dispersed metal particles of various natures into the copolymer composition has a different effect on reducing the relative deformation of the samples and increasing T_g . The glass transition temperature increases from 358 K for the unfilled copolymer to 395 K for the nickel-filled composite. During the introduction of metals into the composition formulation, the degree of deformation for all samples decreases.

TMC analysis allows to determine the glass transition temperatures of copolymers, which have been found to correlate with the glass transition temperatures obtained using dynamic mechanical thermal analysis. DMTA is especially relevant for the study of filled polymer systems, as it makes it possible to detect the influence of the presence of MF particles on the change in the mobility of macromolecules in the boundary surface layers. As a result of adsorption phenomena at the interface between the binder/filler phases, the molecular mobility of the system components changes, which affects the change in the nature of the relaxation processes. The results of DMTA are presented in the form of curves in the temperature dependence of the mechanical losses tangent ($\text{tg } \delta$) (Fig. 1b).

As in the case of TMC, temperature transitions of metal-filled composites, compared to unfilled ones (Fig. 1b, curve 1), are significantly shifted towards higher temperatures. The T_g value of the polymer corresponds to the peak on the curves of the angle of mechanical losses tangent vs. temperature. A specific feature of the obtained composites is the presence of two maxima on the dependence $\text{tg } \delta = f(T)$ (Fig. 1b, curves 2, 3, 4). The presence of two maxima is evidence of the existence of a different structure of the polymer matrix in the interfacial layer on the surface of the metal particle and in the volume.

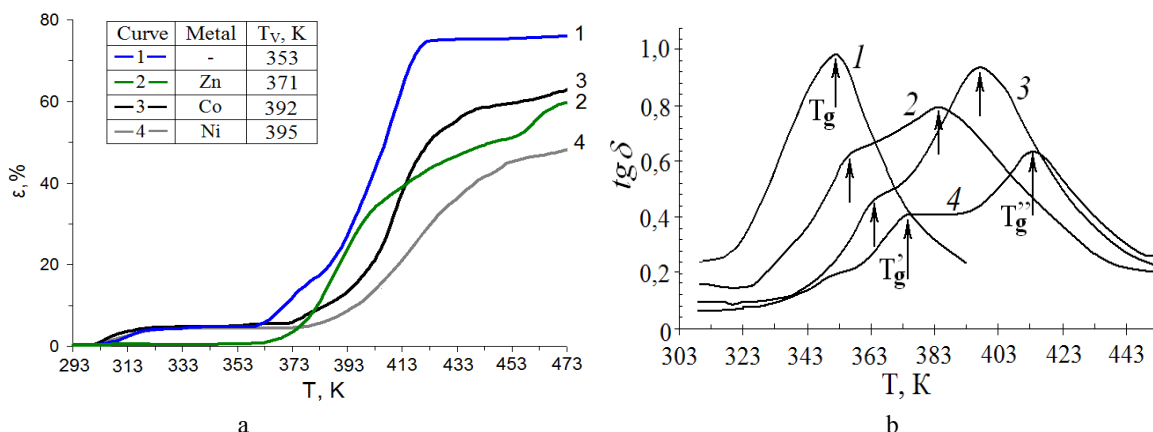


Fig. 1. The effect of the metal nature on the temperature dependence of deformation, Vick heat resistance (a) and the mechanical loss tangent (b) of pHEMA-gr-PVP copolymers (HEMA:PVP=80:20 mass parts; $[Me]=10$ wt.%): 1 – no metal; 2 – Zn; 3 – Co; 4 – Ni

