МІНІСТЕРСТВО ОСВІТИ І НАУКИ УКРАЇНИ

Національний університет “Львівська політехніка”,
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ДВНЗ “Український державний хіміко-технологічний університет”,
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Гуманітарно-технологічний університет ім. Казіміра Пулацького,
Радом, Польща

# X Українсько-польська наукова конференція «Полімери спеціального призначення»

Львів, 21-24 вересня 2020

Тези доповідей

Lviv Polytechnic National University,
Lviv, Ukraine
SHEI “Ukrainian State Chemical Technology University”,
Dnipro, Ukraine
Kazimierz Pulaski University of Humanities and Technology,
Radom, Poland

# X Ukrainian-Polish Scientific conference “Polymers of special applications”

Lviv, September 21-24, 2020

Theses of the reports

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Польща

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# Х Українсько-польської наукової конференції
# «ПОЛІМЕРИ СПЕЦІАЛЬНОГО ПРИЗНАЧЕННЯ»

*Львів, 21-24 вересня 2020*

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2. Technology of polymeric and composite materials.
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# HYDROGEL FILMS STRENGTHENED IN VOLUME THROUGH THE MATRIX POLYMERIZATION

Baran N.M., Suberlyak O.V., Melnyk Yu.Ya, Grytsenko O.M., Kos P.

*Department of Plastic Engineering, Lviv Polytechnic National University, Ukraine, Lviv, 12, St. Bandera str.*

The recent developments and studies in the membrane and polymer engineering are focused on the ways to improve the properties of the known synthetic materials. The leading role in the current research is occupied by the forming of the new composite membranes with functional polymer hydrogels. The combination of the soft polymer hydrogels and rigid polymer membranes properties by the modification technique enables the application of their functionality in the unique manner. Implementing them in one material will result in the large number of further composite system variations.

The forming of strengthened in volume composite hydrogel membranes by matrix polymerization of 2-hydroxyethyl methacrylate (HEMA) and polyvinylpyrrolidone (PVP) reactive compositions has been proposed.

The composite polyamide-hydrogel membranes were created by the polymerization of 2-hydroxyethyl methacrylate (HEMA) and polyvinylpyrrolidone in the presence of potassium persulfate (PPS) initiator and polyamide-polyvinylpyrrolidone complex (PA-6/PVP). The polymerization was performed in the aqueous formic acid solution.

In order to develop the forming technique of strengthened in volume composite polymer membranes, the influence of the reactive composition content, concentration of PA-6/PVP complex in the reactive solution on the physical mechanical properties and osmotic penetration of obtained membranes were investigated.

It has been shown that the created strengthened in volume hydrogel films exhibit the enhanced strength with simultaneously preserved the high osmotic penetration comparable with the initial hydrogel.

Established that the variation in the hydrogel composition  and modifying polymer mixture allow a controlled regulation of the composite membrane properties in the wide range which extends the application capabilities depend on the conditions.

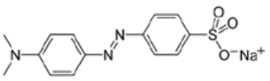
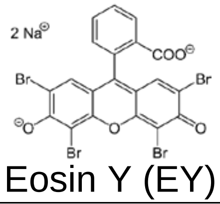
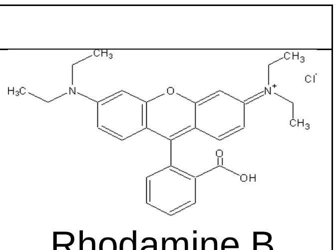
# Ni-Al LAYERED DOUBLE HYDROXIDES SORBENT FOR DECONTAMINATION OF AQUEOUS MEDIA FROM ORGANICS

Bei I., Tolstov O., Slisenko O., Budzinska V.

*Institute of Macromolecular Chemistry of the NAS of Ukraine, Kyiv, Ukraine*

Layered natural and synthetic minerals are prominent materials for using as high performance sorbents due to their appropriate functionality and developed surface. Native or artificial functionality of these sorbents generally promotes a non-selective overall sorption capacity or, in some cases, defined selectivity against to the pollutants of specific chemical structure. Layered double hydroxides (LDH) are synthetic clay-like sorbents with inherent positive charge of the layers. This phenomenon originates from the defects of combined crystal lattice formed by both di- and trivalent metal ions [1]. It is expected that positively charged LDH could be efficient sorbents for anionic type pollutants, namely anionic dyes.

In this work LDH was synthesized by coupling $Ni(OH)_2$ and $Al(OH)_3$ derived from soluble precursors with Ni to Al molar ratio of 2:1 using common procedure [2]. Briefly, mixed solution of $Ni^{2+}$ and $Al^{3+}$ was dropped into sodium carbonate solution under vigorous stirring. The pH 10 was maintained constant by the addition of NaOH. Resulting suspension was kept at 85°C for 6 hrs under vigorous stirring. The precipitate was washed with deionized water and dried at 100°C. The adsorption properties of prepared sorbent as regard to three anionic dyes of different chemical nature were studied.

| Parameters | Dye | | |
|---|---|---|---|
| |  Methyl orange (MO) |  Eosin Y (EY) |  Rhodamine B (RB) |
| Initial concentration, $mmol \cdot L^{-1}$ | 0.05 | 0.05 | 0.025 |
| Adsorption capacity, $mmol \cdot g^{-1}$ | 0.121 | 0.109 | 0.0025 |

Three anionic dyes such as methyl orange, eosin Y and rhodamine B were applied as model compounds for adsorption tests. The results regarding chemical structure of the dyes are summarized in the table.

One can see that adsorption capacity of anionic methyl orange and eosin Y dyes is quite high (40 mg for MO and 75 mg for EY per one gram of sorbent). Moreover, MO dye with more acidic sulfonate groups is characterized by higher level of adsorption capacity. Otherwise, cationic RB is slightly adsorbed by Ni-Al LDH (~1 mg per gram) due to predominant Coulomb repulsion process between positively charged dye molecules and cationic sites of LDH. The synthesized Ni-Al LDH should be applied as efficient hydrogel fillers for purification of aqueous media from organic pollutants.

1. Q. Wang, D. *Chem. Rev.* 2012, Vol. 112(7). P. 4124-4155.
2. G. Starukh, O. Oranska, O. Rozovik. *Nanoscale Res Letts.* 2016. Vol. 11. P. 228-237.

# COMPOSITIONAL IMPACT ON SORPTION PROCESSES FOR LAYERED DOUBLE HYDROXIDES SORBENTS IN DECONTAMINATION OF WATER FROM SOLUBLE DYE

Bei I., Tolstov O., Slisenko O., Budzinska V.

*Institute of Macromolecular Chemistry of the NAS of Ukraine, Kyiv, Ukraine*

Novel advanced materials attract a great interest since their unique properties which could be tailored by variation of their composition, synthesis conditions and other technological parameters. Layered double hydroxides (LDHs), which are also well-known as hydrotalcite-like compounds or anionic clays, represent a class of synthetic layered materials of general formula [1]

$$[M^{II}_{1-x}M^{III}_{x}(OH)_2]^{x+}[An^{y-}_{x/y}\cdot zH_2O]^{x-},$$

where $M^{II}$ and $M^{III}$ are divalent and trivalent metal cations, respectively, $An^{y-}$ is an $y$-valent anion(s) and $x$ has values usually between 0.20 and 0.33. The lamellar structure and anion exchange capacity of LDH make them highly attractive for various technological applications such as inorganic ion-exchangers with improved stability, efficient adsorbent, dispersion stabilizers, catalysts etc.

Here three types of LDHs labelled by cationic composition as Ni-Al, Mg-Al and Zn-Al were synthesized using aluminum nitrate as a source of trivalent metal, and nickel, magnesium and zinc nitrates as precursors for divalent metal hydroxide. Typically, $Me^{2+}$ to $Me^{3+}$ molar ratio was taken as 2:1 for all LDHs obtained. To prepare double hydroxides dispersion the $Me^{2+}$ and $Me^{3+}$ salts was added dropwisely into aqueous solution of $Na_2CO_3$ under vigorous stirring according to [2]. The pH 10 was continuous adjusted by addition of NaOH solution. When the double hydroxides precipitation stage was finished a mixing resulting suspension was stirred for 6 hrs at 85°C to complete the reaction and aging processes resulted in structuration of LDHs. The precipitate was thoroughly washed with deionized water and dried at 100°C before further experiments. Methyl orange was used as model compound to compare a sorption activity of the LDHs synthesized. Initial concentration of the dye solution was 0.05 $mmol\cdot L^{-1}$. A 50 ml portion of dye solution was mixed with 20 mg of a sorbent under vigorous stirring for 6 hours. Amount of the dye adsorbed as mmol per one gram of sorbent was determined by photometry. It was revealed that overall sorption of the dye by Ni-Al LDH is up to two times higher comparing to other LDHs. We suppose a coupling Ni/Al ions provides efficient compaction of LDHs resulted in lower etching and higher adsorption level of LDH against strongly acidic anionic dye.

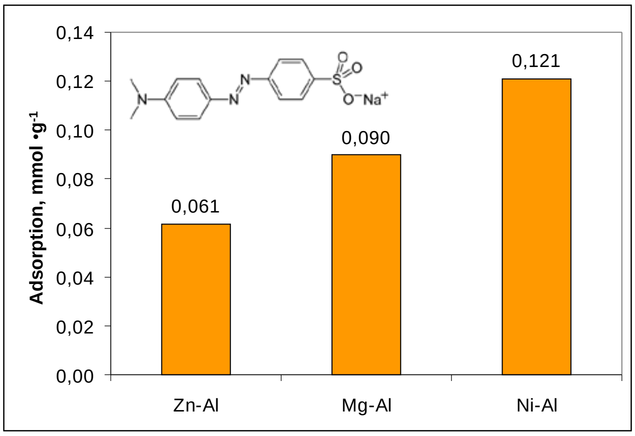


Fig. 1. Composition vs. specific adsorption dependence for all LDHs synthesized

1. F. Kovanda, E. Jindovб, K. Lang et al. *Appl. Clay Sci.* 2010. Vol. 48. P. 260-270.
2. G. Starukh, O. Oranska, O. Rozovik. *Nanoscale Res Letts.* 2016. Vol. 11. P. 228-237.

# COMPOSITE ADSORBENTS FOR ADSORPTIVE HEAT CONVERSION IN VENTILATION SYSTEMS

E.A. Belyanovskaya[1], R.D. Lytovchenko[1], K.M. Sukhyy[1], M.V. Gubinskyi[2], O.O. Yeromin [2], I.V. Sukha[1]

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Inflow air heating is one of the most significant expenditure items for heat supply of residential premises. As a rule for this purpose recuperative heat exchangers are used. However, these devices can be easily blocked with ice, hydrothermal balance of premise being badly disrupted. As promising alternative, regenerators of heat and moisture can be considered. Generally, these devices are based on sensible heat storage materials. So, they affect only temperature and relative humidity of the internal air. As most attractive variants, adsorptive heat-moisture regenerator or open-type heat storage device can be considered. However, design and performance of such devices are strongly determined by adsorbent properties.

The present work is focused on composite adsorbents for adsorptive heat converters in ventilation systems.

Efficiency of adsorptive regenerators based on composites ‘silica gel – sodium sulphate’ and ‘silica gel – sodium acetate’ have been compared when the inflow air warmed in the conditions of a residential apartment. It is shown that in the view of design most convenient materials are adsorbents with limit adsorption which surpass 0.5 kg/kg. Composites which involve 20% of silica gel and 80% of salt are shown to correspond with that requirement. However, composites ‘silica gel – sodium acetate’ occur to be inferior in adsorption and adsorption heat as compared with composites ‘silica gel – sodium acetate’ by a factor of 1.25–2.0. This leads to higher mass of ‘silica gel – $CH_3COONa$’ for supporting the same heat load compared to ‘silica gel – $Na_2SO_4$’. Then performance of adsorptive heat-moisture regenerators was simulated. The highest temperature efficiency factors of both devices based on composite ‘silica gel – sodium sulphate’ and ‘silica gel – sodium acetate’ are stated at airflow speeds of 0.22–0.32 m/s and the time of switching the flows at most of about 5 min. Regenerators based on composites ‘silica gel – sodium sulphate’ are stated to exceed by at least 9–10% the temperature efficiency factors of devices based on ‘silica gel – sodium acetate’. This difference decrease simultaneously when airflow speed, switching over time and difference between temperatures of internal and external air are diminished. Superior performance of regenerators based on ‘silica gel – $Na_2SO_4$’ is shown to result from higher value of maximal adsorption.

This work was supported by Ministry of Education and Science of Ukraine (grant number 0119U002243).

# SYNERGISTIC INFLUENCE OF THE POLYMER MATRIX AND Ni(0) PARTICLES ON THE FORMATION OF METAL-FILLED POLYVINYLPYRROLIDONE COPOLYMERS

[1]Berezhnyy B., [1]Grytsenko O., [1]Baran N., [2]Gaydos I.

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The great interest in metal-filled polymers and their spread in various fields of science and practice is caused by the presence of synergistic effects properties of the polymer matrix and the metal filler. Metal-filled materials based on polymer hydrogels deserve particular attention. Due to their electrical, magnetic and catalytic properties with the combination of the sorption capacity for solvents and low molecular weight compounds, composite hydrogels filled with (nano)particles of nickel are gaining the distribution. Nickel-filled composite copolymers of 2-hydroxyethylmethacrylate (HEMA) with polyvinylpyrrolidone (PVP) and hydrogels based on them were obtained by the methods of polymerization filling and polymerization with simultaneous chemical reduction of nickel ions [1]. The regularities of the mutual influence of the polymerization processes, the formation of nickel particles on the structure and properties of the polymer matrix and Ni(0) particles are investigated. The dependence of the peculiarities of the composite structure formation on the synergetic effects, which were caused by the interaction of the polymer matrix and the metal surface is established. Copolymers are characterized by a unique complex of properties, which is determined by the controlled structure of the formed polymer matrix and the nature of the metal-filler. The combination of polymer and metal phase improves the physico-mechanical, thermo-physical properties of copolymers, as well as gives them electrically conductive properties, catalytic abilities in hydrogen reduction reactions and magnetic susceptibility with small values of coercive force. The presence of Ni(0) particles in the polymer-monomer composition increases the rate of its polymerization, contributes the intensity of the grafting process of polyHEMA to PVP. It was found that Ni(0) particles play the role of additional nodes of the spatial polymer network, which effect on the formation of different cross-linked structure in the interfacial layer on the surface of the particle and in the volume of the polymer. In the presence of a polymer matrix, the reduction process of nickel ions already occur at 60ºC with a uniform distribution of nickel particles in the volume of the copolymer.

It is established that the properties' nature of the change of nickel-filled copolymers mainly depends on the method of introducing the filler into the polymer matrix, which is especially manifested in the composites’ sorption ability and electrical conductivity.

1. Grytsenko, O.; Gajdos, I.; Spišák, E.; Krasinskyi, V.; Suberlyak, O. Novel Ni/pHEMA-gr-PVP composites obtained by polymerization with simultaneous metal deposition: Structure and properties. *Materials*. **2019**, *12*, 1956.

# IMPACT ASSESSMENT OF MORINGA OIL USED AS A BIO-PLASTICIZER AGENT ON PROCESSING AND SELECTED PROPERTIES OF NATURAL RUBBER-BASED VULCANIZATES

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Due to the growing pro-environmental requirements, it is important to replace petrochemical raw materials with substrates obtained from renewable plant sources. The appropriate selection of the composition of the rubber mixture determines desired properties and the highest quality of the obtained material. This research has been undertaken in order to describe the process of producing natural rubber-based vulcanizates with the addition of *Moringa oleifera* seed oil (1, 3, 6, and 12 parts per hundred rubber) as a bio-plasticizer. The optimal vulcanization time was determined using vulcametric curves obtained by means of a rheometry test. The influence of used oil on the vulcanization process was discussed. Moreover, selected mechanical and physicochemical properties, such as tensile properties (tensile strength and elongation at break), abrasion resistance, rebound resilience, and hardness were investigated. In order to define the thermal properties of obtained materials, thermogravimetric analysis was performed. The equilibrium swelling method was applied to determine the crosslink density, the molecular weight of the section between the crosslinks, and the swelling ratio index of the prepared materials. All results were compared with properties of the reference sample (without the addition of *Moringa oleifera* seed oil). It was found that the addition of *Moringa oleifera* oil reduced the crosslinking density, which resulted in the improvement of selected properties of the obtained natural rubber vulcanizates. On the other hand, the higher content of plasticizer extends vulcanization time. It can be stated that increasing the amount of *Moringa oleifera* seed oil causes higher abrasion resistance, lower density, and hardness of natural rubber-based vulcanizates. Moreover, the addition of plasticizer did not deteriorate the thermal stability of materials. All prepared samples were thermally stable up to ca 330 $^{0}$C ($T_{5\%}$- the initial decomposition temperature). The natural rubber-based vulcanizates were successfully prepared using *Moringa oleifera* seed oil as a plasticizer. Obtained research results indicate the great potential of *Moringa oleifera* seed oil as a plasticizer in the rubber industry because meets not only the technical demands but also the ecological requirements.

# ALTERNATIVE WAY TO OBTAIN MONOMERS BASED EPOXY OLIGOMERS

Michael Bratychak

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Among known polymers (oligomers) monomers based epoxy oligomers are of great interest due to the fact that the products on their basis are characterized by a series of good properties. Such type of oligomers is obtained by ionic polymerization of vinyl and diene monomers using the lithium organic compounds. The method is multi-stage and requires the purification of initial compounds and special equipment.

We propose to obtain oligomers with epoxy end-groups on the basis of vinyl and diene monomers via radical polymerization using diepoxy derivatives of azodinitrile compounds or peroxy derivatives of epoxy resins.

Styrene, isoprene, divinyl and the $C_9$ fraction have been used as initial monomers. The $C_9$ fraction is a product of hydrocarbon pyrolysis to ethylene which contains 40-50 wt% of unsaturated compounds, namely styrene, divinylbenzene, indene and pentadiene.

Diepoxy derivatives of azodinitrile compounds have been synthesized o the basis of well-known compounds containing –N=N– bond in their structures and carboxy, hydroxy or chlorohydrin groups as well. Peroxy derivatives of epoxy resins have been synthesized via modification of epoxy resins with hydroperoxides. The effect of initiator amount, temperature and time on the synthesis proceeding has been studied.

The increase in oligomerization temperature decreases the molecular weight and content of double bonds in oligomer and increases the content of epoxy groups. The increase in oligomerization time results in the decrease of epoxy groups content and the increase in molecular weight.

Polydispersion of the synthesized oligomers on the basis of isoprene was found to be 1.9–2.1. To reduce the polydispersion and increase the yield of oligomers with epoxy end-groups the diene monomers were polymerized with addition of initiator. The resulting oligomers were characterized by the molecular weight of 3500–5000.

# INFLUENCE OF THE MODIFIED EPOXY RESIN ADDITION ON PROPERTIES OF PEROXIDE SBR/NBR/XNBR VULCANIZATES

J. Chudzik[1], D. M. Bieliński[1], M. Bratychak[2], Y. Demchuk[2], O. Shyshchak[2], M. Jędrzejczyk[3], G. Celichowski[4]

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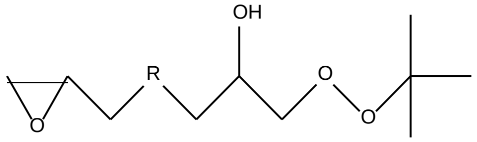
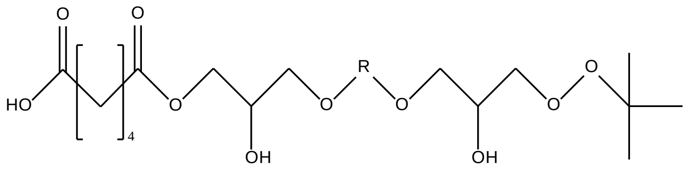
[2] *Lviv Polytechnic National University, Institute of Chemistry and Chemical Technologies, Stepana Bandery St, 12, Lviv, Lviv Oblast, 79000, Ukraine*
[3] *Lodz University of Technology, Institute of General and Ecological Chemistry, Żeromskiego 116, 90-924, Lodz, Poland*
[4] *University of Lodz, Department of Materials Technology and Chemistry, Tamka 12, 91-403, Lodz, Poland*

Nowadays, it is increasingly necessary to use ever-newer polymer composites for increasingly demanding applications. In the case of composites containing a metallic phase, especially with nanometric dimensions, such as nanoparticles, nanotubes or nanowires, it is crucial to ensure good adhesion between the continuous and dispersed phases, which can be enhanced by the addition of polymer proadhesive systems in the form of modified resins. The aim of the study was to examine the effect of the addition of an epoxy resin containing a peroxide group (PO) and the same carboxylated resin (CPO) on mechanical properties of styrene-butadiene rubber (SBR) or nitrile rubber (NBR) or carboxylated nitrile rubber (XNBR) and its adhesion to silver nanowires. Monoperoxy derivative of diglycidyl ether Bisphenol A (PO) and carboxylated peroxy derivative of diglycidyl ether Bisphenol A (CPO) derived from professor Bratychak's team was used in the study. PO or CPO additive has a significant impact on increasing the crosslinking density of rubbers and adhesion to silver nanowires. PO resin itself slightly crosslinks SBR rubber with a relatively short vulcanization time, additionally increasing the adhesion between the rubber matrix and the silver wire. A synergistic effect of PO/CPO on peroxide crosslinking of rubber can be observed. Addition of the resin in combination with application of DCP causes a slight hardening of rubber, whereas using the resin as the only crosslinker makes hardness of the rubber significantly reduced (comparing to peroxide curing), exhibiting a plasticizing effect. It is expected that the addition of resin to rubber-based nanocomposites containing silver nanowires, while significantly improving the interaction at the interface, will have a positive effect on the mechanical properties of this type of composites.



R = $-OC_6H_4C(CH_3)_2C_6H_4O-$

Fig. 1. Monoperoxy derivative of diglycidyl ether Bisphenol A (PO)



R = $-C_6H_4C(CH_3)_2C_6H_4^-$

Fig. 2. Carboxylated peroxy derivative of diglycidyl ether Bisphenol A (CPO)

# RESEARCH OF ADHESIVE STRENGTH POLYVINYLPIROLIDONE COMPOSITIONS

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The high adhesive properties and ability of polyvinylpyrrolidone (PVP) to bind various substances are being used in medical practice for a long time and allow it to apply as a component of medical adhesive compositions.

Thermodynamic approach, which is closely related to the study of interfacial processes, is widely used in the consideration and analysis of adhesion phenomena. A necessary condition for the adhesive strength is wetting the substrate surface. The study of influence of low molecular weight additives of the different surface activity on the structure and adhesive activity of polymer matrices will enable their regulation, which is a necessary condition for the development of water-soluble adhesives of biomedical purposes.

In previous works, the authors conducted research the effect of concentration and nature of low molecular weight additives on the adhesion properties of PVP compositions with 2-hydroxyethyl methacrylate (HEMA). For this purpose the compositions containing PVP (M makes up 28 thousand) of 0.5, 1, 1.5 and 2% content were prepared on the basis of HEMA. Low molecular weight additives with different physical, chemical, structural and other properties, namely: orthophosphate acid, isopropyl alcohol, lecithin were applied in concentrations of 0.3 and 1%. The research was carried out using the substrates of different nature, namely: "organic glass", "silicate glass", "ceramics with a glossy surface", "ceramics with an untreated surface", "steel plate" as well as "bone tissue".

Based on the obtained dependences the values f adhesion work were calculated via the determining the wetting angle. Considering the values of the wetting angle on substrates of different nature, it was found that the introduction of low molecular weight additive improves the adhesion of polyvinylpirolidone compositions with 2-hydroxyethyl methacrylate.

Adhesive strength determination of the adhesive seam of the composition was conducted according to GOST 14759-69.

It was found that for compositions with 0.5% PVP in HEMA, regardless of the additive nature and with increasing concentration the adhesive strength is unstable. The increase of the PVP in HEMA content leads to an increase in the adhesive ability of all additives.

In this manner, the influence of differ structure low molecular weight additives on the adhesive strength of the adhesive seam in compositions based on polyvinylpirolidone has been researched. The adhesive ability of the compositions on substrates of different nature has been characterized.

# STUDY OF THE STRENGTH CHARACTERISTICS OF COMPOSITES BASED ON POLYARYLATE

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Compression test is one of the widely used experimental methods for materials mechanical properties determination. To understand the mechanical behaviour of composites based on aromatic polyester polyarylate the effect of the nature and content of discrete chemical fibers on the physical and mechanical properties of the polymer binder was studied.