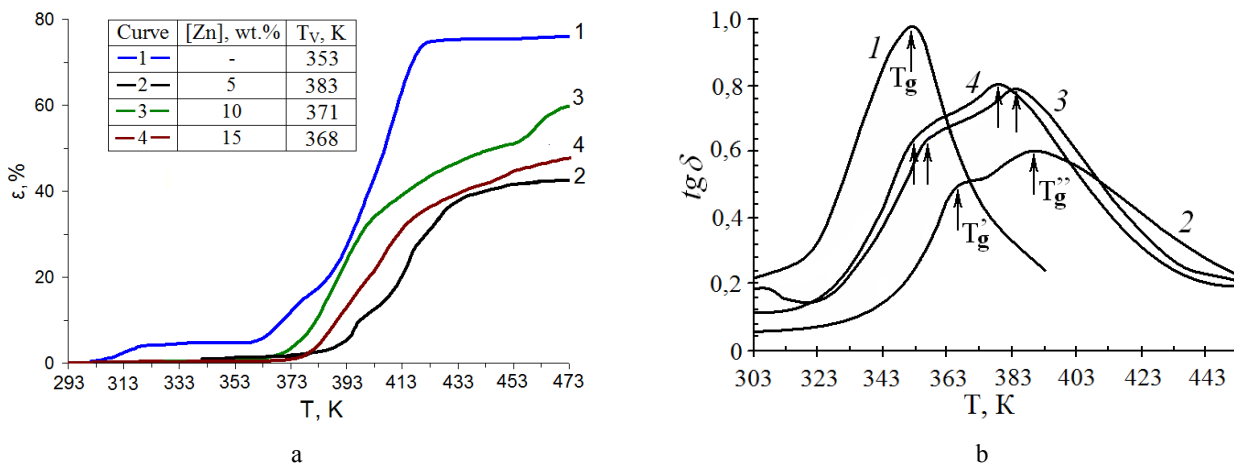


Fig. 2. The effect of Zn content on the temperature dependence of deformation, Vick heat resistance (a) and the tangent of the mechanical loss angle (b) of pHEMA-gr-PVP copolymers (HEMA:PVP= 80:20 mass parts): 1 – no filler; 2 – 5 wt.%; 3 – 10 wt.%; 4 – 15 wt. %

On the curves $tg \delta = f(T)$, the glass transition temperature in the volume of the polymer matrix is marked as T_g' , and the glass transition temperature at the phase boundary as T_g'' . By analyzing the obtained dependences of the mechanical losses tangent, it is possible to draw a conclusion about the effect of the metal nature on the formation of the polymer matrix.

The addition of 10 wt.% of metal to the copolymer composition, in any case, compared to the unfilled material, is accompanied by an increase in the Vick heat resistance. It was found that the glass transition temperature and T_V of pHEMA-gr-PVP copolymers increase in the presence of small amounts of MF (Fig. 1b). However, a further increase in the metal content causes a decrease in T_g and T_V . The obtained DMTA results for copolymers with different zinc contents (Fig. 2b) show that a small increase in the filler content slightly decreases the intensity of the $tg \delta$ peak. However, after reaching a certain MF content, there is an increase in $tg \delta$ and a shift of the

maxima to the region of lower temperatures, which indicates an increase in segmental mobility and a decrease in $T_g' > T_g''$ due to the heterogeneity of the system. Structural changes that cause increased flexibility of macromolecules, usually contribute to lower glass transition temperature. The obtained results are correlated with T_V changes depending on the metal content (Fig. 2a).

One of the main factors affecting the thermo-physical characteristics of the obtained metal-filled composites is the formulation of the original composition. Block copolymers have a fairly high heat resistance, which increases with the increase in PVP content in the composition (Fig. 3a). For each test sample, no transition of the copolymer into a viscous state is observed, which confirms the formation of a crosslinked copolymer. With an increase in the PVP content for zinc-filled materials, a shift in the transition temperature from the glassy state to the highly elastic state towards the region of higher temperatures is observed (Fig. 3b).

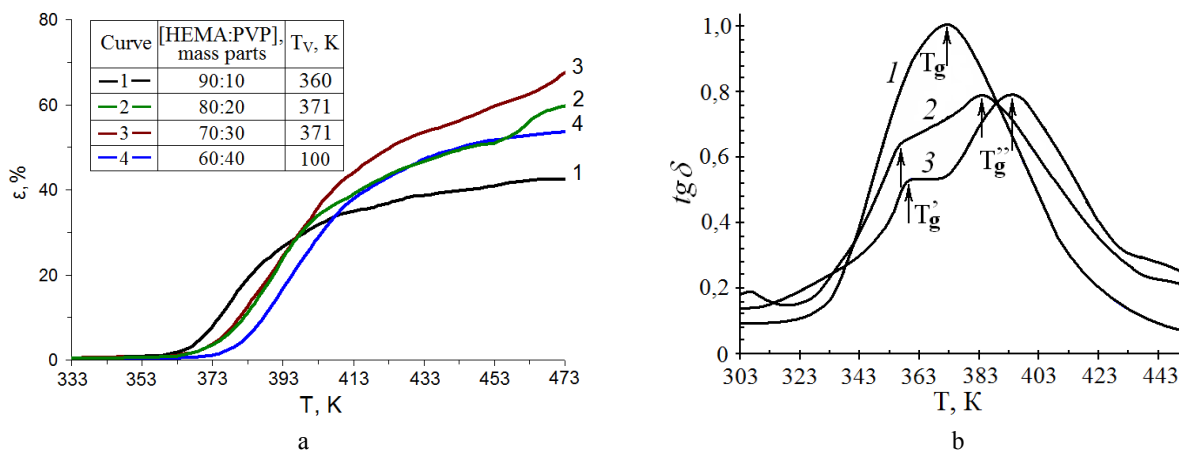


Fig. 3. The effect of the original composition formulation on the temperature dependence of the deformation, the Vick heat resistance (a) and the mechanical loss tangent (b) of metal-filled pHEMA-gr-PVP copolymers ([Zn]=10wt.%) Composition formulation HEMA:PVP, mass parts: 1 – 90:10; 2 – 80:20; 3 – 70:30; 4 – 60:40

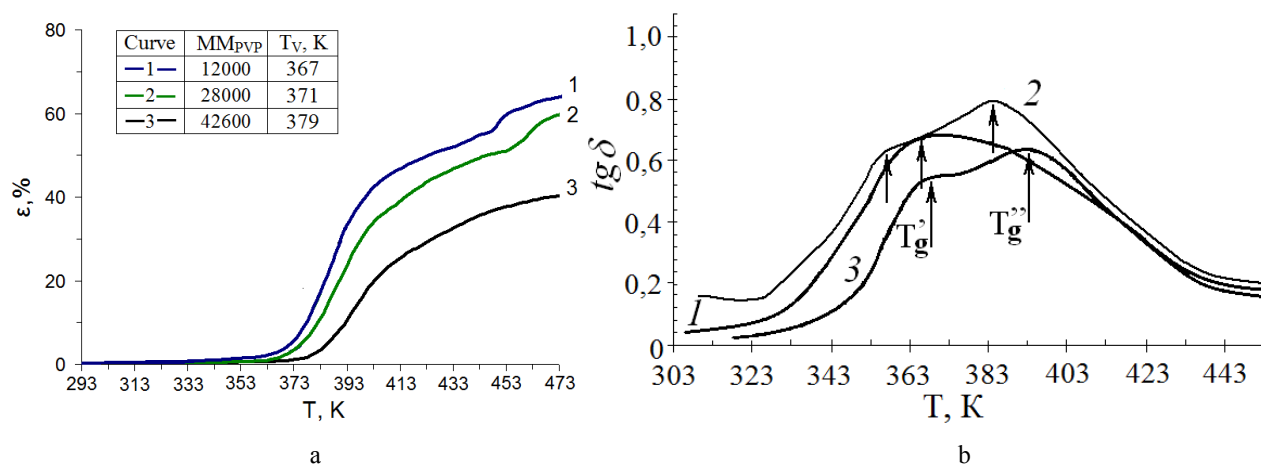


Fig. 4. The effect of MW_{PVP} on the temperature dependence of deformation, Vick heat resistance (a) and the tangent of the mechanical loss angle $tg\delta$ (b) of metal-filled pHEMA-gr-PVP copolymers: ($[Zn]=10$ wt.%; HEMA:PVP=80:20 mass parts): 1 – $12 \cdot 10^3$; 2 – $28 \cdot 10^3$; 3 – $42,6 \cdot 10^3$

From the obtained dependences, it can be concluded that the metal-filled pHEMA-gr-PVP copolymer, which contains a minimum content of PVP, is characterized by the homogeneity of the structure, which is confirmed by one peak on the curve $tg\delta=f(T)$ (Fig. 3b, curve 1). Therefore, the copolymerization of HEMA/PVP compositions with a small amount of PVP occurs without phase separation of the polymer matrix. For composites obtained by polymerization of compositions with a PVP content of more than 20 mass parts, the temperature dependence curve of $tg\delta$ is characterized by the presence of two maxima (Fig. 3b, curves 2, 3). At the same time, an increase in the PVP content in the original composition has little effect on the glass transition temperature change at constant filler content.