Discrete glass fiber M-5, carbon fiber and organic fiber Vniivlon in the amount of 5-35 mass % are used as reinforcing fibrous fillers.

The research data (Table 1) indicate that the fibrous filler nature significantly affects on the composites strength characteristics: more stiffness glass and organic fibers provides the bigger increase of the tensile strength at the compression in comparison with the binder (on 49-92 and 42-85 MPa higher than the polyarylate accordingly).

Table 1. Influence of of the content and fiber nature on strength characteristics of composites based on polyarylate

| Fiber filler | | Tensile strength, MPa | Elasticity modulus, MPa | Destruction work, kJ |
|---|---|---|---|---|
| – | – | 168 | 900 | 2888 |
| Uglen | 5 | 182 | 1138 | 3531 |
| | 15 | 231 | 1163 | 4931 |
| | 25 | 165 | 1263 | 2300 |
| | 35 | 155 | 1375 | 2332 |
| Vniivlon | 5 | 210 | 800 | 3348 |
| | 15 | 231 | 1000 | 2933 |
| | 25 | 242 | 1600 | 2413 |
| | 35 | 253 | 2670 | 2535 |
| Glass fiber | 5 | 217 | 750 | 2760 |
| | 15 | 235 | 1200 | 3115 |
| | 25 | 245 | 2000 | 4020 |
| | 35 | 260 | 2100 | 4636 |

In general, the research results shows us that reinforcing of the complex polyester by discrete chemical polyarylate fibers provides the exceeding of its strength capacities by an average of 24-35%.

# POLYMERIC MICELLES AS DRUG DELIVERY SYSTEMS

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ABSTRACT

Polymeric micelles are one of the modern form that can be used as drug delivery carriers. Thanks to the use of polymer micelles, it is possible to increase the stability of drugs that would normally decompose under normal conditions, or to improve the solubility of substances [1-3]. This leads to increased bioavailability and improve therapy, especially in cancer patients [4].

In this study, seven oligomers with similar chemical structures but different content of monomers, were studied. Oligomers containing epoxy and carboxyl groups formed micelles in two immiscible solvents with different polarity. Micelles were obtained by inverse miniemulsion technique with the use of sonication method to obtain stable emulsion [5].

As surfactants Tween 20 or Span 20 were used. To determine the character, the emulsion was dyed with use of ethanolic solutions of Sudan III and methylene blue [6]. As a result, seven stable emulsions were obtained. Herein, the surface polarity of the micelles and their biocompatibility were studied. For these purposes, we used several experimental and theoretical methods, such as optical microscopy, dynamic light scattering, zeta potential and thermogravimetric analysis. Cytotoxicity of oligomeric micelles were exposed to fibroblasts. For these studies we used 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide assay, which is a widely used colorimetric method determining the number of viable cells in proliferation, cytotoxicity or chemosensitivity assays.

It has been observed that the obtained micelles are made of a hydrophilic shell and a hydrophobic interior, thanks to which it is possible to enclose water insoluble drugs in micelles and their bioavailability can be improved.

ACKNOWLEDGEMENTS

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# METHODS OF PREPARATION AND PROPERTIES OF PECTIN-ALGINATE HYDROGELS. THEIR MORPHOLOGY AND STRUCTURE

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The use of hydrogel dressings, which provide a wet wound healing method, has a number of advantages over traditional gauze dressings. The use of sodium alginate in hydrogel dressings is known, but the use of pectin in the industrial production of such materials is limited. However, in the medical literature and patents there are reports of the ability of pectin to create favorable conditions for the healing of purulent wounds and inflammatory processes of the skin. There is a need to develop a technology for the formation of pectin or pectin-alginate plates, which would meet the requirements for therapeutic hydrogel dressings. The report considers a number of methods for producing hydrogel plates based on pectin and sodium alginate using structuring of polysaccharides with calcium salts.

Table. Comparison of methods for obtaining pectin-alginate plates

| Method | Gel fraction, % | The modulus of elasticity, kPa | Water content at the time of preparation, g /g | Equilibrium degree of swelling, g /g |
|---|---|---|---|---|
| Reactionary formation | 58,9 ± 1,5 | 4,7 ± 0,3 | 18,9 | 29,8 ± 1 |
| Reactionary formation followed by drying | 55,1±1,5 | 3,9 ± 0,3 | 3,8 | 27,3 ± 1 |
| Reactionary formation followed by pressing | 81,5 ± 2 | 13,9 ± 0,3 | 5,1 | 53,2 ± 1,5 |

The paper shows that obtaining plates by forming hydrogels with its subsequent drying does not change the properties of hydrogels. However in the case of obtaining of pectin-alginate hydrogel plates by the method of reactionary formation with subsequent pressing, the polymer macromolecules are ordered, due to which the gel fraction, physical and mechanical properties increase. Due to the ordering of effective crosslinking nodes, the degree of swelling increases, which is an important characteristic of the hydrogel. The preparation of hydrogel plates by the method of reactionary formation with subsequent pressing can be used to create dressings for the treatment of wounds.

# EFFECT OF NANOFILLERS PERCENTAGE ON MECHANICAL PROPERTIES OF PP/MMT NANOCOMPOSITES

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Nowadays, car manufacturers aim to produce lightweight vehicles in order to reduce their fuel’s consumption and $CO_2$ emissions. To achieve this goal, they tend to replace metallic parts by the use of polymeric materials which are reinforced, usually with glass fibre, but it increases the density and the brittleness of the composite. An alternative to glass fibre is to use nanofillers. In more, only 5 wt.% of nanofillers can significantly improve behaviour and properties of a neat polymer compared to at least 20wt.% with glass fibre [1].

Aim of this study was to investigate changes of mechanical properties of PP/MMT nanocomposites. In the study was used PP Mosten PND 33-301 and two types of nanofillers were chosen - Cloisite 20A and Cloisite 3010 (2,4,6wt.%). Samples were prepared by twin-screw extrusion and injection molding to final shape. Mechanical properties of prepared samples were tested on tensile test and Charpy impact test. The samples were exposed at low temperature (-20ºC) and UV chamber for 1440 hours.

Based on the measured values, we can conclude that the addition of nanofillers Cloisite 20A or Cloisite SE 3010 into the PP matrix had no positive effect on tensile strength and elongation of material, for example addition of 6% of Cloisite 20A caused a decrease in tensile strength of 17.1% and material with 6% of organically modified Cloisite SE 3010 showed decrease in tensile strength of 23,7%. Study of influence of addition the Cloisite fillers on resulting impact strength were obtained positive results. After exposure of material to low temperature, the samples show increase of tensile strength. Also the impact strength test showed increase at all samples filled with MMT nanofillers. Examination of the UV degradation effect on the mechanical properties show varying degrees of influence on tested aterials after exposure to UV radiation. Next goal in our progress will be to supply the matrix/filler with compatibilizer to increase the hydrophilicity of polypropylene.

Acknowledgment

This study was supported by the project APVV-17-038.

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# ELECTROSPINNING OF NONWOVEN MATERIALS BASED ON POLYSACCHARIDES

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Electrospinning (ES) is the process of fibers creation due to the action of electrostatic forces on an electrically charged jet of polymer solution or melt. The advantage of this fiber formation method is the possibility of obtaining nonwoven materials with micro- and nanoscale diameter with special properties. These materials are successfully used in medicine and bioengineering for the manufacture of sanitary, cosmetic and medical products. Preference is given to systems of ecological compositions without the use of highly toxic solvents. Modified polysaccharides (cellulose, starch, chitosan) are natural physiologically active macromolecular compounds.

Substantial defect limiting the possibility of practical use of the nonwoven materials formed from water-soluble polymers is their solubility in water which needs additional operation of thermal stabilization to be performed.

Processes for obtaining biocompatible nonwoven polymeric materials by electrospinning method using capillary laboratory with voltage of electric-field of 30 kV were researched in this study.

Compositions of solutions of chitosan in acetic and lactic acid prepared by adding synthetic biocompatible polymers of PVA and PVAc as fiber formers in different proportions were used, which enabled the electrospinning process of nonwoven materials.

Chitosan solutions were prepared in two manners; dissolution of 2% chitosan in 1 % acetic acid and dissolution of 6% chitosan in 70% acetic acid. PVA and PVAc 10% aqueous colloidal solution was prepared separately.

It was found that stable electrospinning of fibers occurs for the following compositions: PVA:chitosan (4: 1 parts by weight), PVAc:chitosan (3: 2 and 4: 1) with lactic acid and PVA: chitosan (5: 1), PVAc:chitosan (3: 1) with acetic acid. For these compositions, a stable process of fiber formation was provided at a distance between the forming and depositing electrodes - 6-9 cm.

The influence of the duration (1-3 h) of thermal stabilization at a temperature of 115 - 120 ° C on the sorption properties of the obtained fibrous materials in distilled water was studied. Samples based on PVA, after thermal stabilization for 3 h are insoluble and reach the maximum equilibrium sorption value of 600-700%. Non-thermostabilized samples based on PVAc reach the maximum sorption of 570%, and after thermal stabilization for 3 h - 450%.

Therefore, thermal stabilization of PVA-based compositions for 3 h leads to the formation of a crosslinked insoluble structure, and for samples based on PVA the thermal stabilization reduces the sorption ability of nonwoven materials of the composite material.

# PSEUDO-POLYAMINO ACIDS OF POLYESTER TYPE AS PROMISING POLYMERS FOR MEDICAL AND BIOMEDICAL APPLICATION

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Polyesters have been widely studied for the last years as materials for different medical applications. A number of synthetic routes to the development of aminofunctional copolyesters were reported. The majority of such approaches are based on the use of tri-functional amino acids. The technique usually includes protection of amine fragments and the use of the other two functional groups (carboxylic, hydroxy, etc.) in polymerization process. Copolyester synthesis usually occurs in severe conditions, i.e. in the presence of strong acids and at high temperatures. One of the ways to overcome these experimental limitations is the use of coupling agents such as dicyclohexylcarbodiimide (DCC) that allows the polyester chain to grow under mild conditions (Steglich esterification). We have developed synthetic approach for polyesters based on the glutamic acid (its N-derivatives) and polyethylene/ polypropylene glycols.

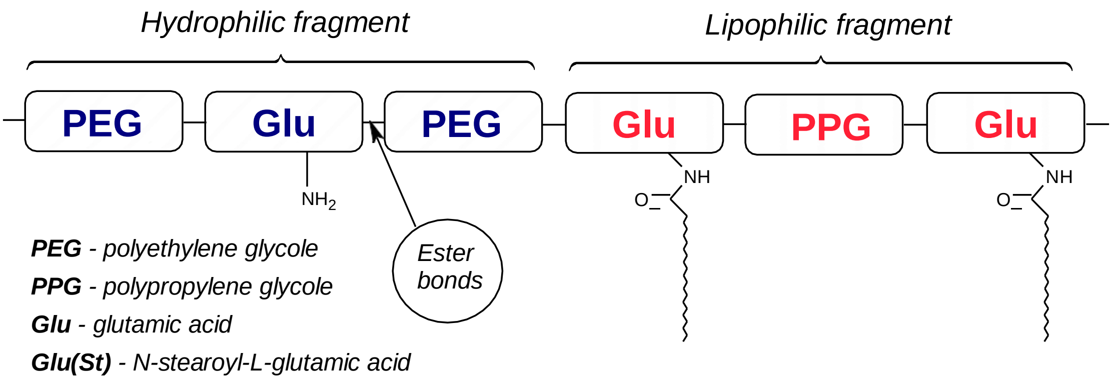

Figure 1. Structure of pseudo-polyamino acids based on glutamic acid and PEG/PPG

As macromolecules of synthesized polyesters are formed of lipophilic and hydrophilic fragments, they possess surface active properties – 1ч2% water dispersions decrease surface tension to 34ч42 mN/m. Particle size of the dispersed phase makes 80ч300 nm according to the dynamic light scattering data depending on the polymer concentration. Dispersed phase particles have complex architecture consisting of lipophilic core and hydrophilic shell. The morphology of particles was studied using methods of small-angle neutron scattering and transmission electron microscopy.

Such particle structure determines their ability to solubilize low-soluble in water organic compounds. In particular, solubilization of toluene and dyes Sudan (III) and curcumin was studied. Its shown that dispersed phase solubilize 0,5 ч 3,0 g of low-soluble compounds per 1 g of polymer in the dispersion depending on the polymer concentration and its composition.

Since the obtained polymers are biocompatible and products of their biodegradation are non-toxic and due to a number of colloidal properties described above, synthesized polyesters are promising materials for dispersed drug delivery systems.

# POLYMERIC BONE SCAFFOLDS

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## INTRODUCTION

Life expectancy increase in most countries of the world is contributing to increasing health care problems. This means, among other things, an increase in the number of people suffering from bone diseases. It results in increasing number of surgical procedures. Those procedures requires functional materials which are: a) more widely available than problematic bone grafts and b) will support therapy by stimulating tissue regeneration. As a response for that demand bone scaffolds were developed and they are used in bone diseases such as fractures, bone defects, osteoporosis, and bone tumors[1]. The purpose of the scaffold is to provide a mechanical support for the regenerated tissue as well as to stimulate the growth of bone tissue. Nowadays, the properties of bone scaffolds are being investigated and new materials are developed to additionally support the therapy by increasing biocompatibility, improving mechanical parameters or accelerating the therapeutic effect as a result of the addition of drugs, growth factors or stem cells.

Scaffold has to meet may requirements, such as biocompatibility, mechanical strength, pore size and bioresorbability. As for biocompatibility, the scaffold not only cannot be toxic[2], but it also has to be at least osteoconductive and preferably osteoinductive[3]. Osteoconductivness means that scaffold allows bone tissues to adhere to scaffolds surface, proliferate and create extracellular structure. Osteoinductivness it is material property, which promotes formation of new tissues and differentiation of precursor cells into osteoblasts[4]. The mechanical strength of scaffold should match the bone strenght[3]. The pore size have effect on tissue growth. Pores are important to allow oxygen, nutrition and cellular respiration products transport[5]. It has ben proven that pore size of 200-350 µm are the best for bone tissue growth[3,6]. Good scaffold also degrades and creates a site for regenerated tissue growth. The degradation speed has to be controlled and adjusted to the rate of tissue growth.

## MATERIALS

The base material for scaffolds was polyurethane (PUR) synthesized using α,ω-dihyroxy(ethylene-butylene adipate) (dHEBA) polyester (trade name Polios 55/20, Purinova, Poland); diisocyanate of cycloaliphatic structure (4,4-methylene bis[cyclohexyl] isocyanate) (HMDI, Sigma Aldrich, Poland), 1,4-butanediol (BDO) as chain extender. The NCO:OH ratio was

0.9. Synthesis scheme can be found on Figure 1. At beginning, with use of Polios 55/20 and HMDI, the urethane prepolymer with 8% free isocyanate groups was obtained (80 °C, 60 min, microwave reactor MR Ertec Nova 09, 675 W, 2.45 GHz). Next step was to add BDO (80 °C, 3 min, microwave reactor MR Ertec Nova 09, 675 W, 2.45 GHz) to form PUR. Obtained material was left in a dyer (80 °C, 24 h) to finish the reaction.

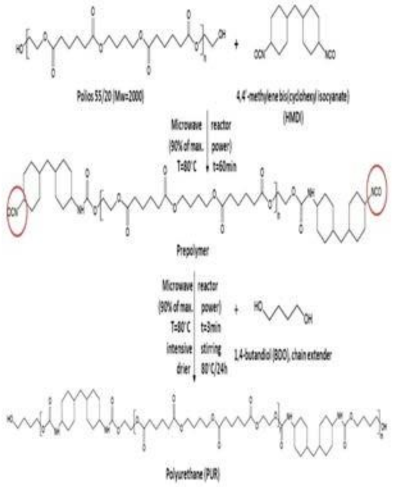

Fig. 1. Polyurethane preparation. Adapted from: *Polyurethane porous scaffolds (PPS) for soft tissue regenerative medicine applications* by J. Kucicska-Lipka, I. Gubanska, M. Pokrywczynska, H. Cieslicski, N. Filipowicz, T. Drewa & H. Janik, 2018, Polymer Bulletin 75, p. 1957-1979[7].

For modification of scaffolds, hydroxyapatite (HA) and gelatin were used. For forming of scaffolds conventional kitchen salt (sodium chloride) and dimethyl sulfoxide (DMSO, Sigma Aldrich, Poland) was used.

Scaffolds were made using solvent-casting particulate leaching (SCPL) method. Three main types of scaffolds were obtained: a) pure PUR, b) PUR modified with HA, c) PUR modified with both HA and gelatin.

*HA modified PUR scaffolds*

Five solutions of 30 wt.% PUR in DMSO were prepared. Following amounts of HA were added 0, 1, 3, 5, 10 wt.% respectively. Then, kitchen salt of crystals size in range of 0.46-0.6 mm was added until complete saturation of solution occurred. The prepared material was moved into silicone ice-cube molds and stored in freezer (-20 °C, 7 days). The next step was to transfer the material into bidistilled water, where kitchen salt was washed out. Water was changed once per two days. After 8 days, samples were taken out and left in room conditions for drying for one week.

*HA-gelatin modified PUR scaffolds*

Solution of 30 wt.% PUR in DMSO was prepared. Kitchen salt of crystals size in range of 0.46-0.6 mm was added until complete saturation of solution occurred. The prepared material was moved into silicone ice-cube molds and stored in freezer (-20 °C, 7 days). The next step was to transfer the material into bidistilled water, where kitchen salt was washed out. Water was changed once per two days. After 8 days, samples were taken out and left in room conditions for drying for one week.

After drying, samples were divided into four groups. Three solutions of 2 wt.% gelatin in distilled water were prepared. Then HA was added to the solutions: 1, 3, 5 wt.% respectively. Then the samples were immersed in prepared solutions (group 1 – not immersed, group 2 – 1 wt.% HA, group 3 – 3 wt.% HA, group 4 – 5 wt.% HA) and placed for 15 minutes into vaccum chamber to improve the penetration of pores. After that time samples were taken out and left in room conditions for drying for one week.

METHODS

*Mechanical properties*

Mechanical testing was concluded on Zwick/Roel Z020 testing machine in compression mode. The pre-force was set to 0.25 N. The crosshead speed was set as 20 mm/min; measurement stopped at 75% of initial height. The average values from 5 tests are presented for each sample type.

*Porosity*

The porosity was calculated as shown bellow:

$$P = \left(1 - \frac{m}{V * \rho}\right) * 100\% , \quad (1)$$

Where:
P – porosity [%];
m – sample mass [g];
V – sample volume [$cm^3$];
$\rho$ – density of solid PUR [$g/cm^3$].
Density of solid PUR was was determined on a hydrostatic balance.

*Microscopy*

The microscopic images were taken on optical microscope (xxxx - nazwa) with 40x and 800x magnifications.

RESULTS

*Mechanical properties*

The average the maximum compressive force, Young's modulus and permanent deformations for HA modified and HA-gelatin modified PUR scaffolds were presented in Table 1. and 2. respectively.

For both scaffold types, the increase in maximum stress at 75% compression was aligned to amount of modifier. The higher amount of modifier is introduced, the higher maximum stress is. It can be observed, that the maximum stress for HA-gelatin modified PUR scaffolds is much higher than for HA modified ones. Interestingly there is big difference between “0” samples (420 ± 22 for HA vs 1000 ± 180 for HA-gelatin). It could be effect of usage of vacuum chamber, that took out remaining water. The alignment of modulus to amount of modifier is not clear due to high standard deviations, but it can be stated that presence of modifier increases the modulus compared to pure PUR scaffold. The permanent deformation of HA modified PUR scaffolds is low – around 3%, and does not change after 24 h. The permanent deformation of HA-gelatin modified PUR scaffolds however is high – up to 13 %, and gets lowered by around 50% after 24 h.

Table 1. Mechanical properties of HA modified PUR scaffolds.

| HA wt.% | $F_{max}$ [kPa] | E [kPa] | Permanent deformation [%] | Permanent deformation after 24 h [%] |
|---|---|---|---|---|
| 0 | 420 ± 22 | 120 ± 28 | 3 ± 1 | 3 ± 1 |
| 1 | 820 ± 72 | 240 ± 110 | 3 ± 1 | 2 ± 1 |
| 3 | 630 ± 78 | 240 ± 110 | 4 ± 1 | 2 ± 1 |
| 5 | 490 ± 60 | 180 ± 37 | 3 ± 1 | 2 ± 1 |
| 10 | 1470 ± 80 | 350 ± 160 | 5 ± 1 | 2 ± 2 |

Table 2. Mechanical properties of HA-gelatin modified PUR scaffolds.

| HA wt.% | $F_{max}$ [kPa] | E [kPa] | Permanent deformation [%] | Permanent deformation after 24h [%] |
|---|---|---|---|---|
| 0 | 1000 ± 180 | 70 ± 33 | 5 ± 2 | 1 ± 2 |
| 1 | 1500 ± 200 | 180 ± 38 | 11 ± 2 | 5 ± 1 |
| 3 | 1600 ± 250 | 130 ± 47 | 13 ± 1 | 6 ± 1 |
| 5 | 2300 ± 150 | 160 ± 71 | 11 ± 1 | 6 ± 2 |

*Porosity*

Calculated porosities for HA modified and HA-gelatin modified PUR scaffolds were presented in Table 3. and 4. respectively. The porosity values are high and for HA-gelatin modified scaffolds are lower than HA modified ones, because gelatin fills up the pores.

Table 3. Porosity of HA modified PUR scaffolds.

| HA wt.% | Porosity [%] |
|---|---|
| 0 | 85.3 ± 0.2 |
| 1 | 80.9 ± 0.8 |
| 3 | 82.6 ± 0.9 |
| 5 | 84.1 ± 1.1 |
| 10 | 77.0 ± 1.1 |

Table 4. Porosity of HA-gelatin modified PUR scaffolds.

| HA wt.% | Porosity [%] |
|---|---|
| 0 | 78.1 ± 1.1 |
| 1 | 75.7 ± 0.2 |
| 3 | 75.4 ± 0.6 |
| 5 | 75.5 ± 0.6 |

*Microscopy*

Microscopic images are presented for HA modified and HA-gelatin modified scaffolds on Fig. 2. and 3. respectively. 40x images of HA modified scaffolds (Fig. 2 a-e) show homogenous, open and connected pores of 0.3-

0.4 mm diameter. 800x images (Fig. 2. f-j) of HA modified scaffolds show micropores of 10-50 µm diameter. 40x images of HA-gelatin modified scaffolds (Fig. 3 a-d) show open and connected pores of 0.3-0.4 mm diameter. 800x images of HA-gelatin modified scaffolds (Fig. 3 e-h) show micropores of 10-30 µm diameter.

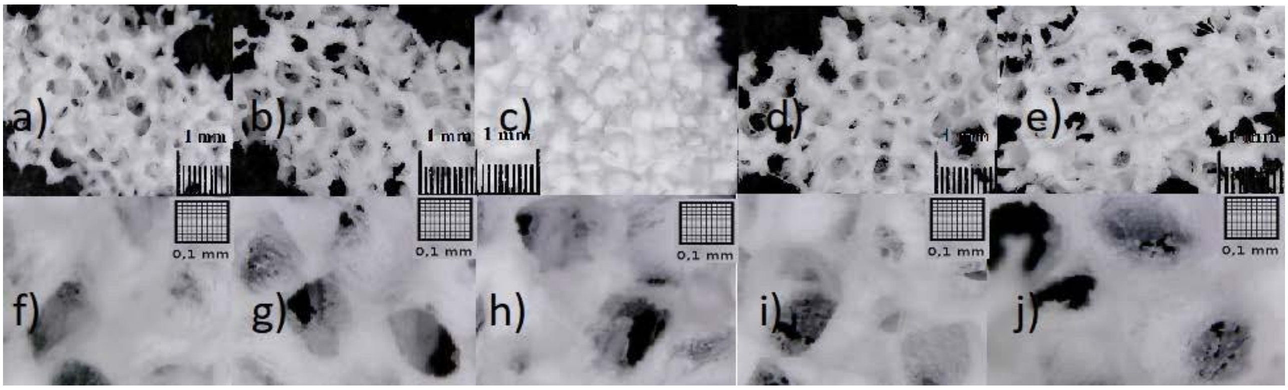

Figure 2. Microscopic images of HA modified PUR scaffolds. a-e 40x; f-j 800x, a,f - 0%, b,g - 1%, c,h - 3%, d,i - 5%, e,j - 10%.