For copolymers synthesized on the PVP basis with a higher molecular weight, the increase in T_V (Fig. 4a) and glass transition temperature is observed, which is confirmed by both TMC (Fig. 4a) and DMTA results (Fig. 4b).

A shift in the glass transition temperature to higher temperatures indicates the formation of a more structured copolymer.

4. Conclusions

It was established that the modification of pHEMA-gr-PVP copolymers by filling them with finely dispersed metal powders improves their thermo-physical characteristics. Depending on the nature and content of the metal filler, the heat resistance of copolymers increases by 10–40 K compared to unfilled copolymers and lays in the range of 360–395 K. The change in heat resistance correlates with the change in the glass transition temperature: the addition of metal filler to the copolymer in every case contributes to the shift of the glass transition

temperature to the region of higher temperatures compared to the unfilled copolymer. Composites filled with nickel have the best thermo-physical properties, and the composites filled with zinc have the worst. At the same time, the results of this work can be used to characterize the structure of metal-filled copolymers. In particular, the conducted studies confirm the synthesis of spatially crosslinked pHEMA-gr-PVP copolymers, as well as the participation of metal filler particles in the formation of additional nodes in the spatial network of the copolymer. With the help of DMTA, it was proved that in the presence of metal particles, a different structure of the polymer network is formed in the interphase layer on the surface of the metal particle and in the volume of the polymer. The obtained results provide an additional opportunity for the controlled synthesis of metal-filled pHEMA-gr-PVP copolymers with the required structure and, accordingly, a set of properties.

References

- [1] Nicolais, L.; Carotenuto, G. *Metal-polymer nanocomposites*; John Wiley & Sons: Hoboken, NJ, USA, 2005.
- [2] Kucherenko, A.; Nikitchuk, O.; Baran, N.; Dulebova, L.; Kuznetsova, M.; Moravskiy, V. Characteristics of Metallized Polymeric Raw Materials. In *Proceedings of the 2021 IEEE 11th International Conference Nanomaterials: Applications & Properties (NAP)*; IEEE: Odessa, 2021. <https://doi.org/10.1109/NAP51885.2021.9568393>
- [3] Saeed, A.; Zaaba, N.; Ismeel, H. A Review: Metal Filled Thermoplastic Composites. *POLYM-PLAST TECH MAT* **2021**, *60*, 1033–1050. <https://doi.org/10.1080/25740881.2021.1882489>
- [4] Hevus, I.; Kohut, A.; Voronov, A. Amphiphilic Invertible Polyurethanes: Synthesis and Properties. *Macromolecules* **2010**, *43*, 7488–7494. <https://doi.org/10.1021/ma101175k>
- [5] Los, P.; Lukomska, A.; Jeziorska, R. Metal-Polymer Composites for Electromagnetic Interference Shielding Applications. *Polimery*

- 2021**, *61*, 663–669. <https://doi.org/10.14314/polimery.2016.663>
- [6] Sapronov, O.; Buketov, A.; Yakushchenko, S.; Syzonenko, O.; Sapronova, A.; Sotsenko, V.; Vorobiov, P.; Lypian, Y.; Sieliverstov, I.; Dobrotvor, I. Application of Synthesized Iron/Titanium Carbide Mixture for Restoration of Water Transport Parts by Epoxy Composites. *Composites: Mechanics, Computations, Applications: An International Journal* **2021**, *12*, 23–35. <https://doi.org/10.1615/CompMechComputAppIntJ.2021039175>
- [7] Moravskiy, V.; Kucherenko, A.; Kuznetsova, M.; Dulebova, L.; Spišák, E. Obtainment and Characterization of Metal-Coated Polyethylene Granules as a Basis for the Development of Heat Storage Systems. *Polymers* **2022**, *14*, 218. <https://doi.org/10.3390/polym14010218>
- [8] Yaman, K. Fractal Characterization of Electrical Conductivity and Mechanical Properties of Copper Particulate Polyester Matrix Composites Using Image Processing. *Polym. Bull.* **2022**, *79*, 3309–3332. <https://doi.org/10.1007/s00289-021-03665-2>
- [9] Buketov, A.V.; Bagliuk, G.A.; Sizonenko, O.M.; Sapronov, O.O.; Smetankin, S.O.; Torpakov, A.S. Effect of Particulate Ti–Al–TiC Reinforcements on the Mechanical Properties of Epoxy Polymer Composites. *Powder Metall. Met. Ceram.* **2023**, *61*, 586–596. <https://doi.org/10.1007/s11106-023-00347-8>
- [10] Moravskiy, V.; Kucherenko, A.; Kuznetsova, M.; Dulebova, L.; Spišák, E.; Majerníková, J. Utilization of Polypropylene in the Production of Metal-Filled Polymer Composites: Development and Characteristics. *Materials* **2020**, *13*, 2856. <https://doi.org/10.3390/ma13122856>
- [11] Mehvari, S.; Sanchez-Vicente, Y.; González, S.; Lafdi, K. Conductivity Behaviour under Pressure of Copper Micro-Additive/Polyurethane Composites (Experimental and Modelling). *Polymers* **2022**, *14*, 1287. <https://doi.org/10.3390/polym14071287>
- [12] Wang, L.; Wang, H.; Huang, X.W.; Song, X.; Hu, M.; Tang, L.; Xue, H.; Gao, J. Superhydrophobic and Superelastic Conductive Rubber Composite for Wearable Strain Sensors with Ultrahigh Sensitivity and Excellent Anti-Corrosion Property. *J. Mater. Chem. A* **2018**, *6*, 24523–24533. <https://doi.org/10.1039/c8ta07847e>
- [13] Li, H.; Yang, P.; Pageni, P.; Tang, C. Recent Advances in Metal-Containing Polymer Hydrogels. *Macromol. Rapid Commun.* **2017**, *38*, 1700109. <https://doi.org/10.1002/marc.201700109>
- [14] Grytsenko, O.; Dulebova, L.; Spišák, E.; Pukach, P. Metal-Filled Polyvinylpyrrolidone Copolymers: Promising Platforms for Creating Sensors. *Polymers* **2023**, *15*, 2259. <https://doi.org/10.3390/polym15102259>
- [15] Kucherenko, A.N.; Moravskiy, V.S.; Kuznetsova, M.Y.; Grytsenko, O.N.; Masyuk, A.S.; Dulebova, L. Regularities of Obtaining Metal-Filled Polymer Composites. In *Nanomaterials in biomedical application and biosensors (NAP-2019)*; Pogrebnjak, A.; Pogorelov, M.; Viter, R., Eds; Springer Proceedings in Physics, vol. 244; Springer: Singapore, 2020; pp. 59–66. https://doi.org/10.1007/978-981-15-3996-1_6
- [16] Hevus, I.; Kohut, A.; Voronov, A. Micellar Assemblies from Amphiphilic Polyurethanes for Size-Controlled Synthesis of Silver Nanoparticles Dispersible both in Polar and Nonpolar Media. *J. Nanopart. Res.* **2012**, *14*, 820. <https://doi.org/10.1007/s11051-012-0820-x>
- [17] El-Shamy, A.G. Polymer/Noble Metal Nanocomposites. In *Nanocomposites – Recent Evolutions*; Sivasankaran, S., Ed.; IntechOpen, London, 2019. <https://doi.org/10.5772/intechopen.79016>
- [18] Khatri, B.; Lappe, K.; Noetzel, D.; Pursche, K.; Hanemann, T. A 3D-Printable Polymer-Metal Soft-Magnetic Functional Composite-Development and Characterization. *Materials* **2018**, *11*, 189. <https://doi.org/10.3390/ma11020189>