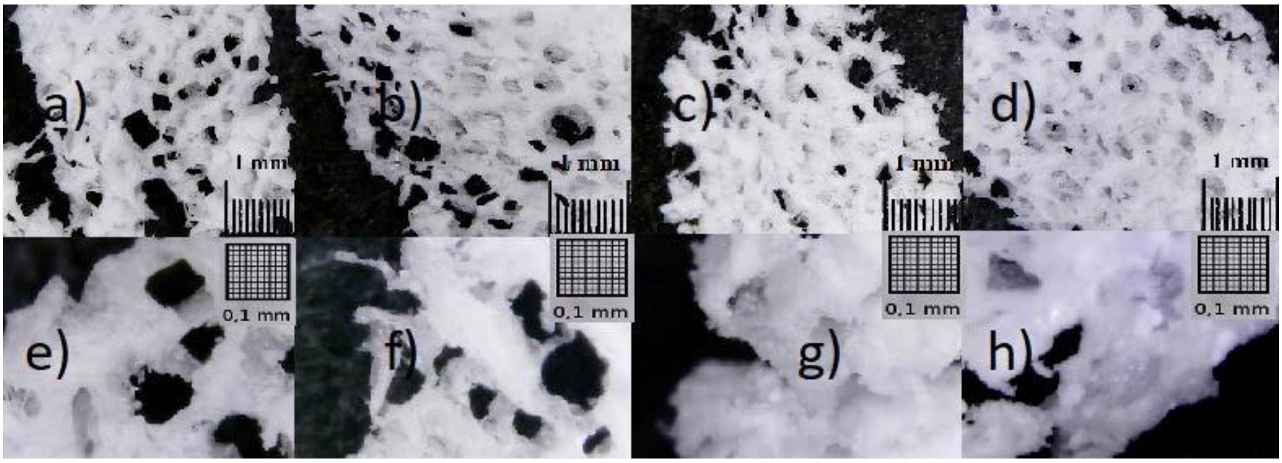

Figure 3. Microscopic images of HA - gelatin modified PUR scaffolds. a-d - 40x; e-h - 800x, a,e - 0%, b,f - 1%, c,g - 3%, d,j - 5%.

CONCLUSIONS

The scaffolds obtained by the SCPL method meet conditions regarding the porosity of bone scaffolds. The pores obtained have uniform dimensions that can be adjusted by selecting the appropriate salt fraction. Both macro- and micropores are formed. Macro- and microporosity will provide a structure suitable for the transport of nutrients and waste products as well as cell migration and the formation of the extracellular tissue structure. The mechanical properties of the more durable samples are similar to those of the spongy bone essence. An additional advantage is the use of materials that increase the biocompatibility of the scaffold and accelerate tissue regeneration - HA and gelatin. It is also worth paying attention to the fact that the decomposition products of the PUR used are not toxic to the body.

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# POLYOLEFINS REVEALING A SHAPE MEMORY EFFECT

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## General concept of shape memory materials

Nowadays, significant amount of polymers are designed as smart and intelligent, as they can change shapes, colors or even perform analysis of surroundings on their own. There are two main conditions, which smart materials have to fulfill. The first one is that smart materials can consistently, reversibly respond to changes in the environment, which surrounds the material. The second one is that the responses of these materials have to be useful such as changes in mechanical properties, geometry, and color, electromagnetic or physical properties.

One of smart materials are shape memory materials (SMMs), which have the ability to revert to their original shape. They can deform into a temporary shape and, after stimulation of change in surrounding environment, return to their original shape. Different triggers can be used to activate the SME such as light, magnetic field, electricity, water or solvent activation, and the most commonly used trigger, heat[1]. SMMs which are temperature-sensitive undergoes a structural change at characteristic transition temperature ($T_{trans}$). They can be permanently and easily deformed, and they will return to their original shape after heating. SME can be classified due to reversibility. One-way SMM can revert from temporary shape to permanent shape, but not vice versa. Two-way means that SMM can change between two shapes with only activation and deactivation of external triggers. SME can be classified also due to amount of remembered shapes. The most basic situation is dual-shape SMM, which means that this material can adopt two shapes: one temporary and one permanent during shape memory cycle. There are also materials with triple- and multi-shape SME, where there is more than one temporary shape which can be programmed[2].

To distinguish one SMM from another specific nomenclature is required. It should consist of trigger type, reversibility, shape numbers which material can adopt and the material name. The example of such naming could be: light induced two-way multi-SME polylactone blend.

Shape memory effect (SME) is not a recent discovery in science. The first thoughts about SME appeared before the outbreak of World War II. The oldest found SMMs are alloys: gold-cadmium, brass (copper-zinc) and nickel-titanium. Later on, more materials were reported as SMMs: polymers[3], ceramics[4] and gels[5].

## 1. Shape memory effect in polymers

Shape memory polymers (SMPs) are one of the material groups which can exhibit SME. The base of polymers SME is the existence of separated phases in the structure of polymers. It can come from cross-links, hydrogen bonds, chain-branches, coiled structure and others[6]. Usually chains are randomly configurated in the volume of polymer. However, they can be blocked by presence of cross-links and partial bonding. SME of polymers depends of transposing between the state of randomly entangled and constrained conformations. Basically polymer networks can be divided into two domains: netpoints (hard segments) and molecular switches (soft segment). With a presence of external trigger, softs segments are flexible, which results in elastic behavior of the whole polymer network. When the external trigger vanishes, polymer network hardens, preserving given shape. Process of exhibiting shape memory property of polymers is as follows:

- Conventional processing of polymer to obtain permanent shape A,
- Programming – deformation of the sample to obtain temporary shape B,
- Recovery – application of and external stimulus, polymer goes back to shape A.

Two last steps can be repeated many times. SME is quantified in cyclic mechanical tests. In those tests strain fixity rates ($R_f$) and strain recovery rates ($R_r$) and stimulus type and factor size are determined[1]:

$$\boxed{R_f(N) = \frac{\varepsilon_u(N)}{\varepsilon_m}} \tag{1}$$

$$\boxed{R_r(N) = \frac{\varepsilon_m - \varepsilon_p(N)}{\varepsilon_m - \varepsilon_p(N-1)}} \tag{2}$$

where:

$\varepsilon_m$ – mechanical deformation

$\varepsilon_u(N)$ – temporary shape

N – number of cycle

$\varepsilon_p(N)$ – restored permanent shape.

Ideally $R_f$ and $R_r$ should be 100%. Typically, such tests are conducted in stress-controlled cycles as shown on Figure 1. Test sample is mounted in dynamic mechanical thermal analysis (DMTA) equipment. The test consists of four steps:

1. Elongation to $\varepsilon_m$ with molecular switches open (temperature above $T_{trans}$) and maintenance of strain to allow polymer chains to relax,
2. With constant stress $\sigma_m$ applied, molecular switches are closed to fix the temporary shape (cooling to temperatuire lesser than $T_{trans}$),

3. Stress is slowly reduced at 0 MPa, strain reduces a bit,
4. Stress is held constant at 0 MPa, and molecular switches are opened (temperature above $T_{trans}$), which results in contraction of test sample and recovery of permanent shape.

Although SME is a complex phenomenon, several models for prediction of SME have been described using uniaxial deformation processes as a start of the deliberations. Two main approaches are used: mechanical modeling[7,8] and thermodynamic one[9,10]. They can predict stress and strain[9], irrecoverable strain[7,9] and temperature-dependent stress and strain[10] for SMP.

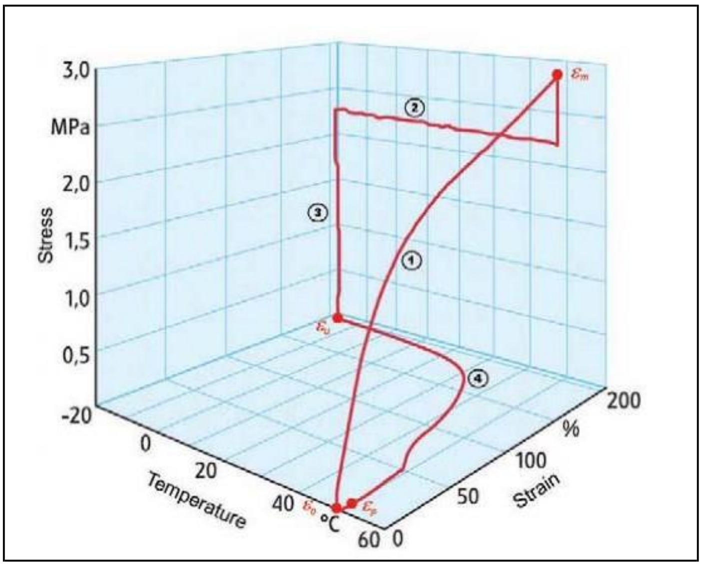

Fig. 1. Stress-strain-temperature diagram of thermally induced shape memory polymer. Adapted from *Shape-Memory Effect From Permanent Shape* by A. Lendlein, S. Kelch, 2002, *Angewandte Chemie* (International ed. in English), p. 2034–2057[1].

## 2. Types of shape memory effect triggers

### *2.1 Temperature*

SMPs with temperature trigger can be divided into two groups: first one with transition temperature of melting point of one of the components ($T_{trans} = T_m$) and the second one with transition temperature of glossy temperature of one of the components ($T_{trans} = T_g$).

The first group ($T_{trans} = T_m$) consist mostly of crystalline polymers. Crystalline state of polymers prohibits chain movement. If the structure consist of two polymer types – soft, with low $T_m$ and hard with high $T_m$. Melting soft one will allow to strain and move chains of the hard one. After cooling down and crystallization, soft chains will form covalent netpoints, whose prevent relaxation of hard chains, thus leading to stable, temporary shape. When material will heat up again to $T > T_m$, soft parts will melt, allowing hard parts to relax and reform the permanent shape. The mostly studied ones are polyurethanes, polyetheresters, block copolymers of polyethyleneterephthalate (PET) and polyethyleneoxide (PEO), block copolymers of polystyrene (PS) and poly(1,4-butadiene)[11].

The second group ($T_{trans} = T_g$) consists mostly of amorphous polymers. When polymer is in the glassy state, the movements of the polymer segments are suspended. When polymer is heated up to the point, where it leaves the glossy state, polymer chains start to move and will form compact random coils, as it is the most favored energetic-wise. If those moving chains were elongated and frozen in glossy state, transition to elastic state will result in shrinkage and restoration of the original compact random coils. This effect can happen in linear copolymers but in cross-linked copolymers (elastomers) it is also possible. Permanent shape of such copolymers is being set during cross-linking and cannot be changed later on. Those cross-links acts as netpoints and are responsible for memorizing the original shape. In such polymer also amorphous chain segments are present, whose act as flexible segments in $T > T_g$. If those cross-links are not permanent, and they are removed above certain temperature and they are restored after cooling down with formation of new "permanent" shape, they are called as vitrimers. The mostly investigated ones are polyesters based on poly(ε-caprolactone) and polyketones (e.g. poly[ethylene-*co*-propene-*co*-cabonoxide])[11].

### *2.2 Indirect thermal triggers*

Activation of thermal triggers does not have to consist only of rising of environment temperature. There are two routes to initiate temperature SME. The first one is to use indirect heating using e.g. irradiation or magnetism. The second one is to lower $T_{trans}$ by using plasticizer e.g. water.

Indirect heating can be performed using different phenomenon. Illumination with infrared light is one of them. Infrared light has wavelengths longer than visible lights. This radiation is being absorbed by SMP, and its molecules changes rotational-vibrational movements, leading to excite vibrational molecules and finally heats up the SMP. This phenomena was presented e.g. in laser-activated polyurethane medical device[13,14]. The infrared absorption capacity and speed of the transition can be improved by addition of conductive fillers into SMP e.g. carbon black, carbon nanotubes and nanoparticles[15].

Other phenomenon used for indirect heating is resistance heating during flow of electric current. Most of polymers are electrical insulator, thus conducting fillers has to be introduced e.g. carbon black, carbon nanotubes, carbon fibers or metal nanoparticles. Such trigger can be used in applications where heating is undesirable e.g. in medical applications[16].

Magnetism is also one of indirect thermal triggers. Addition of magnetic particles and nanoparticles provide inductive heating, when SMP is exposed to alternating magnetic fields. Those particles absorb energy from the alternating magnetic heat and transforms it into heat. Three heat generation mechanisms are possible: eddy current losses (when magnetic particles has low electrical conductivity), rotational losses (when magnetic domains are forced to rotate by magnetic field) and hysteresis losses (when magnetization is being reversed). Such SMPs can be characterized not only by $T_{trans}$, but also by $H_{trans}$, specific transition magnetic field strength[17,18].

Solvent induced SME bases on lowering $T_{trans}$ by swelling of solvent e.g. water. For hydrophilic polymers water can be used[19]. For hydrophobic polymers other solvents may be used e.g. dimethyl sulfoxide (DMSO) and ethanol (EtOH)[20]. Solvent swelling enhances the flexibility of polymer chains. Solvent swelling can also influence internal bonds in vitrimer networks. Swelling initiates bond-exchange reaction, where network topology can be changed. The schematic representation of tetrahydrofuran (THF) swelling in epoxy vitrimer[21] is shown on Figure 2. This phenomenon can be used to shape programming, reconfiguring, and also to weld two parts of vitrimer together or heal the damages of the sample.

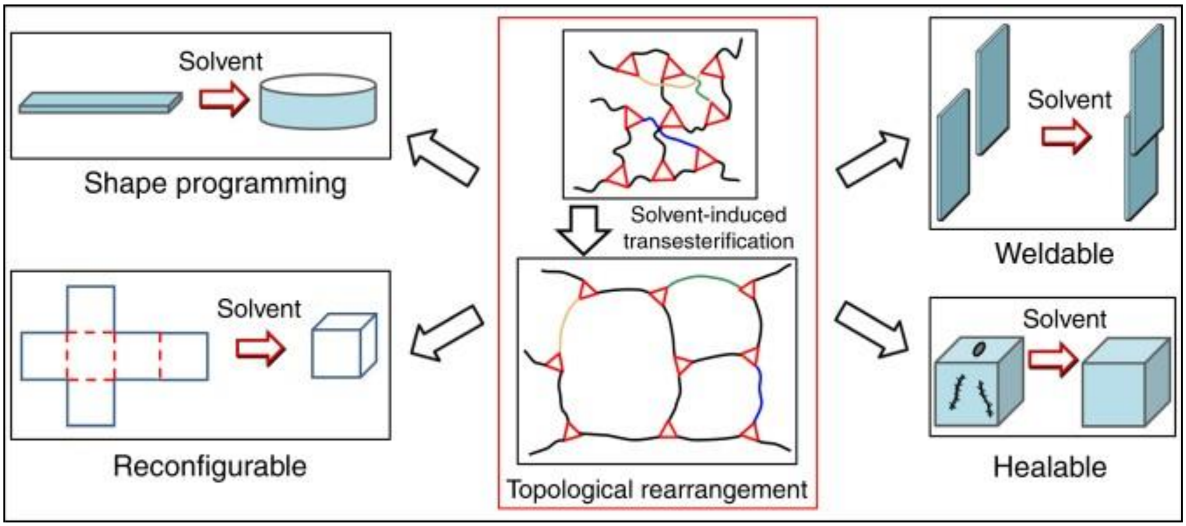

Fig. 2. Schematic of topological rearrangement induced by solvent-activated transesterification, which enables shape programming, reconfiguration, welding and healing of epoxy vitirmer. Adapted from *Solvent-Assisted Programming of Flat Polymer Sheets into Reconfigurable and Self-Healing 3D Structures*, by Y. Yang, E. M. Terentjev, Y. Wei, Y. Ji, Y., 2018, Nat. Commun., 9 (1), p. 1906[21].

### *2.3 Light*

Photoreactive, reversible molecular switches in SMP are used in light induced SME. Polymers using this SME mechanism can have chemical cross-links or interpenetrating network inside its structure. Usually formation of new photoresponsive cross-links are possible using (2+2) cycloaddition reactions (Fig. 3.) of acrylates or star-poly(ethylene glycol)[22] under irradiation of specific light wavelength. Although such SMP are useful, they have disadvantage of non-biodegradability. To obtain this diselenide bonds[23] or biodegradable segments[24] are used.

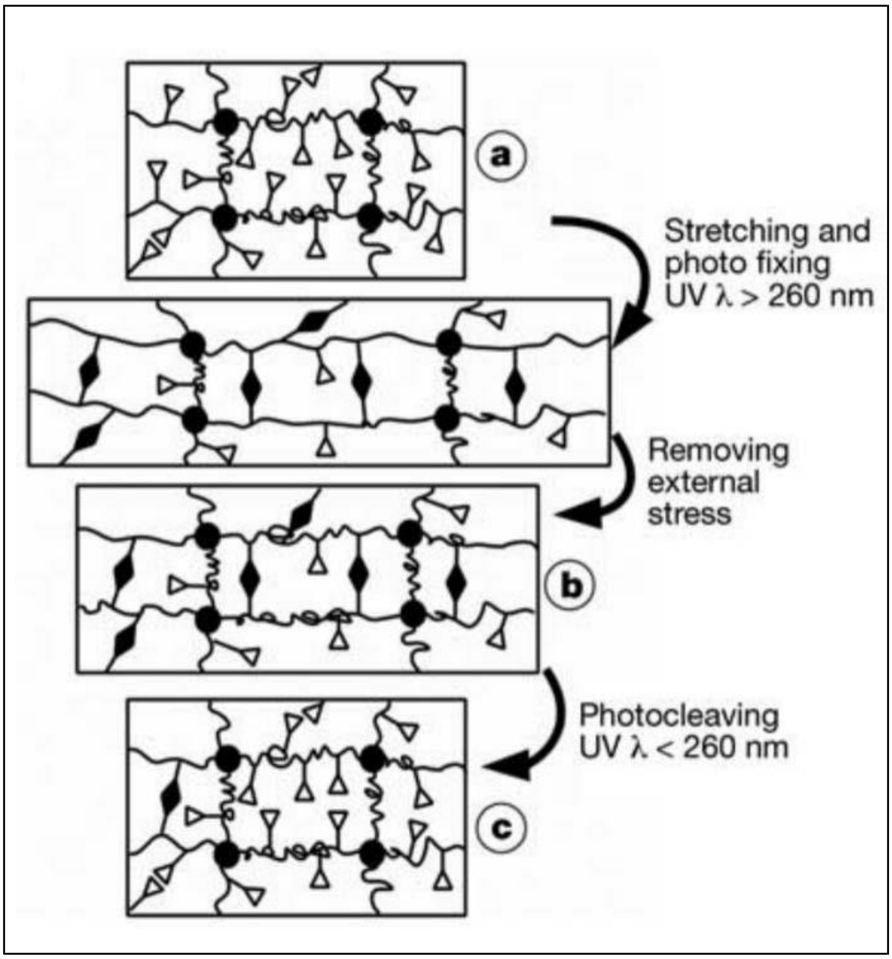

Fig. 3. Shape memory effect of photoresponsive polymer – molecular mechanism. Chromophores (open triangles) are covalently grafted onto polymer permanent network (filled circles – permanent crosslinks). They form photoreversible crosslinks (filled diamonds). Adapted from: *Light-Induced Shape-Memory Polymers,* by: A. Lendlein, H. Jiang, O. Jьnger, R. Langer, 2005, Nature, 434 (7035), p. 879–888[22].

### *3. Shape memory of polyolefins*

Polyolefins are the most widely used polymers in the world. Despite this polyolefin-based SMPs are a novel topics compared to e.g. PU-based SMPs. The reason of it is apolar nature of polyolefin, which requires modification of its structure. The most widely researched type of commercially available polyolefin based SMP is poly(ethylene-co-vinyl acetate) (EVA)[11]. In general, most of polyolefin-based SMPs are one-way and dual-shape. Polyolefin-based SMPs can be divided into 6 groups: composites and nanocomposites, blends, copolymers, cross-linked structures, ionomers and homopolymers. Examples for each group are shown in Table 1.

Table 1. Polyolefin-based shape memory materials

| # | Name | Type of SME* | Trigger | Processability | Ref. |
|---|---|---|---|---|---|
| Homopolymers | | | | | |
| 1. | PE | 1-W/2-S | Temperature | Thermoplastic | 25,26,27 |
| 2. | UHMWPE | 2-W/2-S | Temperature | Thermoplastic | 28 |
| 3. | PP | 2-W/2-S | Temperature | Thermoplastic | 28 |
| Copolymers | | | | | |
| 4. | Poly(ethylene-*co*-1-octene) | 2-W/2-S | Temperature | Thermoplastic | 29 |
| Composites and nanocomposites | | | | | |
| 5. | PE/clay | 1-W/2-S | Temperature | Thermosetting | 30 |
| 6. | LDPE/millable PU/organoclay | 1-W/2-S | Temperature | Thermosetting | 31 |
| 7. | LDPE/montmorillonite/NdFeB | 1-W/2-S | Magnetism | Both | 32 |
| 8. | Polycyclooctene/carbon nanotube/PE | 1-W/3-S | Temperature, electricity | Thermosetting | 33 |
| 9. | SBS/LDPE/$Fe_3O_4$ | 1-W/2-S | Magnetism | Thermoplastic | 34 |
| 10. | Thermoplastic elastomer PE | 1-W/2-S | Temperature, radiation | Thermoplastic | 35 |
| 11. | Foamed Eucommia ulmoides gum/HDPE | 1-W/3-S | Temperature | Thermoplastic | 36 |
| 12. | Glass fiber/SBS/LDPE | 1-W/2-S | Temperature | Thermosetting | 37 |
| 13. | Carbon fiber/SBS/LLDPE | 1-W/2-S | Temperature | Thermosetting | 38 |
| 14. | Trans-1-4-polyisoprene/LDPE/HDPE | 2-W/4-S | Temperature | Thermoplastic | 39 |
| Blends | | | | | |
| 15. | HDPE/poly(ethylene terephthalate) (PET) | 1-W/2-S | Temperature | Thermoplastic | 40 |
| 16. | Poly(vinyl alcochol)/PE | 1-W/3-S | Temperature, water | Thermosetting | 41 |
| 17. | PE/poly(ε-caprolactone) | 2-W/2-S | Temperature | Thermosetting | 42 |
| 18. | LLDPE/PP | 1-W/2-S | Temperature | Thermoplastic | 43 |
| 19. | Polyamide/maleated PE/LDPE | 1-W/2-S | Temperature | Thermoplastic | 44 |
| 20. | Trans-1-4-polyisoprene/LDPE | 1-W/3-S | Temperature | Thermoplastic | 45 |
| Cross-linked structures | | | | | |
| 21. | PP | 1-W/2-S | Temperature | Thermosetting | 46,47 |
| 22. | PE | 1-W/2-S | Temperature | Thermosetting | 7,48,49,50 |
| 23. | PE/PP blends | 1-W/2,3-S | Temperature | Thermosetting | 51,52,43 |
| 24. | PE/carbon black | 1-W/2-S | Temperature | Thermosetting | 53,54 |
| Ionomers | | | | | |
| 25. | Poly(ethylene-*co*-vinyl acetate) | 2-W/2-S | Temperature | Thermosetting | 55,56 |
| 26. | Zinc-neutralized Poly(ethylene-*co*-methacrylic acid) | 1-W/2-S | Temperature | Thermoplastic | 57 |

| # | Name | Type of SME* | Trigger | Processability | Ref. |
|---|---|---|---|---|---|
| 27. | sPP | 1-W/2-S | Temperature | Thermoplastic | [58] |
| 28. | Polyolefin elastomer (POE)/stearic acid (SA) | 1-W/3-S | Temperature, solvent | Thermoplastic | [59] |
| 29. | Zinc neutralized, sulfonated EPDM | 1-W/2-S | Temperature | Thermoplastic | [57] |
| 30. | Sulfonated poly(ethylene-*co*-propylene-*co*-[5-ethylidene-2-norbornene])/fatty acid salts blend | 1-W/2-S | Temperature | Thermoplastic | [60] |
| 31. | Maleated polyolefin elastomer/Nylon 12 | 1-W/2-S | Temperature | Thermoplastic | [61] |
| 32. | Maleated ethylene-propylene-diene rubber (mEPDM)/maleated polyethylene-octene elastomer (mPOE) | 1-W/3-S | Temperature | Thermoplastic | [2] |

* 1-W = one-way; 2-W = two-way; 2-S = dual shape; 3-S = triple shape; 4-S = quadruple shape

The most interesting SMPs are the ones with two-way SME (Entries 2, 3, 4, 15, 18, 25). It is shocking, that many efforts were made to obtain polyolefin-based SMP with two-way SME (ionomers, blends, composites), and it appears nowadays that carbon and hydrogen only based polyolefins exhibits the desired property (Table 1. Entries 2, 3, 4). For UHMWPE (Table 1. Entry 2) the working mechanism utilizes intensive intermolecular entanglements of extremely long PE chains. Above melting temperature, the entanglements can be partially disentangled. The still-entangled chains keep the permanent shape, while those disentangled ones orient under applied force and cooling. During cooling, those previously disentangled chains re-entangle and they preserve the new shape. Two phases are effectively present, one with tendency to form permanent shape, the other with tendency to form programmed shape. Their presence induces internal stresses. When sample is heated up, the crystals consisting of re-entangled chains melts, and the sample returns to permanent shape. When sample is cooled down, re-entangled chains crystallize creating tension which leads to restoration of programmed shape (Fig. 4. a).

2-W SME of PP (Table 1. Entry 3) utilizes broad melting temperature of PP. When sample is heated to certain temperature, low $T_m$ crystals melt. Sample is then stretched and cooled down. Previously melted polymer parts recrystallizes but this time in oriented manner and preserves programmed shape. The presence of two phases induces internal stresses. When temperature is again raised, low $T_m$ crystals starts to melt, releasing the internal stress and sample is back in its permanent shape. When the temperature is lowered, the oriented crystalline part is recreated providing internal stress and the sample reverts to its programed shape (Fig. 4. b). The similar mechanism occurs in PE/1-octene block copolymer (Entry 4), but there 1-octene block acts as low $T_m$ part of polymer. The advantage of this approach is lowered temperature of switch (5 vs 90˚C for temporary shape, 55 vs 150˚C for permanent shape).

The interesting group of polyolefin-based SMPs are ionomers. In this group new net-points (cross-links) are induced by ionic interactions. The material can be prepared by neutralizing functional groups of polymer (Entries 25, 26, 29) or by reacting two functional groups in polymer blends and composited (Entries 28, 30, 31, 32). Interactions between functional groups of polymer chains have to be also considered, but there is no significant research on this topic yet. Carbon-hydrogen only SMPs properties could be further enhanced by addition of functional groups. Functional groups could strengthen the existing physical mechanism or add new covalent bonds mechanism which could lead to another shape allowed to be remembered.

## 4. Shape memory polymers applications

Shape memory polymers have very broad application potential. Some of polymers have already been deployed on the market in form of textiles and packages [62,63]. The other, more sophisticated and more lucrative applications are medical devices and aerospace[64,65]. Polymers are already widely used in medicine in form of implants, medical devices and equipment. The addition of SME and widen the polymer usage even more. Potential medical application of SMP are: minimally invasive surgeries[66], self-deployable stents[67], implants[68], active prosthesis[13,14] and artificial muscles[26].

The most popular use of SMP are heat shrinkable tubes and films. They were firstly made of polynorbornene and styrene-butadiene copolymers. Nowadays polyurethanes are used in most shrinkable applications[69]. Polyurethanes are also used as self-deployable chairs or safe tags[70].

DIRTBag™ self-deployable repair box is based on polystyrene thermoset and is used as preferred solution for isolation repair in Boeing 787[71]. The other applications of this polymer are e.g. PatchNRepair and PatchNprotect by Gemini Materials[72]. Composite Technology Development offers TEMBO polymers as deployable structures[73].

The other applications involve self-healing materials e.g. protective coatings for metal substrates[74,75]. SMPs can be also used for 3D printing of sophisticated by fused deposition modeling (FDM) method[76].

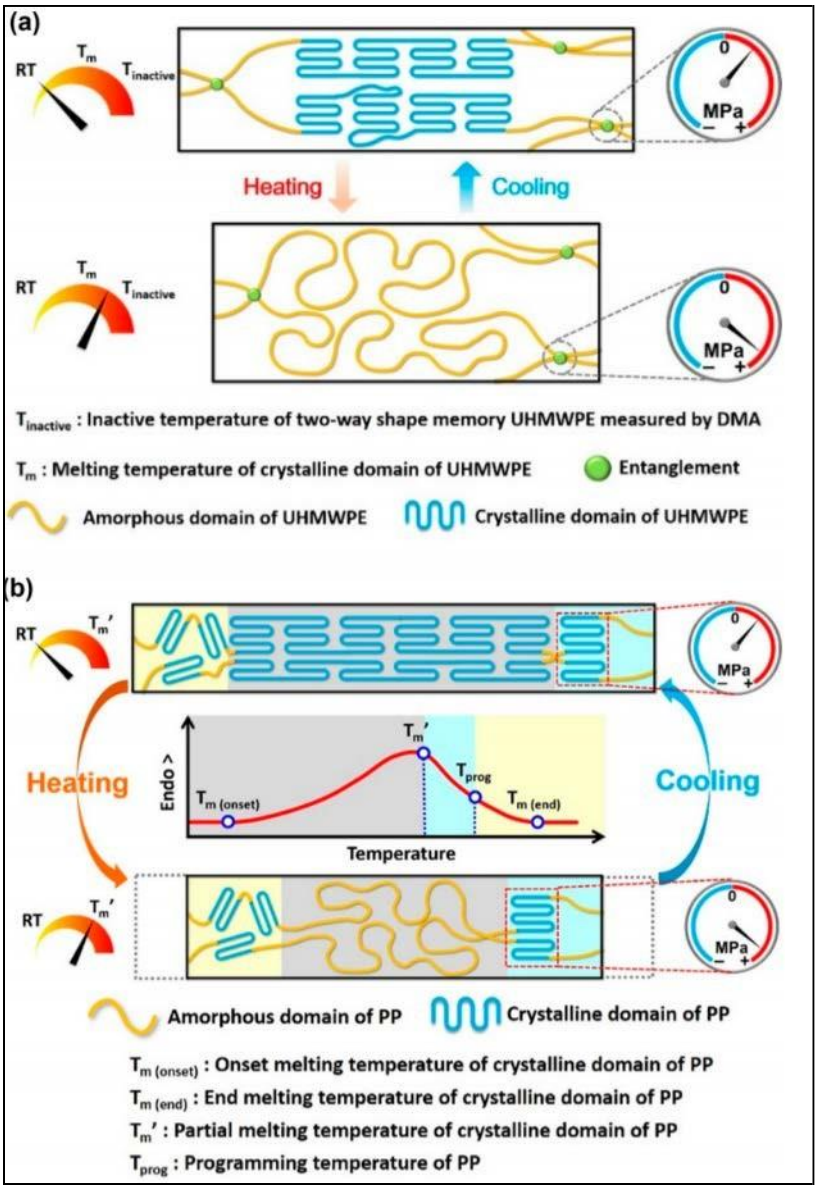

Fig. 4. Principles of reversible SME of a) UHMWPE and b) PP. Adapted from: *Imparting External Stress-Free Two-Way Shape Memory Effect to Commodity Polyolefins by Manipulation of Their Hierarchical Structures* by: L. F. Fan, Y. N. Huang, M. Z. Rong, M. Q. Zhang, X. Chen, 2019, ACS Macro Lett. 2019, 8 (9), p. 1141–1146[28].

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# THE TECHNOLOGICAL PARAMETERS OPTIMIZATION OF THE COPOLYMERIZATION 2-HEMA AND PVP WITH SIMULTANEOUS NI$^{2+}$ REDUCTION

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The urgent problem in technologies of polymeric and composite materials is the development of new uncomplicated, highly effective technologies for the synthesis of metal-filled copolymers of polyvinylpyrrolidone (PVP) and hydrogel materials on their basis.

The basic technological parameters of the process of obtaining nickel-filled hydrogel materials on the basis of copolymers of PVP with 2-hydroxyethyl methacrylate (HEMA) by the method of polymerization with simultaneous recovery of metal ions were investigated. Using a volumometric method, it was established that at pH 7.5-8, the process of chemical reduction of nickel ions is characterized by a high velocity and a small induction period at a temperature of 60-70ºC. The presence of polyvinylpyrrolidone has been found to reduce the duration of the induction period and increase the rate of reduction reaction. The kinetics of heat release during copolymerization of 2-hydroxyethyl methacrylate with polyvinylpyrrolidone initiated by benzoyl peroxide was investigated by a thermometric method. It is established that the exothermic effect of polymerization can be used to create the necessary temperature conditions for Ni$^{2+}$ reduction. The versatile effect of the composition of the original polymer-monomer composition on the basic parameters of the copolymerization exotherm process has been experimentally proved. The diversified effect of the composition of the initial polymer-monomer composition on the main parameters of the exothermy of the copolymerization experiment has been proved experimentally. Depending on the content of polyvinylpyrrolidone, initiator, solvent and initial polymerization temperature, the maximum exothermic temperature varies from 80 to 130 °C, and its time of onset – from 11 to 86 min. In order to decrease the part of experimental losts, the possibility of use the simplex-lattice planning method to optimize compositional formula of polymer-monomer composition. Optimization was carried out for the main parameters of the exotherm process - the time of gelation start, the region of the gel effect and the maximum temperature of the exotherm. The obtained regression equations allow analytically establish the relationship of the parameters of exothermic processes with the technological conditions for the reduction of Ni$^{2+}$ ions, as well as with the formula of the polymer-monomer composition.

The obtained nickel-hydrogel composites are perspective as new materials which are characterized by magnetic, electrical conductive and catalytic properties and can be used as implantable electrochemical biosensors, electro-stimulated drug release, in chemical catalysis, for example reduction reaction of nitrophenols and in hydrogen production reactions, etc.

# RESOURCE-SAVING PAINT AND COATING MATERIALS

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The definition and calculation of the main physical and technical properties of waste treatment of ceramic granite, given in table 1.

Table1.- Physical and technical properties of waste treatment of ceramic granite

| Indicator | Value |
|---|---|
| $M_I$, g/100g | 24,16 |
| $M_{II}$, g/100g | 74,35 |
| Covering capacity, g/m$^2$ | 243.1 |
| pH of the aqueous extract | 8.06 |

The chemical composition of waste treatment of ceramic granite is given in table2.

Table2.- Chemical composition of waste treatment of ceramic granite

| Chemical composition,% | | | | | | |
|---|---|---|---|---|---|---|
| $Al_2O_3$ | $SiO_2$ | $Fe_2O_3$ | $Na_2O$ | $K_2O$ | TiO | CaO |
| 21,4 | 68,0 | 0,9 | 2,9 | 2,0 | 0,80 | 0,60 |

Analysis of the properties of the studied waste allows us to conclude:

The chemical composition of the waste indicates the predominance of $SiO_2$ and $Al_2O_3$ oxides in the waste. Recommendations for the use of the studied waste as fillers for paints and coating materials are formulated.

The pH value of the aqueous extract of waste treatment of ceramic granite guarantees the absence of stimulating action in the processes of electrochemical corrosion.

The values of $M_I$, $M_{II}$ indicate the economic feasibility of using of waste treatment of ceramic granite as fillers for paint and coating materials.

Formulations were prepared and samples of primer GF-021, one of the sales leaders in the range of organo soluble paint and coating materials of Ukraine were obtained.

The properties of GF-021 gray primers were determined according to the standard formulation with the introduction of talc and GF-021 primer as a filler on the basis of waste treatment of ceramic granite in the amount of 25% in the primer formulation.

Physical and technical properties of GF-021 primers and coatings based on them: conditional viscosity, content of non-volatile substances, hardness of coatings, elasticity, resistance to impact, adhesion, resistance to static action of liquids, resistance to nitroenamel meet the requirements of normative and technical documentation GF-021.

# STUDY ON THERMAL, MECHANICAL AND PHYSICAL PROPERTIES OF NOVEL POLYMER COMPOSITION OBTAINED FROM THERMOPLASTIC POLYURETHANE AND POLI(VINYL CHLORIDE)

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Nowadays growing interest of market in novel plastic materials including polymer composition is observed. They find more and more industrial applications and are becoming an equivalent for many other materials. It is related to the possibility of obtaining materials with better mechanical properties, cheaper production and operating costs, or less harmful to health and the environment. The aim of this study was to obtain polymer compositions based on thermoplastic polyurethane (TPU) and poly(vinyl chloride) (PVC). According to literature TPU/PVC compositions characterized compatibility which depends to a large extent on the ratio of rigid to flexible segments in polyurethane. Good compability of these two polymers relieves in the decreasing in glass temperature when content of polyurethane increases.

TPU/PVC composition were prepared using the plasticized PVC pellets (ANWIL S.A, Poland) and synthesized thermoplastic polyurethane at Department of Polymer Technology. TPU were synthesized by means of prepolymer method using 4,4'-diphenylmethane diisocyanate (Borsdorf, Hungary) and polyoxypropylene diol, Rokopol D2002 (PCC Rokita S.A., Poland). As a chain extender bio-propane-1,3-diol extender (DuPont, USA) was used. Twelve compositions with different percentages of PVC and TPU were prepared by using a Brabender mixer and molded by a hydraulic press. The content of TPU in polymer composition was: 100, 90, 80, 70, 60, 50, 40, 30, 20, 10 and 0 wt.% Obtained materials were tested in order to determine the thermal, mechanical and physical properties.

Thermal properties of obtained materials was investigated by thermogravimetric analysis. Results of TGA indicated that increasing amount of TPU in the polymer composition caused increasing in their thermal stability and the beginning of thermal decomposition took a place in the higher temperatures. Mechanical properties were examined in tensile test. Based on obtained results it was found that tensile strength increased with an increasing in PVC content in the composition, while relative elongation at break and permanent after break decreased. The same dependence was observed in hardness and density.

In general, based on conducted measurements, it has been clearly stated that the properties of obtained compositions depend on the percentage of TPU and PVC. The obtained polymer compositions are characterized by properties intermediate to the components used for their preparation.

# EPOKSYDOWO-SZKLANE KOMPOZYTY WARSTWOWE Z POROWATYM RDZENIEM

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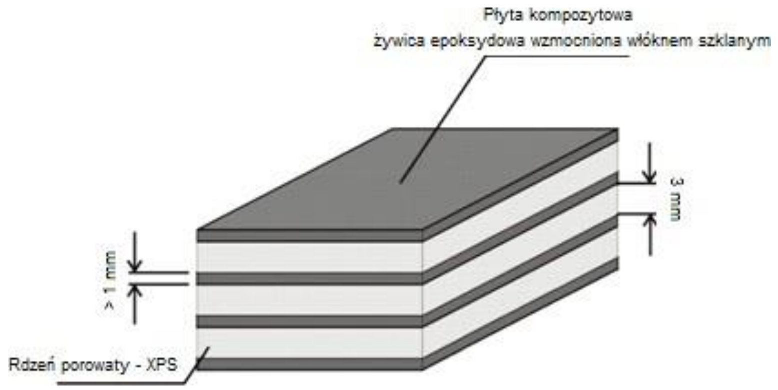
Kompozyty warstwowe, dziкki szerokiemu spektrum zastosowac staj№ siк coraz powszechniej stosowanymi materiaiami konstrukcyjnymi w wielu dziedzinach przemysiu takich jak: budownictwo, lotnictwo, transport, motoryzacja, przemysi elektrotechniczny.

W Katedrze Chemii i Materiaiyw Organicznych Uniwersytetu Technologiczno-Humanistycznego w Radomiu opracowano technikк otrzymywania kompozytyw warstwowych metod№ laminowania rкcznego, ktyrych osnowк stanowiia їywica epoksydowa Epidian 5 wzmocniona wiyknem szklanym, poddana dodatkowo modyfikacji poprzez dodanie poliuretanu Desmocap12 w iloњci 5-15% wagowych. Jako lekki rdzec porowaty zastosowano piyty z ekstradowanego polistyrenu XPS.



Rys. 1 Schemat kompozytu warstwowego

Otrzymane kompozyty zostaiy poddane badaniom wytrzymaioњciowym, tj.: udarnoњж, oznaczenie krytycznego wspyiczynnika intensywnoњci naprкїec, wytrzymaioњж na њciskanie oraz odpornoњж na tryjpunktowe zginanie. Analiza wynikyw wskazuje, їe znaczna poprawa parametryw wytrzymaioњciowych jest zauwaїalna juї przy niewielkim (5%) dodatku poliuretanu w їywicy epoksydowe, gdzie wzrost udarnoњci kompozytu siкgai nawet 70%, a energia zerwania przy tryjpunktowym zginaniu zwiккszyia siк dwukrotnie. Prybki nie iamaiy siк podczas badac, a wysokie wartoњci innych badanych parametryw wytrzymaioњciowych w porywnaniu do niezmodyfikowanej osnowy daj№ obiecuj№ce prognozy dla dalszych prac i moïliwych zastosowac otrzymanych materiaiyw warstwowych.

Kluczowe siowa: ïywica epoksydowa, kompozyty warstwowe, laminat epoksydowo-szklany

# EPOXY-GLASS SANDWICH COMPOSITES WITH A POROUS CORE

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Sandwich composites, because of their wide range of applications, are widely used as construction materials in many fields of such as: construction, aviation, transport, automotive as well as - electrotechnical industry.

In the Department of Chemistry and Organic Materials of the University of Technology and Humanities in Radom were prepared the sandwich composites by manual lamination Epidian 5 (epoxy resin) reinforced with glass fibers and additionally modified by addition of 5 to 15% w/w of polyurethane (Desmocap12) was used as the matrix. Extruded polystyrene plates (XPS) were used as a lightweight porous core.

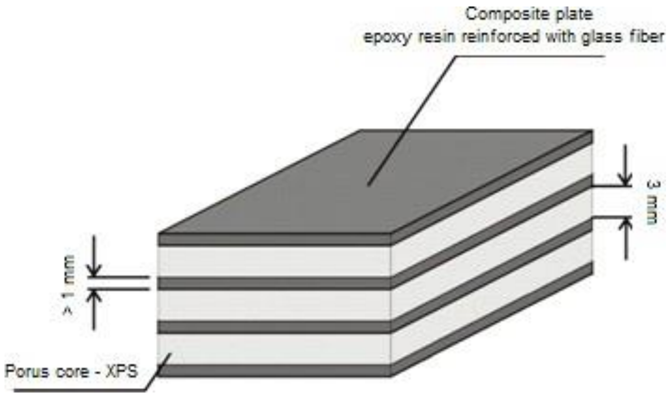

Fig.1 Sandwich composite

The obtained epoxy matrices and sandwich composites, made from joined together above mentoned materials by compression, were subjected to selected strength tests, i.e.: impact strength, compression strength and resistance to three-point bending. The analysis of the results showed a significant improvement in strength parameters. It was observed in composites containing small (5% w/w) addition of polyurethane into the epoxy resin. The impact strength noted for the obtained composites reached 70% higher value in comparison to composite with unmodified epoxy resin and the energy at break at three-point bending increased twice. The samples made of sandwich composites did not break during tests and the observed high values of strength parameters in comparision to the composites with

unmodified matrix are very promising for further investigation and possible applications.

Key words: epoxy resin, layered composites, epoxy-glass laminate

# NOWE MATERIAŁY BIO-POLIURETANOWE OTRZYMYWANE Z WYKORZYSTANIEM GLICERYNY I BIO-1,3-PROPANDIOLU

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## Abstrakt

Niniejsza praca dotyczy nowych materiałów biopoliuretanowych oraz ich właściwości. Materiały otrzymywano metodą prepolimerową. W pierwszym etapie otrzymano prepolimer z wykorzystaniem biopoliolu, a następnie poddano go reakcji z przedłużaczem łańcucha pochodzenia naturalnego bio-1,3-propanodiolem i gliceryną. Biopoliuretany otrzymywano w trzech stosunkach molowych grup izocyjanianowych do hydroksylowych (1.0, 1.1, 1.2). Otrzymane materiały zostały scharakteryzowane za pomocą spektroskopii w podczerwieni (FTIR) oraz w badaniach wytrzymałość przy rozciąganiu i twardości.

## Wstęp

Na przełomie ostatnich lat obserwuje się ogromny wzrost zainteresowania w zakresie syntezy polimerów z monomerów pochodzenia naturalnego. Organizacja European Bioplastics, zdefiniowała pojęcie biotworzyw, jako materiały biopochodne albo biodegradowalne lub materiały charakteryzujące się jednocześnie obydwoma wymienionymi właściwościami. Zainteresowanie otrzymywaniem bio-tworzyw stale wzrasta.

Poliuretany to materiały otrzymywane w wyniku poliaddycji trzech monomerów: diizocyjanianów, oligomeroli i makrocząsteczkowych przedłużaczy łańcucha. Swoje zastosowania uzyskują dzięki szerokiej gamie różnorodnych właściwości. Polimery te, na skalę przemysłową, otrzymuje się głównie z monomerów pochodzenia petrochemicznego. Niemniej jednak wiele prac wskazuje na pozytywny wpływ wprowadzenia do ich syntezy substratów pochodzenia roślinnego. Zamienniki takie charakteryzują się nie tylko mniejszą szkodliwością dla środowiska, lecz przede wszystkim mniejszą toksycznością przy produkcji i uniezależnieniem od surowców kopalnych. Na przełomie kilku ostatnich lat można zaobserwować rosnącą ilość małocząsteczkowych produktów, w tym przedłużaczy łańcucha pochodzenia naturalnego. Są to m.in. bio-1,4-butanodiol (bio-BDO) firmy BASF oraz bio-1,3-propanodiol (bio-PDO) firmy DuPont Tate & Lyle Bio Products [1-4].

W literaturze opisany jest wpływ wybranych przedłużaczy łańcucha na właściwości materiałów poliuretanowych. B.J. Rashmi i in. udowodnili że poliuretany zsyntezowane przy użyciu 1,3-propanodiolu o petrochemicznym pochodzeniu i te otrzymane z bio-zamiennikiem firmy DuPont Company posiadają zbliżone właściwości termiczne i mechaniczne oraz podobną rozpuszczalność [5,6]. Natomiast w swojej publikacji Datta J., Kasprzyk P. i in zbadali wpływ stosunku [NCO]/[OH] prepolimeru przedłużanego za pomocą bio-1,4-butanodiolu (BASF, Niemcy). Na podstawie przeprowadzonych badań wynika że wytrzymałość na rozciąganie, wydłużenie przy zerwaniu oraz twardość materiału rośnie wraz z rosnącym stosunkiem molowym grup [NCO]/[OH] [7].

Celem poniższej pracy, było zbadanie wpływu stosunku molowego grup NCO/OH na strukturę chemiczną i wybrane właściwości otrzymanych przy użyciu monomerów pochodzenia roślinnego materiałów bio-poliuretanowych.

## CZĘŚĆ EKSPERYMENTALNA

### Otrzymywanie elastomerów poliuretanowych

W pierwszym etapie prac zsyntezowano prepolimer z wykorzystaniem (4,4′-diizocyjanianu difenylometanu), MDI (Borsdorf, Węgry) oraz poliolu poliestrowego Priplast 3238-LQ-(GD) (Corda, Polska). Zawartość nieprzereagowanych grup izocyjanianowych w prepolimerze wynosiła 8,35%. Następnie prepolimer przedłużano za pomocą makrocząsteczkowego glikolu, bio-1,3-propandiol, bio-PDO Zamea®, (DuPont, USA),), gliceryny roślinnej o czystości 99,5% (Rafinferia Trzebinia S.A., Polska) i ich mieszaniny w stosunku 1:1. Reakcja w drugim etapie była katalizowana przy użyciu diazobicyklooktanu (Sigma Aldrich, Niemcy). Poliuretany otrzymano w trzech stosunkach molowych [NCO]/[OH]: 1.0,1.1,1.2.