- [19] Burhannuddin, N.L.; Nordin, N.A.; Mazlan, S.A. Physico-chemical Characterization and Rheological Properties of Magnetic Elastomers Containing Different Shapes of Corroded Carbonyl Iron Particles. *Sci. Rep.* **2021**, *11*, 868. <https://doi.org/10.1038/s41598-020-80539-z>
- [20] Amoabeng, D.; Velankar, S. A Review of Conductive Polymer Composites Filled with Low Melting Point Metal Alloys. *Polym. Eng. Sci.* **2017**, *58*, 1010–1019. <https://doi.org/10.1002/pen.24774>
- [21] Grujić, A.; Stajić-Trošić, J.; Stijepović, M.; Stevanović, J.; Aleksić, R. Magnetic and Dynamic Mechanical Properties of Nd-Fe-B Composite Materials with Polymer Matrix. In *Metal, Ceramic and Polymeric Composites for Various Uses*; Cuppoletti, J., Ed.; InTechOpen: Rijeka, Croatia, 2011; pp. 524–526. <https://doi.org/10.5772/18599>
- [22] Ranga Reddy, P.A.; Mohana Raju, K.; Subbarami Reddy, N. A Review on Polymer Nanocomposites: Monometallic and Bimetallic Nanoparticles for Biomedical, Optical and Engineering Applications. *Chem. Sci. Rev. Lett.* **2013**, *1*, 228–235.
- [23] Rozik, N.; Asaad, J.; Mansour, S.; Gomaa, E. Effect of Aluminum and Aluminum/Nickel Hybrid Fillers on the Properties of Epoxy Composites. *Proc. Inst. Mech. Eng. L* **2016**, *230*, 550–557. <https://doi.org/10.1177/1464420715581523>
- [24] Kohut, A.; Voronov, A.; Samaryk, V.; Peukert, W. Amphiphilic Invertible Polyesters as Reducing and Stabilizing Agents in the Formation of Metal Nanoparticles. *Macromol. Rapid Commun.* **2007**, *28*, 1410–1414. <https://doi.org/10.1002/marc.200700312>
- [25] Moravskiy, V.; Kucherenko, A.; Kuznetsova, M.; Dziaman, I.; Grytsenko, O.; Dulebova, L. Studying the Effect of Concentration Factors on the Process of Chemical Metallization of Powdered Polyvinylchloride. *East. Eur. J. Enterp. Technol.* **2018**, *3*, 40–47. <https://doi.org/10.15587/1729-4061.2018.131446>
- [26] Kuntiyi, O.; Mazur, A.; Kytysya, A.; Karpenko, O.; Bazylyak, L.; Mertsalo, I.; Pokynbroda, T.; Prokopalo, A. Electrochemical Synthesis of Silver Nanoparticles in Solutions of Rhamnolipid. *Micro Nano Lett.* **2020**, *15*, 802–807. <https://doi.org/10.1049/mnl.2020.0195>
- [27] Reverberi, A.P.; Salerno, M.; Lauciello, S.; Fabiano, B. Synthesis of Copper Nanoparticles in Ethylene Glycol by Chemical REDUCTION with Vanadium (+2) Salts. *Materials* **2016**, *9*, 809. <https://doi.org/10.3390/ma9100809>
- [28] Tarnavchuk, I.; Voronov, A.; Kohut, A.; Nosova, N.; Varvarenko, S.; Samaryk, V.; Voronov, S. Reactive Hydrogel Networks for the Fabrication of Metal-Polymer Nanocomposites. *Macromol. Rapid Commun.* **2009**, *30*, 1564–1569. <https://doi.org/10.1002/marc.200900285>
- [29] Grytsenko, O.; Naumenko, O.; Suberlyak, O.; Dulebova, L.; Berezhnyy, B. Optimization of the Technological Parameters of the Graft Copolymerization of 2-Hydroxyethyl Methacrylate with Polyvinylpyrrolidone for Nickel Deposition from Salts. *Vopr. Khimii i Khimicheskoi Tekhnologii* **2020**, *1*, 25–32. <https://doi.org/10.32434/0321-4095-2020-128-1-25-32>
- [30] Moravskiy, V.; Dziaman, I.; Suberliak, S.; Grytsenko, O.; Kuznetsova, M. Features of the Production of Metal-Filled Composites by Metallization of Polymeric Raw Materials. In *2017 IEEE 7th International Conference Nanomaterials: Application & Properties (NAP)*; IEEE: Odessa, Ukraine, 2017. <https://doi.org/10.1109/NAP.2017.8190265>
- [31] Chudzik, J.; Bieliński, D.M.; Bratychak, M.; Demchuk, Y.; Astakhova, O.; Jędrzejczyk, M.; Celichowski, G. Influence of Modified Epoxy Resins on Peroxide Curing, Mechanical Properties and Adhesion of SBR, NBR and XNBR to Silver Wires. Part I: Application of Monoperoxy Derivative of Epoxy Resin (PO).