### Metodyka badań

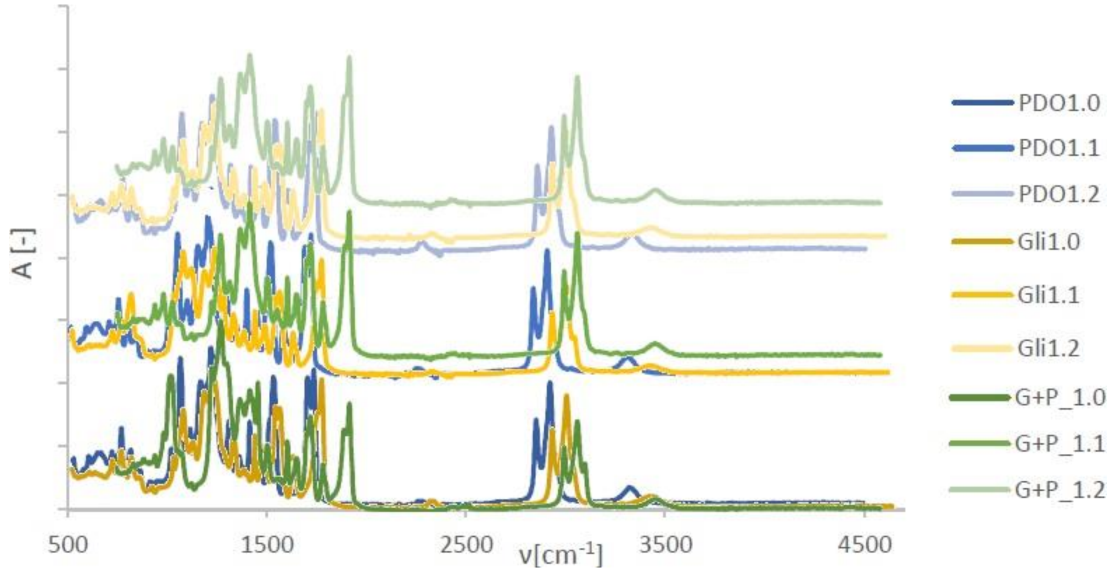
Badania spektroskopowe w podczerwieni wykonano przy użyciu spektrometru FTIR Nicolet 8700, firmy ThermoElectron Corporation. Widma były rejestrowane w zakresie liczby falowej 525 – 4500 cm$^{-1}$, przy rozdzielczości aparatu 4 cm$^{-1}$ oraz z 64 skanami.

Pomiary wytrzymałości na rozciąganie wykonano przy użyciu maszyny wytrzymałościowej Zwick/Roell Z020 zaopatrzonej w ekstensometry. Pomiary przeprowadzono według normy PN-EN ISO 527-1:2012 oraz PN-EN ISO 527-2:2012.

Pomiar twardości Shore’a został wykonany przy pomocy twardościomierza cyfrowego (model 3130) firmy Zwick/Roell typu A, zgodnie z normą PN-EN ISO 868:2005.

### Wyniki i dyskusja

Na podstawie analizy widm FTIR (**Rysunek 1**) określono strukturę chemiczną otrzymanych bio-poliuretanowów. Zaobserwowano charakterystyczne pasma absorpcyjne grupy uretanowej w zakresie liczby falowej: 3400-3300 cm$^{-1}$ (-NH), 1730-1700 cm$^{-1}$(C=O) i 1535 cm$^{-1}$ (NH i CN) i 1100 cm$^{-1}$ (C(O)O). Nie zarejestrowano pasma absorpcyjnego w zakresie liczby falowej 2270cm$^{-1}$, które jest charakterystyczne dla grupy NCO co wskazuje na pełne przereagowanie monomerów [8].



Rysunek 1 Widma FTIR elastomerów bio-poliuretanowych

Wytrzymałość przy zerwaniu, TSb, wydłużenie przy zerwaniu Ɛb i odkształcenie trwałe po zerwaniu Ɛt zestawiono w **Tabeli 1**. Generalnie zauważono, że wytrzymałość przy rozciąganiu i wydłużenie przy zerwaniu zależą od stosunku molowego grup NCO/OH. Na podstawie przeprowadzonych badań stwierdzono, że najwyższą wytrzymałością na rozciąganie charakteryzuje się bio-poliuretan otrzymany przy użyciu bio-PDO, a najniższymi wartościami materiały na bazie glicerolu. Ta sama zależność została zaobserwowana w przypadku wydłużenia przy zerwaniu. Wytrzymałość otrzymanych materiałów mieści się w granicy od 4,1 do 12,8 MPa. Wszystkie otrzymane materiały charakteryzują się bardzo niską wartości odkształcenia trwałego przy zerwaniu.

Tabela 1 Wartości właściwości mechanicznych elastomeru bio-poliuretanowego

| | *Gliceryna* | | | *bio-PDO* | | | *Gliceryna + bio-PDO* | | |
|---|---|---|---|---|---|---|---|---|---|
| | *$TS_b$ [MPa]* | *$\varepsilon_b$ [%]* | *$\varepsilon_t$ [%]* | *$TS_b$ [MPa]* | *$\varepsilon_b$ [%]* | *$\varepsilon_t$ [%]* | *$TS_b$ [MPa]* | *$\varepsilon_b$ [%]* | *$\varepsilon_t$ [%]* |
| **1.0** | 9,2 ± 1,2 | 60 ± 5,0 | 0 | 12,8 ± 0,6 | 237 ± 34,2 | 17 | 11,0 ± 0,8 | 93 ± 9,7 | 2 |
| **1.1** | 7,8 ± 1,0 | 42 ± 7,2 | 0 | 10,3 ± 1,9 | 111 ± 53,6 | 8 | 9,3 ± 1,6 | 68 ± 14,4 | 1 |
| **1.2** | 4,1 ± 0,6 | 25 ± 4,1 | 1 | 5,9 ± 1,4 | 49 ± 17,8 | 1 | 8,4 ± 1,1 | 54 ± 8,7 | 0 |

Analizując twardość otrzymanych bio-poliuretanów (**Tabela 2**) zauważono zarówno wpływ zastosowanego środka przedłużającego jak również wpływu stosunku molowego NCO/OH. Materiały, do syntezy których wykorzystano bio-1,3-propanodiol charakteryzują się najwyższą twardością, przy czym twardość maleje wraz ze wzrostem stosunku molowego NCO/OH.

Bio-poliuretany otrzymywane z udziałem gliceryny posiadają twardość obniżoną o ok 10-15 °ShA zależnie od stosunku molowego reagentów.

Tabela 2 Wyniki twardości otrzymanych materiałów.

| | **bio-PDO** | **Gliceryna** | **Gliceryna + bio-PDO** |
|---|---|---|---|
| **1.0** | 88,1±0,3 | 73,8±0,4 | 64,9±0,3 |
| **1.1** | 87,5±0,4 | 75,0±0,5 | 81,1±0,5 |
| **1.2** | 77,8±0,3 | 78,7±0,3 | 83,1±0,4 |

## Podsumowanie

Na podstawie przeprowadzonych badań określono wpływ monomerów pochodzenia naturalnego na wybrane właściwości materiałów bio-poliuretanowych. Analiza FTIR wykazała że wszystkie materiały wykazują podobieństwo w strukturze chemicznej. Widma spektroskopowe potwierdziły pełne przereagowanie grup izocyjanianowych w każdym otrzymanym materiale. Najlepszymi właściwościami mechanicznymi charakteryzował się bio-poliuretan przedłużany za pomocą bio-PDO, co wynika z liniowego charakteru budowy tego przedłużacza. Największą twardością charakteryzowały się również materiały syntezowane przy użyciu bio-PDO. Zastosowanie gliceryny jako środka przedłużającego wpływa na obniżenie wytrzymałości na zerwanie, wydłużenia przy zerwaniu oraz twardości. Materiały które przedłużane były mieszaniną glikolu i gliceryny charakteryzowały się właściwościami pośrednimi. Wyniki badań dowodzą, że otrzymane materiały wykazują zbliżone właściwości do materiałów syntezowanych przy użyciu monomerów pochodzenia petrochemicznego.

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# NANOCOMPOSITES BASED ON POLYAMIDE AND MONTMORILLONITE OBTAINED FROM SOLUTION

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Previous studies and established regularities have substantiated the feasibility of obtaining polyamide (PA-6) based nanocomposites and montmorillonite (MMT) modified with polyvinylpyrrolidone (PVP) since it forms a technological mixture with polypropylene [1]. However, obtaining a uniform distribution of MMT in the PA-6 during modification in the melt causes considerable difficulties due to the high viscosity. Therefore, it became necessary to find a method for obtaining a homogeneous nanocomposite based on PA-6 and modified MMT. According to our assumptions, a mixing of PA-6 with montmorillonite-polyvinylpyrrolidone mixture (MPM) in formic acid solution is promising. Both PA-6 and MPM are dissolved in formic acid, thus the homogeneous molecular mixing is expected.

Therefore, the aim of the study was to investigate the method for obtaining nanocomposite based on PA-6 with MPM by mixing in formic acid solution and to establish its structure, technological and thermophysical properties.

A new method for obtaining a nanocomposite based on PA-6 polyamide with montmorillonite pre-intercalated with polyvinylpyrrolidone, has been developed. The method consists of mixing components in formic acid solution.

X-ray studies have shown the identity of the supramolecular structure of the synthesized nanocomposite and PA-6, precipitated from formic acid solution. At the same time, the results of thermogravimetric and other analysis show significant differences in the structure and properties of PA-6/MPM nanocomposite and pure PA-6. In particular, the comparison of MPM modified polyamide and original PA-6 shows a higher degree of crystallinity and thermal resistance higher by 16 °C for the synthesized nanocomposite. The resulting PA-6/MPM is characterized by MFI value which is higher by 10 units than that of pure PA-6; this indicates the formation of an inversion mixture with lower viscosity.

The presence of PVP in the structure of the obtained nanocomposite was confirmed by IR spectroscopy, and the presence of exfoliated MMT was confirmed by X-ray diffractometric analysis of the nanocomposite pyrolysis residue.

Aknowlegment

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1. Krasinskyi V., Suberlyak O., Zemke V. et al. The Role of Polyvinylpyrrolidone in the Formation of Nanocomposites Based on acompatible Polycaproamide and Polypropylene / Chemistry & Chemical Technology, 2019, 13(1), 59–63.

# FUNCTIONALISED POLYOLEFINS; SYNTHESIS, PROPERTIES AND APPLICATIONS

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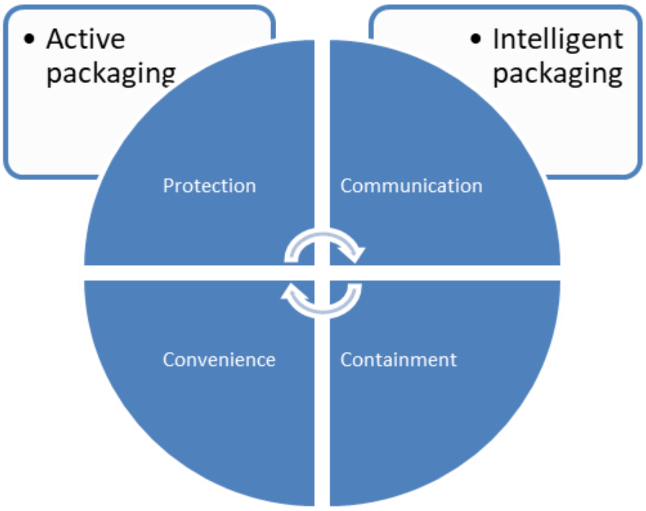
Plastic packaging cover a significant part of worldwide industry. Since recent 50 years production has increased from 15 million tonnes in 1964 to 311 million tonnes of in 2014. Packaging represent 26% of total volume of plastic production. Half of this amount belongs to polyethylene (PE), 21% to polypropylene (PP), 15% to poly(ethylene terephthalate) (PET) and the rest to PS, PVC and others [1]. Basically, packaging has a 4 functions (fig.1): protection, communication, convenience, containment. The package protect product against influence of external environment, communicate with customer as a marketing tool, provide clients easy to use and is able to contain product with different shape and size [2]. Active and intelligent packaging in easy, visible way provide information about food quality and surrounding environment [3]. Every year food packaging technologies are evolving. It is a response for growing requirement of modern society [4].



The article reports characterization of functional polypropylene, copolymers based on this PP and their utilization as intelligent sensors for food packaging industry. Such functional materials are able to interact with pH or oxygen sensors therefore might belong to the group of "intelligent polymers".

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# IMPROVING THE TECHNOLOGY OF SYNTHESIS AND ADVANCE PROPERTIES OF UREA-FORMALDEHYDE POLYFOAM

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One of the most common raw materials for synthetic polymer foam, such as foam, is urea-formaldehyde resin (CFS). Urea-formaldehyde foam (CFP) is the cheapest and most technological heat and sound insulation building material. For the production of polyfoam, urea-formaldehyde resin with a reduced content of free formaldehyde is mainly used. During curing and drying of KFP a huge amount of gaseous formaldehyde is released. At the same time, the concentration of formaldehyde in the working area significantly exceeds its maximum allowable concentration for humans (MPC-0.5 mg / m3). In addition, it has another disadvantage, after curing and drying, it decreases in volume, has a linear shrinkage of more than 7%, and a volume shrinkage of more than 15%. This negatively affects its operational and thermal insulation properties of CFP.

In the presented work, a successful attempt was made to reduce the diffusion of free formaldehyde content and reduce the shrinkage of the foam. This was realized by introducing chemical formaldehyde acceptors into the CFP in the technological process of foam production. To do this, we also conducted a number of experiments with the addition of special chemical foaming agents to the CF resin to reduce the linear and bulk shrinkage of the dried foam. The paper describes the technology of foaming KFS and the properties of urea-formaldehyde foam, by using special formaldehyde acceptors to reduce its concentration during the preparation and use of KFP foam.

In the experimental part, with the help of a special automatic formaldehyde analyzer MIS-98170, the content and diffusion of gaseous formaldehyde from polyfoam, before and after the introduction of chemical formaldehyde acceptors were investigated. As a result of the conducted researches the most effective, ecological acceptors of formaldehyde which reduce concentration and emission of free formaldehyde in 2-3 times were chosen. And also special, additional chemical foaming agents which reduce shrinkage of polyfoam to 2-4% were used. In addition optimum protections paint and varnish coverings for reduction of water and moisture absorption of KF of polyfoam were selected.

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# SYNTHESIS OF PEROXIDE-CONTAINING HETERO-CHAIN AMPHIPHILIC OLIGOMERS BASED ON BIS-PEROXYOXETANES AND POLYETHYLENE GLYCOLS

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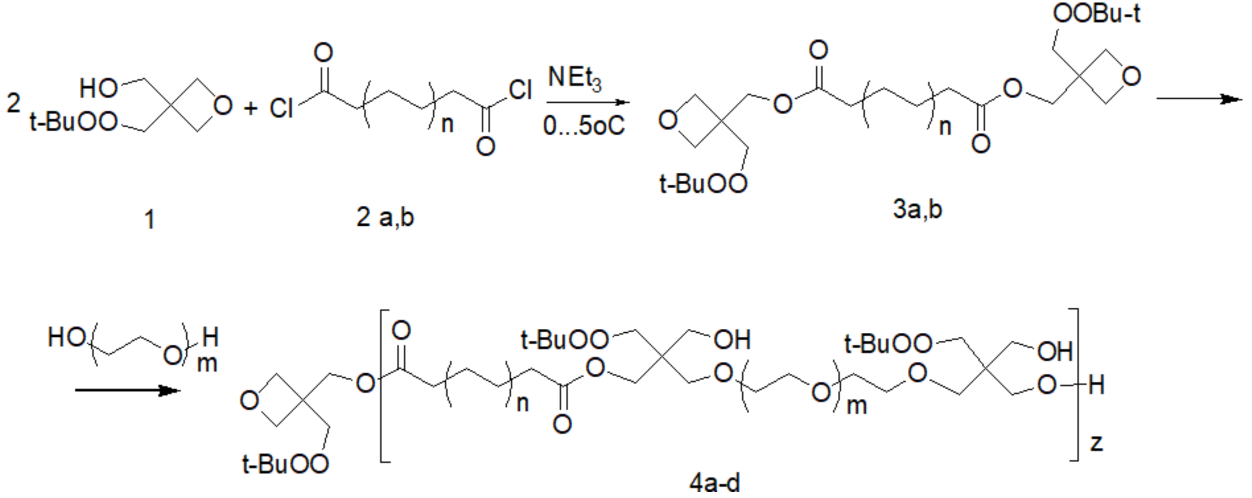
Surface-active oligomers of branched structure are used as effective carriers of drug substances, materials for obtaining nanosensors, modifiers of the interfacial surface of colloidal systems, and so on. Such oligomers are obtained by both condensation reactions and free radical polymerization. We have synthesized surface-active heterochain oligomers containing peroxyalkyl and hydroxymethyl groups. This will allow to obtain surface-active brush-like copolymers of different structure by means of graft copolymerization initiated by peroxide groups or polymer-like transformations by hydroxyl groups.

As monomers for the introduction of peroxide-containing fragments into the molecules of oligomers used peroxide-containing bis-oxetanes, which were synthesized by acylation of peroxide-containing oxetane (1) by the hydroxyl group of dichlorohydrides of sebacic (2a) and dodecanedicarboxylic (2b) acids.

Reaction of the obtained bis-peroxioxetanes (3a, b) with polyethylene glycols of different molecular weight when used as a catalyst $BF_3 \cdot OEt_2$ synthesized oligoesters (4a-d) containing as substituents of the main chain regularly located peroxide-containing fragments and hydroxymethyl:



1 2 a,b 3a,b 4a-d

For the obtained macroinitiators, the dependences of the surface tension of aqueous solutions on the concentration at the interface of the aqueous solution of the substance - air and the values of the critical concentrations of micelle formation were determined.

# COALESCENTS BASED ON ORGANOBORON IONIC LIQUIDS FOR WATERBORNE COATINGS

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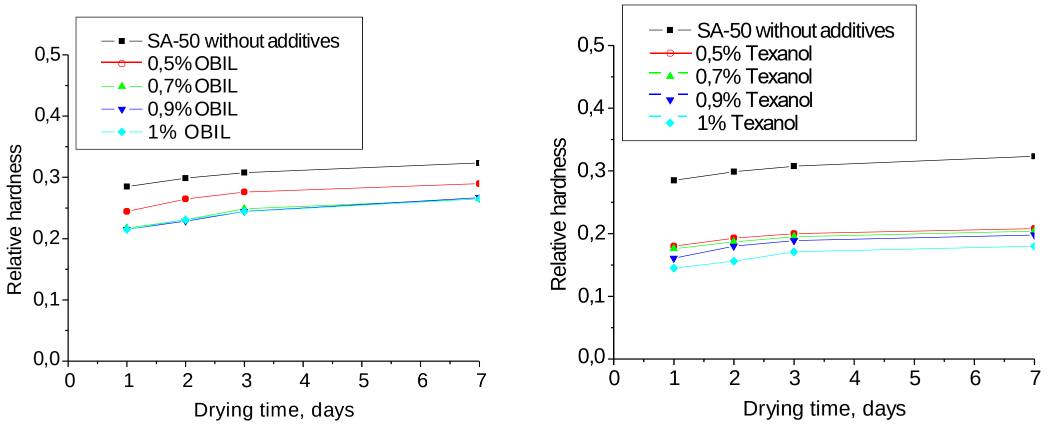
Waterborne coatings (WCs) became widely utilized in the last couple of decades due to a combination of low volatile organic compounds (VOC) content and, as a result, low toxicity, non-flammability, high drying speed, better adhesion to substrates compared to traditional solvent-based coatings etc. Waterborne coatings contain coalescents – compounds that decrease the minimum film forming temperature (MFFT) of the polymer binder and increase film formation efficiency.

In the decades since as WCs started being widely utilized, large number of coalescents were developed, however, after European Union has passed the 2004/42/EC directive which significantly limited VOC content in WCs, a need arose to develop new coalescents with low volatility (of high boiling point).

We propose the use of organoboron ionic liquids (OBIL) synthesized by interaction of boric acid with diethanol amines as coalescents for styrene-acrylic dispersion with MFFT of 18°C and urethane-acrylic dispersions with MFFT of 4-40$^{o}$C. OBILs were synthesized via original procedure and exhibit $T_{b.p.}$ = 270$^{o}$C, pH = 9-10. Approximate cost of OBILs is $2,8-3,5/kg.

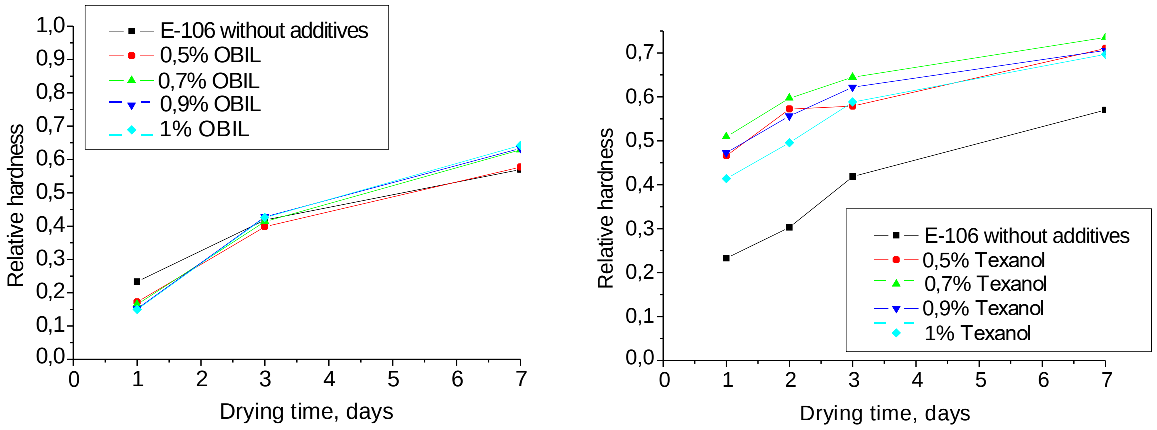
Figures 1-3 show comparison of relative hardness of films formed by styrene-acrylic dispersion Tritex SA-50, urethane-acrylic Neopac E-106 and mixture of Neopac E-106 and Joncryl HYB 6336 (30:70 wt. %) with different amounts of OBILs and Texanol® (Eastman Chemical Company) added.



a

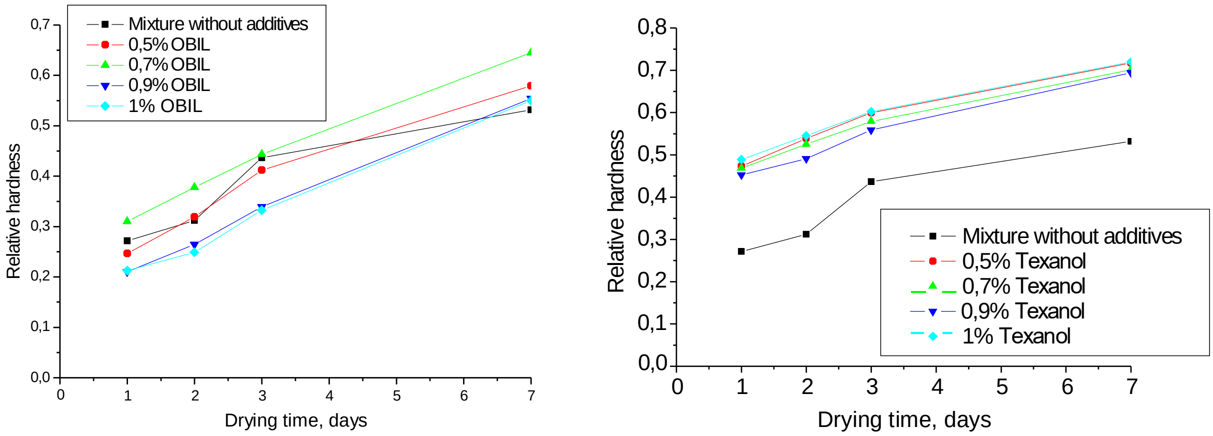
b

Fig. 1. Dependence of relative hardness of films formed by styrene-acrylic dispersion Tritex SA-50 (a, b) on coalescent concentration: OBIL (a) and Texanol® (b)



a b

Fig. 2. Dependence of relative hardness of films formed by urethane-acrylic dispersion Neopac E-106 (a, b) on coalescent concentration: OBIL (a) and Texanol® (b)



a b

Fig. 3. Dependence of relative hardness of films formed from mixture of Neopac E-106 and Joncryl HYB 6336 (30:70 wt. %) (a, b) on coalescent concentration: OBIL (a) and Texanol® (b)

Thus, films formed from OBIL-modified urethane-acrylic dispersions exhibited higher levels of relative hardness compared to unmodified WCs.

Films formed from OBIL-modified styrene-acrylic dispersion exhibited lower relative hardness, which suggests that OBILs act as plasticizers in styrene-acrylic films. However, relative hardness of films with OBILs was higher than that of films with Texanol®.

Films, formed from OBIL-modified pigmented coatings with Tritex SA-50 as a binder, exhibited slight increase in hardness without change of their decorative properties.

# EFFECT OF POLYPROPYLENE ADDITION ON THE PROPERTIES OF MODIFIED BITUMEN

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Abstract

This paper relates to the modification of road bitumen of penetration grade 70/100 with four different types of polypropylene homopolymers which vary in molecular weight distribution, degree of crystallinity and, therefore, with tacticity of its backbone chains. As part of the conducted researches, the influence of incorporating such modifiers on the final properties of resulting polymer-modified bitumen (PMB) was investigated, emphasizing the impact of differences in characteristics of the used polymer materials. Differential scanning calorimetry (DSC) analysis was applied to define the structural variations of the used bitumen modifiers. In order to test its performance in the bitumen, the penetration test, ring and ball test and the dynamic viscosity test were carried out on the produced PMB samples. The hot-storage stability test of modified bitumens was also included in the researches, to check if the samples meet the necessary requirements to use them in the road application. The results show that the properties of PMBs modified with various types of polypropylenes depend on the backbone chain conformation and molecular weight distribution of the applied modifiers.

Keywords: polymer-modified bitumen, polypropylene, tacticity.

## INTRODUCTION

One of the most popular, and thus tested bitumen modification methods is their modification with the use of high-molecular-weight macromolecules of synthetic origins – polymers. Bitumen modification with polymers occurs in two different ways: by mixing them physically with the bitumen or by chemical reactions which take place between them. During the last 50 years of researches, there has been an increasing interest in bitumen modification, resulting in extensive knowledge of e.g., the types of polymers that can be used for this purpose. Among them, there are compounds from the group of plastomers, e.g. polyethylene (PE), polypropylene (PP), ethylene-vinyl acetate (EVA), ethylene butyl acrylate (EBA) copolymer. However, the greatest interest from a technological point of view concerns the polymers of the group of thermoplastic elastomers (TPE) such as styrene-butadiene-styrene (SBS), styrene-isoprene-styrene (SIS) and styrene-ethylene /butylene-styrene (SEBS) block copolymers[1 – 2].

Some plastomers are used in the asphalt industry as an alternative to elastomers, e.g. in the road construction. Unlike elastomers, thermoplastic plastomers usually do not form a physical lattice in the bitumen, but dispersed in it, they act as a filler for the colloidal system of bitumen, at the same time increasing its viscosity[3]. Comparing the plastomeric asphalt binders with elastomeric ones, they are characterized by a greater tendency to create permanent deformations in the pavement. Also, plastomeric asphalt binders have a greater stiffness at elevated temperatures, which results in the lack of improvement in the elastic properties of the pavement. Bitumen modification with plastomers, usually does not increase its resistance to low temperature cracking (it does not significantly affect the brittle point of the properties of the pavement. Bitumen modification with plastomers, usually does not increase its resistance to low temperature cracking (it does not significantly affect the brittle point of the neat bitumen, or even some-times increases it) and affects the penetration more than its softening point values (in opposite to modifiers from the group of thermoplastic elastomers). Due to the relatively low cost of these bitumen modifiers and their beneficial effect on the properties of the neat bitumen, the most common group of plastomeric asphalt binders are polyolefin-modified bitumens[4].

Polyolefin bitumen modifiers are attractive in terms of application. Their low price resulting from raw material and production costs, availability, and thermal properties, which significantly affect the technical parameters of the produced polymer-modified bitumen. One of the first used (1970) bitumen modifiers was atactic polypropylene (aPP) - until then a it was a waste by-product in the production of isotactic polypropylene (iPP), since then polyolefins as bitumen modifiers have been looked at more closely[1, 5]. Simple polyolefins such as PP or PE incorporated into the hot bitumen in the form of granules, powders, or fibers usually swell by absorbing bitumen group components with a lower molecular weight than the polymer (mainly aliphatic oils). As a result of this, a two-phase structure is created, consisting of a polyolefin phase (dispersed phase) dispersed in the bitumen matrix (continuous phase). As the concentration of polyolefins in the bitumen increases, the phenomenon of phase inversion is observed. The addition of polymer disturbs the thermodynamic equilibrium of the colloidal structure of the neat bitumen, making the formed system instable. Thus, as in all cases of polymer modified bitumen, the aim is to ensure that the bitumen after modification with polyolefins is macroscopically homogeneous and consists of two interpenetrating continuous phases in terms of microstructure, which would improve its performance[6].

Long, poorly branched chains of conventional polyolefins tend to come closer together and thicken, so they might crystallize, which in turn leads to a lack of interaction between the bitumen and modifier, resulting in an unstable modified binder. The low compatibility of the bitumen with polyolefins such as

PP and PE can be explained by the apolarity of these modifiers and the poor interaction with bitumen group components (maltenes and asphaltenes). Moreover, at high temperatures polyolefins are characterized by higher viscosity and lower density than the neat bitumen, which makes them prone to separating in the upper layer of the modified binder. PP and PE-modified bitumens tend to be unstable systems, so they are used in the waterproofing applications, most commonly in the form of heat-sealable roofing felts, where the polymer-asphalt binder is used to produce the waterproofing material practically immediately after mixing at high temperature. However, the progress in the synthesis of polyolefins made it possible to obtain materials that meet the broader requirements for PMB. The use of thermoplastic polymers is effective for the amount of modifier in proportion to the weight of asphalt used, ranging from 2 wt.% to 10 wt.% (usually, however, these values do not exceed 5 wt.%) [5, 7 – 8].

## MATERIALS

Road bitumen of penetration grade 70/100 (LOTOS Asfalt Sp. z o.o.) was the raw material used for the modification process. Its properties are presented in Table 1. Four different types of polypropylene homopolymers produced by SABIC were used as the neat bitumen modifiers, namely PP-500, PP-520, PP-531, and PP-575. Their characteristics are presented in Table 2.

## METHODS

Upon the modification, the bitumen was heated in a can to a temperature of 180°C for 1 hour in a laboratory dryer. The hot bitumen container was then placed on a heating element to maintain a constant temperature of 180°C.The hot bitumen container was then placed on a heating element to maintain a constant temperature of 180°C. Next, the homogenizer head was mounted and the thermometer was placed in the can. The next step was to start mixing the bitumen, keeping the temperature of 180°C and the speed of the homogenizer at 3000-4000 RPM. After the temperature stabilized at the level of 180°C, the bitumen modification was started by adding small portions of the weighed amount of granulated polymer. The study established the incorporation of each type of a modifier to the bitumen in the concentration range of 2,5 wt.%. and 5,0 wt.% based on the final weight of the PMB. It was aimed at assessing the influence of the amount of the modifier used in the obtained PMB on its final physicochemical properties and the hot-storage stability. The process of homogenization of polymers with bitumen was carried out for 1 hour with an emphasis on controlling the temperature conditions, which were regulated by the appropriate setting of the power of the heating element and the speed of the stirrer's rotation. In the described procedure, an *IKA T50 basic ULTRA - TURRAX* laboratory homogenizer with a mixing rotor type S 50N - G 45M was used.

Table 1. The properties of the neat bitumen 70/100

| Parameter | Unit | Value | Test method |
|---|---|---|---|
| Penetration at 25$^o$C | 0,1 mm | 70 – 100 | PN-EN 1426 |
| Softening point | °C | 43 – 51 | PN-EN 1427 |
| Brittle point | °C | ≤ -10 | PN-EN 12593 |
| Flash point | °C | ≥ 230 | PN-EN ISO 2592 |
| Solubility | %m/m | ≥ 99,0 | PN-EN 12592 |
| Mass change | %m/m | ≤ 0,8 | PN-EN 12607-1 |

Table 2. The characteristics of bitumen modifiers

| Parameter | PP-500 | PP-520 | PP-531 | PP-575 |
|---|---|---|---|---|
| Density [kg/m$^3$] | 905 | 905 | 905 | 905 |
| MFI [dg/10 min.] (230°C, 2,16kg) | 3,1 | 10,5 | 3,0 | 10,5 |
| Tensile modulus [MPa] | 1550 | 1700 | 1600 | 1800 |
| Elongation at break [%] | 10 | 9 | 9 | 9 |
| Stress at yield [MPa] | 36 | 37 | 37 | 36 |
| Vicat softening temperature [°C] (at 10N) | 152 | 154 | 156 | 154 |

Differential scanning calorimetry (DSC) method was performed using a DSC Q100 apparatus (TA Instruments). The measurements were carried out at a heating and cooling rate of 10°C/min. from -60°C to 230°C. The transitions (melting and crystallization) were derived from the second heating and cooling curves of the received thermograms.

Directly after the homogenization process, the dynamic viscosity of the obtained PMB was determined using a *TermoElectron - Haake Viscotester 2 Plus* viscometer. The determination was performed each time after the measurement result was determined at 180°C, by immersing the measuring head of the viscometer in the PMB to the depth determined by the scale placed above the test cylinder.

The penetration test was performed following the PN-EN 1426: 2015-08 standard using penetrometer *Petrotest* PNR.

The ring and ball test was carried out in accordance with the procedure contained in the PN - EN 1427: 2015-08 standard.

The hot-storage stability test (so-called tube test) was performed following the PN-EN 13399 standard. Then, the softening point of the samples obtained in the tube test were tested, in accordance with the PN-EN 1427 standard. The PMB stability was assessed following the PN-EN.

## RESULTS AND DISCUSSION

Based on the DSC curves analysis the enthalpies and temperatures of phase transitions of the PP modifiers were determined and presented in Table 3. It was observed that the highest melting temperature was obtained for PP-520 (115,6 °C) and for PP-520 (113,1 °C) sample. The two remaining samples had similar melting temperatures of ≈ 105°C. Due to the obtained values, it was possible to determine the content of the crystalline phase in all polypropylene modifiers. For this purpose, the following dependencies were used to calculate the degree of crystallinity of polypropylene:

$$W_C = \frac{\Delta H_M}{\Delta H_{M100\%}} \cdot 100\%$$

$W_c$ – crystalline phase content [%]
$\Delta H_M$ – melting enthalpy of a given polymer [J/g]
$\Delta H_{M100\%}$ – melting enthalpy of 100% crystalline polymer

Table 3. DSC analysis results for modifiers samples

| Parameter | PP-500 | PP-520 | PP-531 | PP-575 |
|---|---|---|---|---|
| $\Delta H_M$ [J/g] | 104,9 | 115,6 | 104,8 | 113,1 |
| $T_M$ [°C] | 158,9 | 159,3 | 160,4 | 159,9 |
| $\Delta H_C$ [J/g] | 100,3 | 111,2 | 102,5 | 109,0 |
| $T_C$ [°C] | 108,9 | 110,1 | 108,8 | 112,6 |

On this basis, the crystalline contents of a given modifiers were computed and presented in Table 4. Melting enthalpy the fully crystalline polypropylene is a material constant, reported in the literature[8]. Its value is equal to 207 J/g.

Table 4. Phase content of the tested polymers

| Parameter | PP-500 | PP-520 | PP-531 | PP-575 |
|---|---|---|---|---|
| Crystalline phase content [%] | 50,7 | 55,9 | 50,6 | 54,6 |
| Amorphous phase content [%] | 49,3 | 44,1 | 49,4 | 45,4 |

The term of tacticity of polypropylene is related to the notion of stereoregularity in the backbone chain of a polymer. A given polymer is stereoregular when its chain structure can be reconstructed by translating a dyad (two adjacent mers) of a specific spatial configuration along a fixed plane. Therefore, only those polymers with stereoregular structure are tactical, so they include iso- (the methyl groups are distributed on the same side of the polymer backbone chain) and syndiotactic (formally, it is an alternating copolymer of two enantiomers of polypropylene configuration units) forms. Non-stereoregular polymers are atactic (the methyl groups are distributed on both sides of the carbon chain in no fixed order)[9].

As the types of polypropylene used in the modification (according to the manufacturer's data) are homopolymers, the more likely the stereoregularity of their chain can be considered. On the other hand, the presence of atacticity, i.e. the lack of stereoregularity in the macromolecule chain, is directly related to the content of the amorphous phase. Thus, it can be concluded that PP - 500P is atactic in about 49% same as the PP-531, while PP - 520P is amporphous in only about 44%. PP-575 has a little bit higher crystalline phase in its structure than PP-520. Because to obtain largely syndiotactic sequences of the polypropylene chain it is required to use highly stereospecific catalysts of a certain type, it can only be assumed that the crystalline phase of the described modifiers consists mainly of the isotactic form of PP. The properties of the tested PMBs are presented in Table 5.

The addition of various types of polypropylene to the bitumen increased the dynamic viscosity of the binders at 180$^c$C. PP-500 and PP-531 polypropylenes (more atactic) influence this parameter to a greater extent as compared to PP-520 and PP-575 PMB samples. There is also an increase in the viscosity of polymer modified bitumen along with the content of the modifiers used in the bitumen, and the increase of this parameter in both cases is similar and amounts to approx. 0,3 [Pas].

The increase in the viscosity of polymer modified bitumen compared to unmodified bitumen is because the types of polypropylene used are typical thermoplastic materials, therefore, at high homogenization temperature, they melt and swell under the influence of asphalt group components, significantly affecting the parameter. Taking into account that thermoplastics have high values of dynamic viscosity in the molten state about asphalt, they will increase this parameter about the resulting polymer binder. The greater impact on the dynamic viscosity of binders with the addition of the PP-500/PP-531 modifiers can be explained by its better solubility in the resin components of asphalt compared to PP-520/PP-575 polypropylene. The degree of tacticity of the latter is greater and it contains more crystalline phase that interact poorly with asphalt without improving the rheological properties of the binders. Besides, the melt polymer PP-500 has a lower melt flow index, which makes it more viscous than polypropylene PP-520 in the same state. As a result, the addition of a more atactic polypropylene to the hot asphalt will increase the dynamic viscosity of the binders to a greater extent. The results of penetration after homogenization show that PP-531 and PP-500 modified bitumen is characterized by higher hardness than PP 575/PP-520 PMB. In the case of modified bitumens, each used amount of PP-531 and PP-575 achieved lower penetration values, compared to the conventional 70/100 bitumen. Also, there was a sudden increase in hardness with the addition 5 wt.% of PP-531to the bitumen, compared to samples containing 2.5 wt. of this modifier. There is a visible tendency of penetration decrease along with the higher mass fraction of polypropylene in the asphalt. After homogenization, the modified bitumen PP-531PH shows the lowest penetration and resistance to deformation under the influence of external forces.

Table 5. Results of tested PMBs

| Type of modifier | Modifier [wt.%] | Bitumen [wt.%] | Viscosity 180°C [Pas] | Avg. Penetration [0,1 mm] | Avg. Softening point [°C] | Δ Softening point [°C] |
|---|---|---|---|---|---|---|
| Neat Bitumen | 0,00% | 100,00% | 0,04 | 74,00 | 45,70 | 0,10 |
| PP-500 | 2,50% | 97,50% | 0,10 | 17,00 | 54,10 | 88,40 |
| | 5,00% | 95,00% | 0,10 | 29,00 | 58,10 | 87,20 |
| PP-520 | 2,50% | 97,50% | 0,08 | 20,00 | 51,20 | 78,50 |
| | 5,00% | 95,00% | 0,10 | 17,00 | 54,90 | 89,70 |
| PP-531 | 2,50% | 97,50% | 0,10 | 47,00 | 50,20 | 90,00 |
| | 5,00% | 95,00% | 0,30 | 31,00 | 52,10 | 89,90 |
| PP-575 | 2,50% | 97,50% | 0,06 | 21,00 | 51,50 | 90,50 |
| | 5,00% | 95,00% | 0,10 | 18,00 | 54,30 | 87,60 |

The obtained test results of ring and ball test proved that with the increase of polypropylene content in the modified bitumen, its softening point increases. These values were higher for PMBs prepared with more isotactic polypropylenes, as they have higher melting temperatures than their more atactic analogues.

The storage stability tests of the polymer-modified bitumen showed that the developed binders are instable, which is manifested by the separation of the polymer phase from the samples, which migrates to the top of the tube, making it rich in the polymer phase. This results in a great difference in the penetration values for polypropylene-modified bitumens.

## CONCLUSIONS

The research carried out in this paper is generally consistent with the expectations resulting from the literature study on the modification of bitumen with increased the hardness of the obtained binders and slightly increased their softening point. The modifiers with a higher degree of atacticity (PP-500P; PP575) turned out to be more effective bitumen modifier. The obtained polymer-asphalt binders are not, however, stable in the liquid state at high temperatures, which disqualifies them from being used in road application. Therefore, the scope of research on this subject should be extended in the search for chemical compounds improving this parameter. Due to the significant increase in the dynamic viscosity of the modified binders and the increase in their temperature resistance, it is assumed that they can be successfully used in the production of waterproofing materials (roofing felt or waterproofing coats).

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# INFLUENCE OF TALC ON MORPHOLOGY AND PROPERTIES OF POLYLACTIDE

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Today due to the low level of reuse of polymeric materials, the most acceptable and generally accepted direction in the development of chemistry and technology of polymeric and composite materials is the use of biodegradable polymers that are capable of controlled decomposition in environmental conditions by external factors. In this regard, the most promising is polylactide (PLA) - a biocompatible biodegradable thermoplastic polymeric material derived from renewable raw materials.

At the same time, the morphology and operational (tensile strength, modulus of elasticity, surface hardness, heat resistance, etc.) characteristics of polymers, in particular polylactide, significantly depend on the content of applications of different nature. Therefore, the directed action on the morphology of polylactide, in particular its additional heat treatment, and the introduction of the nucleator of the crystallization process - talc can regulate the properties of the material in a wide range.

In this work, polylactide of company NatureWorks Ingeo 2500 HP, as well as fine talc filler - Algol Chemicals Finntalc M05 were used to obtain polymer composite materials.

Based on the results of FTIR spectroscopic and X-ray diffraction studies, the effect of heat treatment on the supramolecular structure of polylactide and on the change in intermolecular interactions under the influence of talc was revealed. In particular, an increase in the value of the degree of crystallinity of the polylactide and a decrease in the size of the crystallites after the heat treatment process at a temperature of 120 °C for 3-10 min.

The hardness of the obtained polylactide materials was studied, in particular, there is an increase in hardness due to the introduction of filler and additional heat treatment. The highest value of hardness of 242 MPa is characteristic of the heat-treated material with 2% wt. of talc.

It was found that the addition of talc to the PLA and additional heat treatment contributes to a significant increase in the values of Vicat softening point of polylactide materials by 50-60 K. The greatest impact on Vicat softening point has additional heat treatment. The introduction of 2% wt. talc allows you to reduce the required heat treatment time to achieve high values of Vicat softening point.

There is also an increase in the modulus of deformation by 45-95% and the modulus of elasticity by 15-50% of polylactide materials under the action of filler and heat treatment, in particular, the highest values are characteristic of heat-treated samples with talc content of 2% wt.

# INFLUENCE OF CALCIUM-CONTAINING FILLERS ON ELASTIC-DEFORMATION PROPERTIES OF POLYLACTIDE

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The search for optimal materials for implants, the development of various biodegradable biocomposites based on polymers from natural raw materials is a promising direction of technology of polymer and composite materials. In this regard, promising are materials based on polylactide (PLA) and calcium-containing fillers.

For polylactide composite materials, along with strength and thermophysical properties, elastic, highly-elastic and plastic characteristics are of great importance. Studies of the deformation properties of polymeric materials are also necessary to understand the behavior of the material under load of different types and their morphological features.

In this work, polylactide of company NatureWorks Ingeo 2500 HP, as well as fine fillers of calcium orthophosphate and calcium hydrogen phosphate were used to obtain polymer composite materials. Also, for the targeted effect on the morphology of the obtained materials, additional heat treatment of the obtained materials was performed at 120 °C for 10 min.

Based on the carry out research, was found the deformation modulus increased by 60-95% and the elastic modulus by 35-75% of polylactide materials under the action of filler and heat treatment, in particular, the highest values are characteristic of heat-treated samples with a filler content of 2% wt. It should be noted that the effect of calcium hydrogen phosphate is more significant than orthophosphate.

Based on the module-deformation method of calculation, data on the fractions of elastic, highly elastic and plastic components in the total deformation are obtained. It was found that the introduction of the filler and additional heat treatment leads to a decrease in the part of the elastic component and an increase in the part of the plastic component, while the part of the highly elastic component is almost unchanged.

The surface hardness of the obtained polylactide materials was studied, in particular, there was an increase in hardness with the introduction of filler and additional heat treatment. The highest value of hardness of 299 MPa is characteristic of the heat-treated material with 2% wt. calcium orthophosphate. It was found that the addition of fillers and additional heat treatment contributes to the growth of the structure coefficient of the material that characterizes the spatial fluctuation grid of the polymer. In this case, the greatest influence on the coefficient of the structure has an additional heat treatment.

Using thermomechanical analysis, it was found that the addition of filler has almost no effect on the nature of thermomechanical curves, at the same time heat treatment contributes to a significant increase in the degree of crystallinity of PLA and, accordingly, shifting its melting temperature to higher temperatures.

# MODIFICATION OF HYDROGEL MEMBRANES BY THE LAYERED SILICATES

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The hurried development of polymer hydrogels physico-chemistry has played a revolutionary role in sphere's extension of their practical application, in particular in the creation of membranes with adjustable permeability.

Polymer hydrogels have low mechanical strength and their swelling degree strongly depends on the medium of solution which significantly limits their applying. Obtaining of compositions based on polymer hydrogels via

adding into their composition of various compounds can significantly improve their physico-chemical characteristics.

Polymer-clay compositions are of considerable scientific interest. Clay particles give hydrogels the new properties, improve their mechanical properties as well as prevent collapse. The clay particles themselves included in the hydrogel, also acquire new properties; in particular, it can be chemically modified without coagulation.

To create polymer-silicate materials the ability of layered silicates to intercalate monomers and polymers in their interlayer space is used, followed by stratification of filler particles into monolayers with a thickness of 1 nm. Thereby the dispersion of nanoparticles in the polymer matrix is being achieved. In the natural state the layered silicates, natural ion exchangers are characterized by high hydrophilicity, which allows them to be used for modification of hydrogel materials during synthesis by polymerization of compositions in an aqueous medium. Among the clay materials for the production of hydrogel polymer composites the montmorillonite (MMT) is promising material which has good thixotropic and sorption properties.

The work purpose was to study an influence of montmorillonite content on swelling, mechanical strength and permeability of composite film hydrogel membranes based on 2-hydroxyethyl methacrylate (HEMA) with polyvinylpyrrolidone (PVP) copolymers.

It was determined that the composite hydrogel membranes obtained by modification of hydrogels based on HEMA/PVP copolymers with montmorillonite during the film synthesis via radical polymerization in an aqueous medium are characterized by high sorption capacity, mechanical strength and osmotic permeability (at the low MMT content). It is shown that an increase of MMT content in the composition of hydrogel HEMA/PVP membranes leads to a decrease of their permeability and elasticity and an increase of the swelling degree and strength during the breakthrough.

# METALLIZATION OF POLYMER GRANULES

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For various industries of considerable interest are metal-filled polymers in which the fillers are metal powders or metal fibers. Such metal-filled polymers are characterized by high strength, heat resistance, thermal and electrical conductivity. Some polymers of this type due to their cheapness and availability replace non-ferrous and precious metals in the manufacture of bearing liners, products with high thermal conductivity and low friction, others are used in radio engineering, to protect against electromagnetic radiation, in the manufacture of conductive parts, catalytic systems, etc.

The paper presents the results of research that formed the basis for the development of metallization technology of granular polymer raw materials.

A new method of giving the surface of polymer granules catalytic properties has been proposed. Activation of the polymer surface occurred as a result of treatment of granules in a ball mill with powder of active metal (relative to Cu), in this case Zn. This joint treatment in a ball mill allows to obtain a polymer surface saturated with particles of catalytically active metal, which are fast fixed on the surface of the granules. For chemical deposition of copper on the activated surface of polymer granules, a copper solution of the following composition was used: $CuSO_4$ $5H_2O$; EDTA-$Na_2$ ($C_{10}H_{14}N_2Na_2O_8 \cdot 2H_2O$); NaOH; formaldehyde. As a result of the deposition of copper in the solution of chemical metallization, a high-quality metal surface was obtained, which covers the surface of the polymer granules with a solid layer. The results of the study of the metallized surface of polymer granules by electron microscopy show that copper during deposition from solution forms a solid, dense coating on the polymer surface.

The developed technology can be used to obtain high-tech metal-containing polymer composite materials. The introduction of metal into the polymer matrix in the form of a metal coating formed on the polymer surface will provide metal-containing polymer composites, which are characterized by a uniform distribution of the metal in the polymer matrix. Obtaining such metal-filled composites will occur directly during the processing of metallized polymeric raw materials into products using standard equipment without complicating the processing technology.