- Materials* **2021**, *14*, 1320. <https://doi.org/10.3390/ma14051320>
- [32] Sahiner, N.; Butun, S.; Ozay, O.; Dibek, B. Utilization of Smart Hydrogel-Metal Composites as Catalysis Media. *J. Colloid Interface Sci.* **2012**, *373*, 122–128. <https://doi.org/10.1016/j.jcis.2011.08.080>
- [33] Veerubhotla, K.; Lee, C.H. Design of Biodegradable 3D-Printed Cardiovascular Stent. *Bioprinting* **2022**, *26*, e00204. <https://doi.org/10.1016/j.bprint.2022.e00204>
- [34] Echeverria, C.; Fernandes, S.N.; Godinho, M.H.; Borges, J.P.; Soares, P.I.P. Functional Stimuli-Responsive Gels: Hydrogels and Microgels. *Gels* **2018**, *4*, 54. <https://doi.org/10.3390/gels4020054>
- [35] Pablos, J.L.; Jiménez-Holguín, J.; Salcedo, S.S.; Salinas, A.J.; Corrales, T.; Vallet-Regí, M. New Photocrosslinked 3D Foamed Scaffolds Based on Gelma Copolymers: Potential Application in Bone Tissue Engineering. *Gels* **2023**, *9*, 403. <https://doi.org/10.3390/gels9050403>
- [36] Suberlyak, O.; Skorokhoda, V. Hydrogels Based on Polyvinylpyrrolidone Copolymers. In *Hydrogels*; Haider, S.; Haider, A., Eds.; IntechOpen: London, United Kingdom, 2018; pp. 136–214. <https://doi.org/10.5772/intechopen.72082>
- [37] Khan, S.; Ullah, A.; Ullah, K.; Rehman, N. Insight into Hydrogels. *Des Monomers Polym* **2016**, *19*, 456–478. <http://dx.doi.org/10.1080/15685551.2016.1169380>
- [38] Jumadilov, T.; Abilov, Z.; Kondauron, R.; Himersen, H.; Yeskalieva, G.; Akylbekova, M.; Akimov, A. Influence of Hydrogels Initial State on their Electrochemical and Volume-Gravimetric Properties in Intergel System Polyacrylic Acid Hydrogel and Poly-4-vinylpyridine Hydrogel. *Chem. Chem. Technol.* **2015**, *9*, 459–462. <https://doi.org/10.23939/chcht09.04.459>
- [39] Gibas, I.; Janik, H. Review: Synthetic Polymer Hydrogels for Biomedical Applications. *Chem. Chem. Technol.* **2010**, *4*, 297–304. <https://doi.org/10.23939/chcht04.04.297>
- [40] Maikovyich, O.; Nosova, N.; Yakoviv, M.; Dron, I.; Stasiuk, A.; Samaryk, V.; Voronov, S. Composite Materials Based on Polyacrylamide and Gelatin Reinforced with Polypropylene Microfiber. *Vopr. Khimii i Khimicheskoi Tekhnologii* **2021**, *1*, 45–54.
- [41] Majcher, M.J.; Hoare, T. Applications of Hydrogels. In *Functional Biopolymers. Polymers and Polymeric Composites: A Reference Series*; Jafar Mazumder, M.; Sheardown, H.; Al-Ahmed, A., Eds.; Springer, Cham, 2019; pp 453–490. https://doi.org/10.1007/978-3-319-95990-0_17
- [42] Bercea, M. Bioinspired Hydrogels as Platforms for Life-Science Applications: Challenges and Opportunities. *Polymers* **2022**, *14*, 2365. <https://doi.org/10.3390/polym14122365>
- [43] Zhang, Y.S.; Khademhosseini, A. Advances in Engineering Hydrogels. *Science* **2017**, *356*, eaaf3627. <https://doi.org/10.1126/science.aaf3627>
- [44] Dong, W.; Yao, D.; Yang, L. Soft Bimodal Sensor Array Based on Conductive Hydrogel for Driving Status Monitoring. *Sensors* **2020**, *20*, 1641. <https://doi.org/10.3390/s20061641>
- [45] Samaryk, V.; Varvarenko, S.; Nosova, N.; Fihurka, N.; Musyanovych, A.; Landfester, K.; Popadyuk, N.; Voronov, S. Optical Properties of Hydrogels Filled with Dispersed Nanoparticles. *Chem. Chem. Technol.* **2017**, *11*, 449–453. <https://doi.org/10.23939/chcht11.04.449>
- [46] Grytsenko, O.; Dulebova, L.; Suberlyak, O.; Skorokhoda, V.; Spišák, E.; Gajdos, I. Features of Structure and Properties of pHEMA-gr-PVP Block Copolymers, Obtained in the Presence of Fe²⁺. *Materials* **2020**, *13*, 4580. <https://doi.org/10.3390/ma13204580>
- [47] Grytsenko, O.; Dulebova, L.; Spišák, E.; Berezhnyy, B. New Materials Based on Polyvinylpyrrolidone-Containing Copolymers with Ferromagnetic Fillers. *Materials* **2022**, *15*, 5183. <https://doi.org/10.3390/ma15155183>
- [48] Grytsenko, O.; Pukach, P.; Suberlyak, O.; Moravskiy, V.; Kovalchuk, R.; Berezhnyy, B. The Scheffé's Method in the Study of Mathematical Model of the Polymeric Hydrogels Composite Structures Optimization. *Math. Model. Comput.* **2019**, *6*, 258–267. <https://doi.org/10.23939/mmc2019.02.258>
- [49] Grytsenko, O.; Pukach, P.; Suberlyak, O.; Shakhovska, N.; Karovič Jr., V. Usage of Mathematical Modeling and Optimization in Development of Hydrogel Medical Dressings Production. *Electronics* **2021**, *10*, 620. <https://doi.org/10.3390/electronics10050620>
- [50] Suberlyak, O.; Grytsenko, O.; Baran, N.; Yatsulchak, G.; Berezhnyy, B. Formation Features of Tubular Products on the Basis of Composite Hydrogels. *Chem. Chem. Technol.* **2020**, *14*, 312–317. <https://doi.org/10.23939/chcht14.03.312>