# SYNTHESIS OF LINEAR SEGMENTED POLYURETHANES AS COMPONENTS OF EPOXYURETHANE COMPOSITIONS

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It is known that modifiers such as segmented polyurethanes (SPU) significantly increase the physical and mechanical characteristics of epoxypolymer compositions, including their elasticity, adhesive strength, and the like. SPUs are many block copolymers that are composed of so-called hard (polar) and soft (non-polar) segments. The multiphase structure of the SPU is due to the repulsive interaction of dissimilar parts and the thermodynamic incompatibility of hard and soft segments at low temperatures. The microphase structure of the separation of polyurethanes depends on many factors, namely: the structure and molecular weight of the soft segment, the nature of the chain extender, the content and interactions of the hard segment. As a rule, phase separation occurs during the curing of epoxyurethane compositions. The conditions for the synthesis of SPU based on PPG-1000 and 2,4-2.6 toluene diisocyanates (80/20) and SPU based on PPG-1000 and isophorone diisocyanate (IPDI) were studied. The chain extender is 1,4-butanediol, or 1,3-hydroxybenzene, or 4,4'-dihydroxy-2,2-diphenylpropane. The calculated MM of these SPU is ~ 13000 g / mol.

The effective heat of activation of a viscous flow has been determined by the rheological properties of the SPU at various temperatures. The fact of the formation of the SPU was confirmed by IR spectrometry. According to the phase state diagrams of mixtures of the epoxydian oligomer DER-331 with synthesized SPU (50:50) obtained by the method of light scattering from the heating rate of the mixture, it was determined that SPU are compatible and homogeneous with DER-331 from room temperature to 180 ° C.

# INVESTIGATION OF THE PROCESS OF STRUCTURING POLYSACCHARIDES BY N-DERIVATIVES OF GLUTAMIC ACID IN THE STEGLICH REACTION

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The research of forming biomaterials based on polysaccharides is mainly in three directions. There are the creation of hydrogels with special properties, microhydrogels and drug delivery systems. Interest to polysaccharides is due to the fact that polysaccharides are tolerant to the human body. This fact explains wide efforts of researchers to form polymer polysaccharide-based materials for medical and biomedical purposes.

The report sets out a number of studies in dextrin’s modification to produce a functional product with branched structure of macromolecules (figure 1).

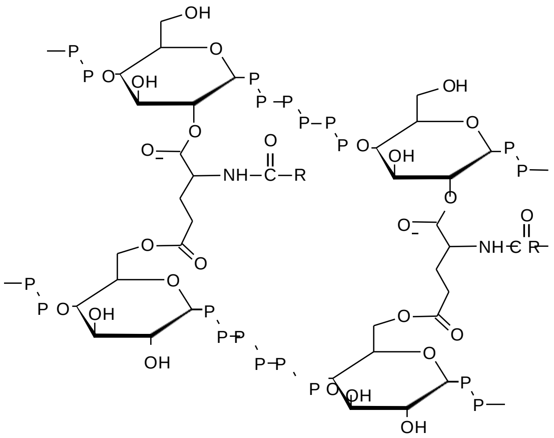

Figure 1. Structure of modified dextrin, where P - glucopyranoside residue

To ensure branching of dextrin macromolecules, modification was carried out using the bifunctional agents N- derivatives of glutamic acid. The residue in the N-position provides introduction of required function. Cross-linking was performed via the Steglich reaction in soft, controlled conditions.

In this report the effect of process conditions on the structure of the resulting products was studied. It was shown, that the reaction leads to the formation of products with branched and 3D-structured nature of macrochains. The resulting products have different properties.

We have studied the conditions of separation and showed the dependence of their properties on the degree of cross-linking and branching. It was shown that the modified polysaccharides macromolecules with branched structure form well-stabilized aqueous dispersion in aqueous medium, and macromolecules with 3D-structured macrochains form microhydrogel in an aqueous medium.

In this report the results of studies of aqueous dispersions and microhydrogels formation, their ability to solubilize insoluble in water organic compounds and their release them in lipophilic medium are presented. Cytological studies of toxicity of obtained polymeric materials were conducted. The complex research suggests that obtained polymers are perspective as polymer materials for medical and biomedical use.

# FORMATION OF CROSS-LINKED POLYACRYLAMIDE NETWORKS WITH SIMULTANEOUS FIXING TO THE POLYPROPYLENE SURFACE

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The research is devoted to the development of technology for producing hydrogel therapeutic agents with high physical and mechanical properties on the basis of acrylamide copolymers. An increase in the physico-mechanical properties of polyacrylamide hydrogels is achieved by covalent grafting of the gel-forming polymer to the polypropylene surface. Hydrogel structure provides biocompatibility with tissues of living organism, the ability to adsorb and release drugs, atraumatic technique; the reinforcing polymer material provides necessary mechanical strength during the technological operations in the production and application of this hydrogel material. A peculiarity proposed in this work is the covalent attachment of the gel-forming polymer to the polypropylene surface allowing the resulting material to be integrated in a coherent structure and thus obtaining the characteristics of a composite.

In this paper presents the experimental results regarding the comonomers radical copolymerization, which is simultaneously initiated by two peroxide initiators. One of the initiator is localized in the reaction volume, and the second one is covalently grafted to the polymer surface. The following items are discussed in this section: the dynamics of the of acrylamide polymerization process; copolymerization of acrylamide, N,N-methylenebisacrylamide and potassium acrylate; the formation of polymer network points; the effect of process conditions and reaction mixture composition on the time and conversion of gelation. The comparison of the formation rates of the gel-forming polymer macromolecules, which were initiated from the reaction volume and from the surface of the reinforcing material, was of special attention. It is shown that the consistency of mentioned two processes is the basis for hydrogel grafting to the surface.

A mathematical model for the formation of polymer network of acrylamide, N,N-methylenebisacrylamide and potassium acrylate copolymer was obtained using statistical methods. The model well describes the experimental data and explains the nature of the main factors effect on the time and conversion of gelation, as well as the ratio between sol- and gel-fractions during the whole hydrogel formation process.

Based on the experimental results and predictive data generated by the mathematical model, the basic regularities of the formation of a three-dimensional hydrogel network (formation of polymer molecules, cross-linking) before the system gelation (conversion > 5-7%) and after it till deep stages of copolymerization (conversion> 75-85%) were examined. Dependences of the basic parameters of the hydrogel formation (rate, copolymer composition, average degree of polymerization, density of cross-linking, ratio between sol and gel fractions) on the process conditions were obtained. This allowed to demonstrate that the grafting to the surface is realized after the gel point and the majority of covalent bonds that provide the grafting of the gel-forming polymer to the surface is formed in deep stages (conversion > 75-85%).

# POLYANILINE NANOTUBES – CARBON NANO-ONIONS NANOCOMPOSITE AS A NOVEL ELECTRODE MATERIAL FOR ELECTROCHEMICAL SENSING OF DAIDZEIN

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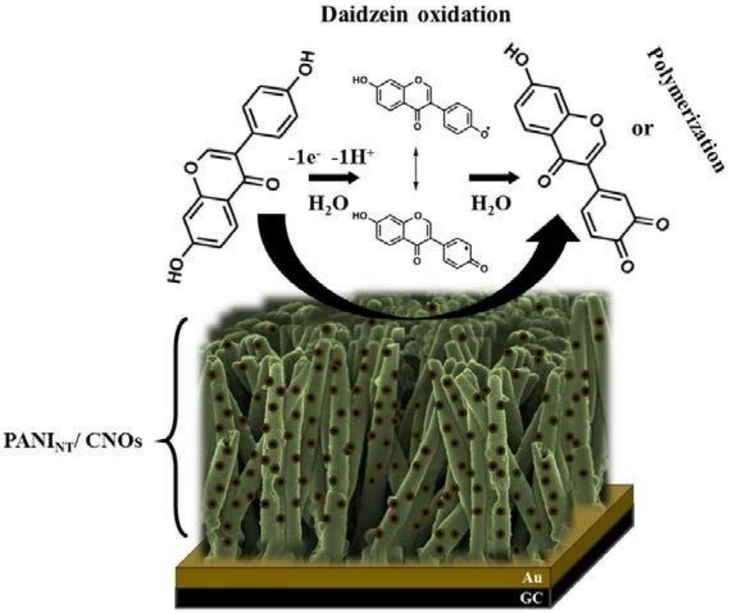
## GRAPHICAL ABSTRACT



## ABSTRACT

Carbon-based nanomaterials, such as graphene, carbon nanotubes (CNTs), carbon nanofibers, carbon nano-onions (CNOs) or fullerenes, are currently one of the most attractive nanostructures [1–4]. The unique mechanical, chemical, optical and electrical properties of CNOs are related to their shape, size and surface area, what makes them useful in multiple nanodevices. Considerable effort is currently devoted to the preparation, characterization and application of CNOs nanocomposites [3]. Many of them are suitable for chemical or electrochemical detection. Their biocompatibility also makes them useful as biosensor agents [5].The electrochemical biosensors are promising tools for important biological compounds determination and environmental analysis. Such devices can operate under mild conditions and are easy to miniaturize [6].

In this study glassy carbon electrode (GCE) surfaces were modified with nanocomposites containing conductive polyaniline nanotubes ($PANI_{nt}$) and carbon nano-onions (CNOs). The $PANI_{nt}$/CNOs nanocomposites exhibit the ability to oxidize daidzein (DA). Herein we report a simple and sensitive way for DA determination at concentrations between 1 and 10 µM by linear sweep voltammetry using a nanostructured GCE/$PANI_{nt}$/CNOs system. The electrochemical behaviour of DA was examined in PBS buffer (pH 7.4) using an electrode modified with the oxidized CNOs or their derivatives contatining carboxyl and benzylamino functional groups. The results indicate good selectivity and sensitivity of $PANI_{nt}$/CNOs nanocomposites against DA molecules. The characteristic direct electrooxidation of DA was observed at +0.65 V and +0.8 V vs. Ag/AgCl at pH 7.4.

ACKNOWLEDGEMENTS

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# NEW POLYOLS OBTAINED FROM WOOD WASTE AS RAW MATERIALS FOR THE PRODUCTION OF WOOD-POLYMER COMPOSITES

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The problem of wood waste generation and associated risks are an increasingly noticeable challenges for the modern science. Waste management of post-industrial and post-use waste should be included to the very important and difficult problems that Polish society is struggling with. According to the Waste Directive [2008/98 / EC], waste is defined as any substance or object that the holder discards, intends to discard or is required to dispose [1]. We divide wood waste into industrial waste, which arise during the production of finished products, and post-use waste. The first group includes shavings, sawdust, bark, wood dust, as well as large and small pieces of wood from the processing of wood. The largest sources of wood wastes are the sawmill industry (63%), production of particle boards and chipboards (14%) and the furniture industry (13%). The most abundant among industrial waste are sawdust and shavings and bark [1,2].

The previously mentioned directive also indicates the waste management hierarchy which says that preparation for re-use and recycling is more desirable than other recovery processes (e.g. energy) and disposal. It should be emphasized that the two least desirable methods of utilizing this waste are still widely used in Poland, therefore the scientists are looking for new methods of management of this resource. One of the known methods of managing this waste in order to obtain a full-value product is production of wood polymer composites (WPC) [1,3].

WPC are materials made of polymeric matrix and shredded wood which act as a filler. The most commonly used materials for the matrix are thermoplastics such as polyethylene (low and high density), polypropylene, poly (vinyl chloride) or polyurethane. Various forms of wood are used as the dispersed phase: splinters, shavings, wood chips, fibers and wood flour, predominantly from conifers. The amount of wood particles in WPC can reach up to 90% of the weight of the composite, however, due to the high moisture absorption, it is limited to 50 - 65%. Higher filler content may result in cracking of the material at the interface of phases. In order to improve the properties of these materials, coupling agents, which improve the compatibility between the polymer phase and the dispersed wood phase, auxiliary agents such as antioxidants, UV stabilizers, biocides, flame retardants are used. Due to environmental protection, it is desirable that as much as possible substances used in the production of WPC should came from renewable sources. One of such ideas of such a solution is the use of a bio-polyol, obtained through liquefaction process, in production of polyurethane matrix. [4,5,6]

Liquefaction is the process of converting solid biomass into liquid. It can run indirectly, where it is first converted into synthesis gas, from which alcohols and alkanes are then synthesized. Direct liquefaction takes place in protic solvents such as water, phenols or low carbon alcohols. It is the main method of biomass conversion because the reaction conditions are milder, the process is easier to control and has a higher efficiency. Obtaining bio-polyol in the liquefaction process consists in the reaction of biomass with a solvent in the form of polyhydric alcohol in addition of catalyst. All biomass components are reacted, while the kinetics of the process is determined by the liquefaction of the cellulose itself, as the slowest process. During the reaction a wide range of substances can be obtained. The most important of them are glycosidic alcohols, which in the next stage can transform into levulinates [7,8].

In this work bio-polyols were prepared by liquefaction of chip waste at a temperature of 150 °C for 6 hours in three different solvents - glycerol, poly(ethylene glycol) (PEG 400) and their mixture in a 1:1 ratio. To accelerate the reaction 3% wt. of concentrated sulphuric acid was added as a catalyst. Properties such as hydroxyl number, biomass conversion and rheology of obtained bio-based polyols were investigated.

## 2. Experimental

### *2.1. Two-step preparation of bio-based polyols*

Liquefaction of chip waste was carried out in a three-neck reactor under atmospheric pressure. The mixture was stirred constantly using mechanical stirrer. The reactor was heated by heating mantle. In this reaction glycerol, PEG 400 and 50/50% wt. mixture of PEG400 and glycerol, was used as a solvent. To catalyze the reaction 3% wt. of 95% sulfuric acid was added. The mass ratio of chip waste to the solvent was 1:10. In the first step, the liquefaction was conducted using three different solvents systems to determine the impact of solvent influence on the course of the reaction and properties of obtained polyols. Samples of the product were collected every hour to study the change of hydroxyl number and biomass conversion during reaction. In the second step the obtained product was neutralized with sodium hydroxide (NaOH) to pH ≈ 7 and then dried under vacuum for 2h to remove excess water.

## 3. Results and discussion

The hydroxyl number of obtained polyols was determined according to PN-EN 1240:2011. Figure 1. shows change in the hydroxyl number as a function of reaction time for 3 polyols coded Polyol P (liquefied in PEG 400), Polyol G (liquefied in glycerol), Polyol M ((liquefied in 1:1 wt./wt. of PEG 400 and glycerol). All polyols show an initial drop in hydroxyl number and a slight increase on the end of the reaction. Reduction of the number of hydroxyl groups can be caused by condensation of glycerin with itself and the biomass. An increase in LOH at the end of the reaction indicates that the biomass chains are broken down into smaller ones. Table 1 shows the change in hydroxyl number after the second synthesis step (neutralization + drying). During the neutralization process, water particles are formed due to the reaction of NaOH with $H_2SO_4$. For samples of Polyol P and G, an increase in LOH was observed after neutralization, which may result from not receiving all the water in the drying process. No change in the hydroxyl number of polyol M proves that the drying process was correctly conducted for this substance [9].

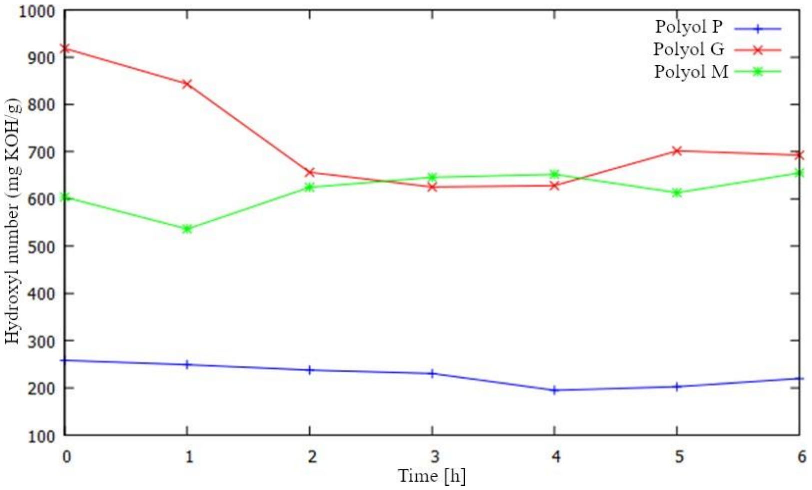

Figure 1. Changes in the hydroxyl number during the biomass liquefaction reaction

Table 3. Hydroxyl number before and after the neutralization process.

| Polyol | $L_{OH}$ before neutralization [mgKOH/g] | $L_{OH}$ after neutralization [mgKOH/g] | Biomass conversion [%] |
|---|---|---|---|
| **Polyol P** | 220 ± 11 | 260 ± 16 | 94,9 ± 1.6 |
| **Polyol G** | 692 ± 26 | 725 ± 32 | 90,4 ± 1,3 |
| **Polyol M** | 655 ± 21 | 650 ± 29 | 93,8 ± 1.4 |

Figure 2. shows the biomass conversion as a function of the reaction time for obtained polyols and table 1. shows final degree of biomass conversion. During the liquefaction process, long chains of biomass decompose to lower molecular weight components. These components can react with used solvent, which is associated with an increase of biomass conversion. First stage of liquefaction process is determined by degradation

of biomass under the influence of sulfuric acid, what explains greatest increase in conversion in the first hour of process. Later, the degradation products may repolymerize into insoluble xylosides and glucosides, which presence decreases the rate of biomass conversion. The increasing degree of biomass conversion proves the correct course of the reaction. The highest efficiency is when using PEG 400 as the solvent and the lowest when using glycerol. There is the greatest increase in conversion in the first hour. The decrease in the hydroxyl number and the increase in biomass conversion proves the correct course of the reaction [10].

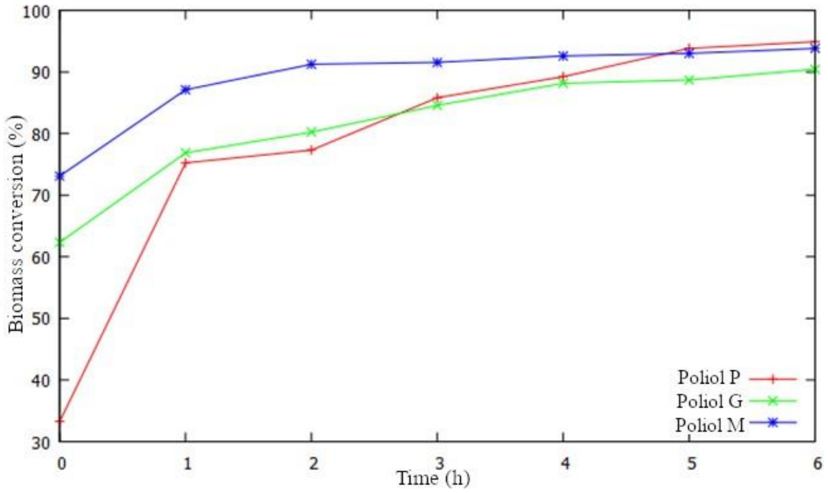

Figure 2. Change of the degree of biomass conversion during its liquefaction reaction

Figure 3 shows the shear stresses and viscosity of polyols at 30 °C and 50 °C. The obtained bio-polyols show a linear flow that can be described as a Newtonian fluid. On the basis of the obtained curves, it was noticed that the shear stress decreased with increasing temperature. This effect is due to the greater mobility of the macromolecules and the free space between them. Polyol G has the highest viscosity of 4.98 Pa·s at 30 °C. Obtained polyols are a rheologically stable fluids because the deviation of the flow curve hysteresis is small.

## 4. Conclusions

In this work bio-based polyols during liquefaction of chip waste using glycerol, PEG 400 and their mixture were obtained. The impact of different kind of solvent on variation of hydroxyl value biomass conversion and rheological properties has been determined. Polyol M has hydroxyl value comparable to the commercially available polyols, high biomass conversion and suitable viscosity and it is expected to be the best in the further production of polyurethane materials. Polyols obtained during research may be used in manufacturing of WPCs with a polyurethane matrix.

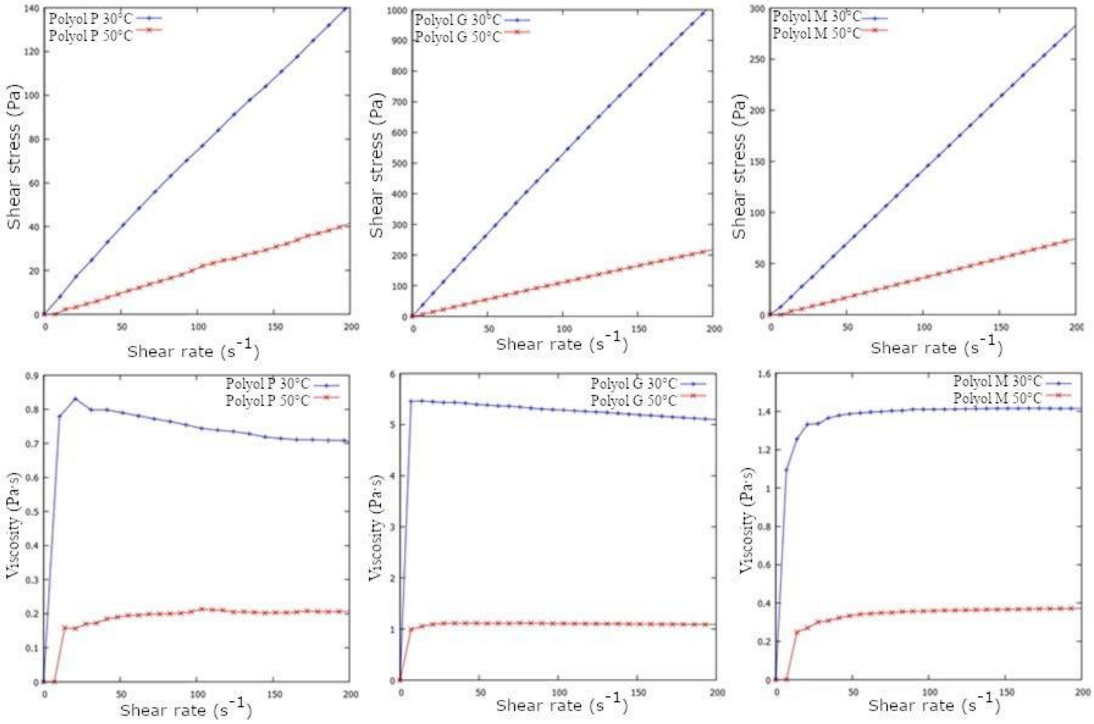

Figure 3. The flow and viscosity curves of obtained polyol at different temperatures

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# PROPERTIES OF EPOXY WEAR-RESISTANT COMPOSITE MATERIALS UNDER CONTACT-DYNAMIC LOADING

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A significant amount of industrial equipment in Ukraine and in the world works in conditions of abrasive-erosive wear under dynamic loading (hydrocyclones, soil and slurry pumps, etc.). To protect and restore equipment used epoxy composite materials with high-Mohs fillers — silicon and boron carbides, silicon nitride, corundum. To develop new competitive epoxy wear-resistant composite materials, it is necessary to study their behavior in contact with solid particles of the medium, taking into account the influence of the elastic and viscous components of the strain energy.

In the study unfilled and filled (20-300 parts by weight) of silicon carbide F-1000 with a particle size of 5-7 µm, epoxy compositions based on ED-20 resin was used. The compositions cured by polyamines of various world manufacturers (PEPA, CeTePox, Epikure F-205, Polyamine B, Ancamine 2692, 2752) according to the regime: 20°C × 24 h + 100°C × 3 h. The dynamic properties of epoxy compositions were determined at 22 ± 2°C by indentation method using a rigid indenter in a single pulsed mode. Viscoelastic properties were characterized using the Maxwell and Kelvin-Voigt models.

The influence of the components of the strain energy - elastic and viscous, on the course of the main (penetration) and passive (rebound) phases of the process was determined, and straight-line relationships between these parameters for unfilled epoxy compositions are established. For composites filled with silicon carbide, the character of these dependences changes to nonlinear, which is associated with the contribution to the deformation process of their formed disperse structure.

Was been shown that at elevated filler concentrations typical of industrial compositions (> 200 parts by weight per 100 parts by weight of ED-20), an increase in intense gas-abrasive wear of materials is observed due to a decrease in the interaction of the polymer with the filler at the interface.

The wear resistance of industrial epoxy composites correlates with the main parameters of their deformation under contact-dynamic loading: the ratio of the active and passive phases of the process, the maximum strain, the ratio of the components (elastic and viscous) of the deformation energy. Based on these parameters, it is proposed to use multidispersed silicon carbide in the developed wear-resistant epoxy material.