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ТЕПЛОФІЗИЧНІ ВЛАСТИВОСТІ КОМПОЗИЦІЙНИХ МЕТАЛОНАПОВНЕНИХ КОПОЛІМЕРІВ ПОЛІВІНІЛПІРОЛІДОНУ

Анотація. Досліджено вплив присутності дрібнодисперсних металевих наповнювачів різної природи (Zn, Co, Ni) на теплофізичні характеристики (теплостійкість за Віка, температура склування) блочних кополімерів полівінілпіролідону з 2-гідроксіетилметакрилатом. Встановлено, що теплостійкість одержаних композитів є значно вищою за теплостійкість ненаповнених кополімерів і лежить у межах 360–395K залежно від природи та вмісту металевих наповнювачів. Зміна теплостійкості корелює зі зміною температури склування, яку оцінювали на основі результатів термомеханічного та динамічного механічного термічного аналізів. Результати роботи є додатковим джерелом характеристики структури металонаповнених кополімерів і підтверджують участь частинки металевих наповнювачів у формуванні вузлів просторової сітки кополімеру, а також доводять факт утворення різної структури полімерної сітки в міжфазному шарі на поверхні металевих частинки і в об'ємі полімеру.

Ключові слова: полівінілпіролідон, 2-гідроксіетилметакрилат, кополімери, металонаповнені полімери, теплостійкість, температура склування.