# CHOICE OF CRYSTAL HYDRATES FOR COMPOSITE ADSORBENTS WITH USE OF POLYMERIC QUARTERLY AMMONIA SALTS

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The urgency of selecting crystalline hydrates for composite adsorbents is the use of innovative adsorbents with additional properties. 'Porous matrix salt' composites have been recognized as promising materials for the adsorption conversion of heat due to their increased sorption capacity for widespread working liquids (water, methanol, and ammonia).

Materials for the transformation of sorption thermal energy, including the reduction of temperature potential, are today one of the key areas of research through initiatives by the international community to reduce greenhouse gas emissions and reduce primary fuel consumption. However, the current state of the art in this field is strongly limited by the insufficient sorption properties of adsorption materials.

This work is devoted to the development of sol-gel technology for the synthesis of organic - inorganic nanocomposites 'silica gel - sodium sulfate' and 'silica gel - sodium acetate' using polymer quaternary ammonium salts and study their properties and performance as materials of energy conversion.

The technological process of production of composite sorbents consists of the following stages: preparation of an aqueous solution of silicate glass and polymer quaternary ammonium salt, the formation of embryos of silicate phase, the formation of silicon-oxygen matrix, drying and fractionation of the sorbent.

The technological principles of obtaining a new class of sorption composite materials "silica gel-$Na_2SO_4$" and 'silica gel-$CH_3COONa$' using the polymer quaternary ammonium salt have been developed. It is shown that such composite sorbents are characterized by high rates of water sorption at the level of 0.42 - 0.65 g-g. The regeneration temperature for the 'silica gel-$N_{a2}SO_4$' composite is 60 $^oC$, and for 'silica gel-$CH_3COONa$' it is 100 $^oC$.

It has been shown that the sorption properties of the synthesized composite sorbents 'silica gel crystalline hydrate' are not a linear combination of the properties of silica gel and a massive salt, but the speed of the water sorption process is three times higher. The hydration process changes from the kinetic regime characteristic of the massive salt to the diffusion mode, in which the limiting stage is the transport of water to the salt via the system of pores of the silicon oxygen matrix.

# IMPROVEMENT OF TECHNOLOGY FOR DRY LECITHIN RECEIVING FROM THE PHOSPHATIDE CONCENTRATE

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One of the major trends in the development of the food industry is to improve the technology of obtaining dry lecithin in order to obtain environmentally friendly food and their production. Such products are distinguished by the presence in their composition of ingredients that are used in addition to traditional food and energy, with a number of specific physiological functions. The creation of such products is not possible without the use of dietary supplements, and the creation of the latter is impossible without special technology and equipment. Therefore, research focused on technology and equipment development is relevant.

Due to the imperfection of the production technology, the receipt of the product will be offered and substantiated with a new solvent, which is either absent or almost absent in lecithin, which will greatly improve the quality of the product obtained. Also use new equipment to produce purer lecithin with less solvent concentration and lower production costs.

Lecithin's, esters of choline amino alcohols and phosphoric acid diglyceride, are the most important representatives of phospholipids. By their nature, lecithin's belong to the most common group of polar lipids that make up the cell membranes of all living organisms.

In the industry, lecithin is obtained from by-products of vegetable oils, such as soybean, sunflower, rapeseed, flax, cotton, olive. The main processes for the production of lecithin that affect the quality of the final product are acetone extraction of phosphatide concentrate (system liquid - solid), filtration and drying of the finished product.

Modern technology for the production of dry lecithin is used as a degreasing agent acetone. The concentration of such a solvent is acceptable for food, but acetone is a toxic substance. The presence of acetone at the manufacturing plant puts employees at risk. Changing the solvent will make the resulting product more environmentally friendly, increase its scope and reduce its impact on production workers.

At this time, the transport (or storage) of the phosphatide concentrate is to maintain the temperature parameters, which affects the cost of the final product. Therefore, changing technology and equipment are the solution to several production problems.

# FLUORINE-CONTAINING DERIVATIVES OF EPOXY RESINS

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To obtain epoxy resins based polymeric coatings with high chemical stability, durability, plasticity and hydrophobycity the resins are modified with fluorine-containing compounds. However, such compositions have an essential drawback: fluorine compounds are not chemically bound with the cross-linked structure based on epoxy resin and thus the final products are nondurable.

In this research we consider the possibility of obtaining fluorine-containing derivatives of epoxy resins, in which fluorine-containing fragments would be chemically bound with oligomer molecules. To preserve the reactivity of the formed compounds it is important to synthesize the compounds containing epoxy group and fluorine-containing fragment simultaneously.

The initial compounds for the synthesis were industrial epoxy dianic resins ED-24, ED-22 and ED-20. The fluorine-containing modifiers were fluorine-containing alcohol-telomers $HOCH_2(CF_2–CF_2)_3H$, $HOCH_2(CF_2–CF_2)_4H$, $HOCH_2(CF_2–CF_2)_6H$ and fluorine-containing alcohol with carboxy group $HOCH_2(CF_2–CF_2)_3COOH$. The reaction catalysts were Crown-ether and benzyltriethylammonium chloride. 2-Propanol and toluene were used as the solvents.

We studied the effect of initial compounds ratio, nature and amount of the catalyst, nature of solvent and fluorine-containing compound, as well as temperature and process time on the rate of target components obtaining. The synthesis procedures were developed. The structure of the synthesized oligomers was confirmed by spectral analyses. We propose to use the synthesized oligomers as active additives for polymeric mixtures based on the industrial resins ED-20 and ED-22.

# MODELING AND INVESTIGATION OF THE SWELLING KINETICS OF HYDROGELS BASED ON SODIUM SALT OF ACRYLIC ACID AND 2-AMINOETHYL-3-AMINOPROPYLTRIMETOXYSILANE

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Organic-inorganic hydrogels were synthesized by simultaneous cross-linking processing - a combination of free radical polymerization of sodium salt of acrylic acid (AANa) in a presence of *N,N'*-methylenebisacrylamide and hydrolysis followed by catalytically-induced condensation of 2-aminoethyl-3-aminopropyl-trimetoxysilane (APTMS, from 5 to 20 wt.%) to form a network structure. The FTIR method confirms incorporation of polyAPTMS into the PAA matrix and formation of intercomponent H-bonds. The introduction of PAPTMS increases swelling degree of the hydrogel as well as thermal stability.

The incorporation of the PAPTMS increases the swelling capabilities of the hydrogels (the maximum water absorbency is 70 g/g when 10 wt.% of PAPTMS is incorporated). The swelling behavior of the hydrogel composites is non-Fickian, and the swelling process fits the Schott's model at low concentration of PAPTMS. The sorption curve of PAANa/PAPTMS = 80/20 sample differs from other samples and the kinetics parameters were interpreted as a result of a combination of two simultaneous processes: first-order kinetics with a very small rate constant and the overall autocatalytic process with its two rate constants. The swelling process starts by the disruption of H-bonds after penetration of water molecules inside the sample and the decreasing of hydrophobicity of the medium occurs due to ionization of carboxylic groups. In fact, this means that the penetration of new water molecules will be easier because the medium becomes more and more hydrophilic. This explanation justifies the autocatalytic mechanism of the swelling process. Despite the fact that the autocatalytic mechanism is in a good agreement with the experimental data, there is some discrepancy on the initial stage of swelling. A first order equation was used to describe this stage. The combination of two mechanisms at 80/20 ratio (contribution of autocatalytic process is 80%) gives the best fitting.

# APPLICATION OF PSEUDO-POLYAMINO ACIDS TO CREATE ANTIBACTERIAL DRUGS WITH HIGH ANTIMICROBIAL EFFECT

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D. D. Ostapiv, N. G. Nosova, V. Y. Samaryk, V. V. Vlizlo

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The creation and using of the novel nanometric carriers for the drugs delivery and biologically active substances is an relevant task of the modern pharmaceutical industry. Among the compounds which capable of binding and transporting a variety of substances to cells may include pseudopolyamino acids that do not contain peptide bonds.

These compounds do not cause in optimal concentrations side effects when entering the body and during metabolism, proved to be quite effective bases for dispersed delivery systems of therapeutic agents into the cell. In particular, this applies to nanometric carriers based on N-derivatives of glutamic acid and diols of various natures. The polyphosphate esters are obtained by the Steglich reaction using polypolyethyleneglycolethylphosphate as a diol with N-stearoylglutamic acid (Fig. 1). The structure of the obtained polyphosphate esters was confirmed by IR spectroscopy, $^{1}H$, $^{31}P$ NMR spectroscopy.

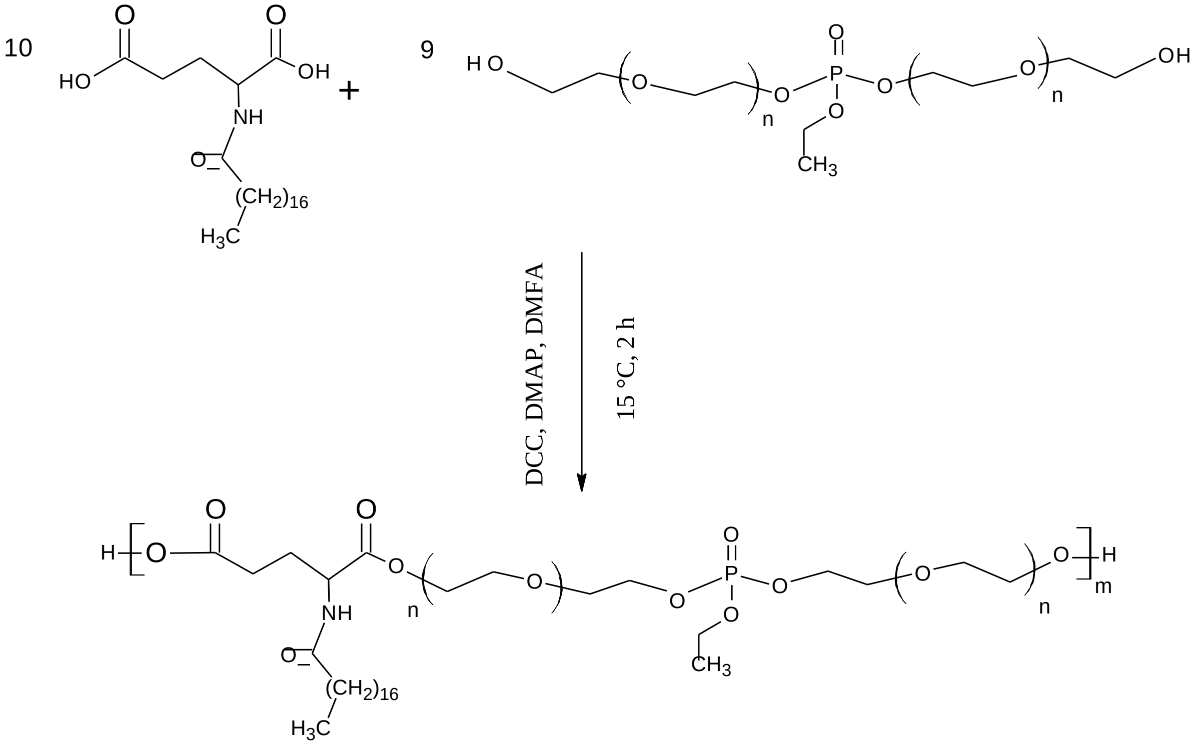

Figure 1. Scheme of obtaining of polyphosphatesters

This report presents the results of studies about the formation of aqueous dispersions of pseudopolyamino acids, the particles of that is binding with antibacterial drugs, including doxycycline and enrofloxacin. Such drug increases the effectiveness of industrial antibiotics by increasing the permeability of target cells and the study of the effect of the obtained complexes on the resistance of microorganisms to them. Biochemical studies have shown a decrease in antibiotic toxicity and an increase in bactericidal action.

# TEMPERATURE-SENSITIVE GRAFTED POLYMER BRUSHES WITH TRANSITIONS BASED ON LOW CRITICAL SOLUTION TEMPERATURE: SYNTHESIS, PROPERTIES, AND APPLICATIONS

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Temperature-responsivity of polymer brushes may be driven by different mechanisms, from which the lower critical solution temperature (LCST) is the most famous one. The using of the grafted temperature-responsive polymer brushes based on LCST opens numerous opportunities for fabrication of “smart” or responsive surfaces. The overwhelming majority of previously reported temperature-responsive grafted polymer brush coatings was based on PNIPAM and POEGMA, despite a fact that a wide range of other thermoresponsive polymers demonstrate similar properties. In this work we not only describe in details fabrication, mechanisms of action and application of well-known PNIPAM and POEGMA grafted brush coatings but also point to other types of thermoresponsive grafted brushes.

# POLYMERIC IONIC LIQUIDS OF IONENE TYPE IN THE TECHNOLOGY OF PRODUCTION OF OFFSET PRINTING PAINTS

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Paints and varnishes for offset printing occupy about 70% of the total market of products and components for printing. The emergence of new sales markets for offset products necessitates the study of optimization of printing paints with improved performance properties. Thus, packaging products require more and more resistant coatings to aggressive environments, and label products require the most wear-resistant coatings. The solution of the environmental aspects of the coating and their impact on the health of the consumer is relevant.

That is why special attention should be paid to the development of offset inks of a new composition with improved technological parameters based on available domestic components. With the advent of new compositions of printing paints it is necessary to develop and test the technology of their manufacture. Created a new offset paint of the following composition: yellow powder pigment (iron oxide R313 Tongchem, 18%), white pigment ($TiO_2$, 2%), urethane-alkyd varnish (41%), solvent (orthoxylol, 25%), polymerized linseed oil (10%), universal desiccant (manganese salts, 2%). The effective use of a small amount of polymeric ionic liquid of ionene type as a dispersant of offset printing paints is proposed.

Systematic researches of new offset printing paints are carried out. The influence of components of offset printing paint on its operational properties is revealed. It is established that the new yellow offset printing paint has better performance than prototypes of domestic and imported manufacturers. The optical density and gloss of the new yellow offset printing paint are 1.2 times higher than the prototype of the imported offset paint, and the viscosity and hardness are 1.5 times and 1.1 times, respectively. Acid resistance and alkali resistance of the new offset printing paints does not change. The adhesion of the new yellow offset printing paints has excellent results.

A new offset printing paints can be recommended before being stored on any absorbent surfaces (paper, cardboard, textiles), as well as on all types of printing films.

# POLYMERIC IONIC LIQUIDS AND IONIC LIQUIDS OF IONENE TYPE AS CATALYSTS OF CHEMICAL REACTIONS

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Ionic liquids are promising solvents, catalytic media in the creation of safe industries, as well as for the implementation of a simplified technological scheme for chemical reactions. This is due to the properties of ionic liquids: low vapor pressure in a wide range of temperatures, low toxicity, unique solubility of various organic and inorganic compounds. The main task of ionic liquid chemistry is the development of new polymeric ionic liquids and their monomeric analogues with specified properties (materials with high ionic conductivity while maintaining their liquid state in a wide range of temperatures).

Therefore, the development of scientific bases of the approach to the creation of methods for the synthesis of new monomers and polymeric ionic liquids based on them, which will meet modern requirements and predict the relative level of their properties aimed at solving urgent problems of society, is relevant.

This scientific work is aimed at the development of new polymeric ionic liquids and ionic liquids of the ionene type to obtain solvents and catalytic media of a simplified energy-saving technological scheme for chemical reactions.

Laboratory researches on expediency of application of polymeric ionic liquids and ionic liquids of ionene type as catalytic environments in organic synthesis or synthesis of polymers are carried out. The effectiveness of their use as catalysts for the synthesis of mono- and diacylglycerols of fatty acids has been confirmed. The influence of temperature and reaction time, the amount of catalyst and the molar ratio of fat-glycerol on the yield of the obtained product was studied. Synthesized products of glycerolysis of sunflower oil can be used as surfactants in foods industry.

# CONTINUOUS PROCESSING OF EXTRUSION CRUMB RUBBER AND RECYCLED POLYURETHANE FOAM TO DEVELOPE AND PRODUCE A NEW MATERIAL FOR ASPHALT MODIFICATION

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ABSTRACT

The goal of the this study is the combined of crumb rubber (CR) and flexible type of recycled polyurethane foam (PUF) to develop and producing a new composite materials for using as modifying-asphalt. The composite materials is prepared during the extrusion process using a single-screw extruding machine under heating and shear forces system. A method for producing a modified asphalt is made in a two steps process. In the first step, recycled polyurethane foam in form of a small pieces which is previously mechanically milled is mixed with crumb rubber powder, and then extruded. In the second step, the composite material and extruded polyurethane foam alone are blended with the virgin asphalt for producing two different modifications. The modification process of asphalt binder is blended at a temperature 180$^o$C, and mixing speed of 3000 rpm into finished products. According to the results, the finished product is asphalt in the amount of up to 85 wt%, and composite materials which comprises from crumb rubber powder and flexible type of recycled polyurethane foam in the amount of 15, 20 and 25 wt%. The weight fraction of crumb rubber and recycled polyurethane foam in proportion of 50-75 wt% and 25-50 wt% respectively. The presence of recycled polyurethane foam helping to improve the storage stability of modified asphalt, homogenous distribution and complete melting into asphalt matrix, which is one of the major initial properties of the finished product. Recycled polyurethane foam alone and composites modified asphalt are also improved the basic physical properties, such as softening point, penetration degree, and viscosity, and rheological parameter such as, loss and storage modulus, rutting resistance parameter of the asphalt binders. The modified asphalt obtained can advantageously be used for road pavement and roofing materials.

INTRODUCTION

Bitumen matrix is the black-coloured product coming from the bottom of the vacuum distillation columns in the crude oil refineries [1]. Due to interesting potential characteristics of bitumen such as impermeability, adhesivity, elasticity, resistance to the influence of weathering, chemicals, which make it the most suitable engineering material as a binder of mineral aggregates in paving and roofing applications [1-6]. Yet, conventional bitumen's in roads are usually sensitive to the increased traffic volume and vehicle loads due to its visco-elastic nature [4].

Yet, the management and recycling approach of waste tire rubbers (WTR) are still challenge for industry, engineers and scientists, due to the vulcanization process during the initial stages for the production of rubber tires. In addition, scrap tires constitute about 80% of the total waste rubbers generated annually [7]. In regard to waste tires, it was reported that about 1.5 billion used tires are generated globally every year [8]. However, from an environmental point of view, the utilization of waste tire rubber as a bitumen modifier may contribute to solve a waste disposal problem, since the development of the automotive industries may produce huge numbers of tires worldwide every year [9, 10]. Another most problematic waste to the environment today is polyurethane foams (PUF) including both types of foams, flexible and rigid foams [11]. Tires [7], and polyurethane foams are high-quality products which should meet all safety requirements in order to be put into service. The cross-linked structure of both materials made them difficult to be recycle in another applications. Due to the irreversible chemical structure of the elastomers, however, a primary or secondary recycling is only possible to a limited extent. Therefore, such waste materials represent a serious disposal problem [12].

However, the main benefits of using an extrusion process for the processing of asphalt modifiers as initial process are: in one aspect, extrusion process give a high compatibility between the crumb rubber and recycled polyurethane foam than conventional mixing and the manually mixing methods in other hand the flexibility of polyurethane foam with the elasticity of crumb rubber together make a good composites in a form of powder during the processing. A second embodiment relates to a method of combining crumb rubber with polyurethane foam using extrusion process, that when crumb rubber powder is composite with polyurethane foam by extrusion process, the elasticity of crumb rubber powder will keep polyurethane foam at the fluffy condition. A third embodiment relates to a method of combining crumb rubber with polyurethane foam using extrusion process, the final composites having a complete conversion of crumb rubber and recycled polyurethane foam to composite material up to 100% in form of powder materials with an uniform size and high elasticity., since polyurethane foam have a very small density, the extruding of recycled polyurethane foam could be reduced the volume of material many times than using ground or cutting process (conventional mixing process). A fourth embodiment relates to modified asphalt mixture by extruded recycled polyurethane foam. This product having high storage stability and guaranteeing better dispersion of it into asphalt matrix at the same time compared to similar product made with the asphalt modification using the same proportion of crumb rubber alone. A fifth embodiment relates to the asphalt modifications. The use of extrusion technique to produce the extruded composite materials allows reducing the energy costs due to minimizing mixing speed to 2000-3000 rpm and a modification temperature up to about 160 $^{o}$C compared with 220$^{o}$C and 6000 rpm needed for asphalt modification with crumb rubber and recycled polyurethane foam which are added separately one by one without previously extrusion process for obtaining a complete melting of polyurethane foam into asphalt matrix. Finally, relates to the environmental protection by reducing the gas emissions due to slightly reduction of modification temperature, speed of mixing, and mixing time.

## MATERIALS AND METHODS

The asphalt type (70/100) penetration grade was used as a matrix; it was supplied by Lotos Company in Poland. The physical properties of this asphalt were characterized by the following: (i) softening point of 44$^{o}$C using ring & ball test; (ii) penetration degree of 85 dmm; (iii) viscosity of 0.44 dPa.s at 165$^{o}$C; (iv) ductility and elastic recovery of 100 cm and 5%, respectively;
(v) bulk density of 1.0296. Finally, the chemical constituent of the asphalt included 6.8 wt% saturates, 64.2 wt% aromatics, 16.2wt % resins, and 12.7 wt% asphaltene. The crumb rubber was obtained from scrap tires with a particle size of 0.4 mm after sieving at the laboratory; it was supplied by Orzeł company in Poland. Scrap polyurethane foam was collected from the polyurethane foam waste at the laboratory.

### *1.1. Penetration test*

PNR12 model – a German-made automatic Penetrometer was used to measure the penetration point according to the European Standard EN1426 test. In this test, the sample (virgin/modified asphalt) was initially thermo-stated in a water bath at 25$^{o}$C for 60 min., then the penetration of a standard needle under a total standard load of 100 g into each sample was measured and reported over a range of 1- 10 mm.

### *1.2. Softening point test*

Softening point temperature (SPT) using ring and ball test was carried out on all samples according to the PN-EN 1427 standard. In this test, disks of the samples were cast in shouldered rings, and then the disks were trimmed to remove excess of asphalt. Next, the disks were heated at a constant rate of 5oC/min in a water bath by using special apparatus.

### *1.3. Storage stability test*

Storage stability is considered a very important parameter for initial properties on modified asphalt, especially for storage and transportation. The storage stability test was conducted according to the PN-EN 13399 standard. The test was carried out as follows: each sample of the studied product was separately poured into an aluminium tube of 37 mm in diameter, 173 mm in height, and sealed. Next, it was stored vertically at 180 ± 2$^{o}$C during 72 hours. Then, the tube was subjected to freezing at 5°C for 24 h to completely solidify. Finally, the tube was cut horizontally into three equal parts. The top and bottom ends of the tube were then melted into separate small beakers and analyzed for their softening point temperature using ring and ball test. According to the standard EN 13399:2010, the good storage stability of the sample implies that the difference between the softening point temperature of the top and the bottom parts of the tube could be less than 2°C. The viscosities of the samples were determined at temperature of 180°C by Digital Readout Rotational Viscometer, model visco-tester 2 Plus, HAAKE Inc, made in Germany.

## EXPERIMENTAL SECTION

### *Experiment 1*

Asphalt modification by extruded material is carried out in two approaches. The first modified asphalt binder is prepared by the addition of extruded composite material which is previously prepared at content level of 15 wt%, while the weight fractions of crumb rubber and recycled polyurethane foam mixture are 75 wt% and 25 wt%, respectively. In contrast, the other approach is carried out by blending virgin asphalt with 15 wt% of extruded polyurethane foam alone. In the first case of modified asphalt blend, approximately 400 gram of the asphalt, was added to the reactor at 180°C, with an initial mixing speed of 1500 rpm for 15 min, followed by the addition of 15 wt% of composite materials. Only then is the mixing speed of 3000 rpm applied for another 60 min to obtain the finished product. Likewise, this was applied for the second approach binder. Results obtained including softening point, penetration test, viscosity and storage stability test for asphalt modified wit 15 wt% of composites and processed polyurethane foam are presented in Tables (1-4).

*Experiment* 2: If, use content level of 20 wt% of composite materials, and everything else being equal, in experiment 1, a finished product with a the softening point, penetration and viscosity values were found to be 64.5°C, 40 (0.1mm, and 14 dPas, respectively, while storage stability was obtained to be 4 (0.1mm) for penetration and 6.5°C for softening point.

*Experiment* 3: If, use weight fraction of crumb rubber and recycled polyurethane foam mixture of 50 wt% and 50 wt%, respectively, and everything else being equal, in experiment 2, a finished product with a softening point, penetration, and viscosity values of 59.5°C, 43 (0.1mm) and 8.0 dPas, respectively were obtained, while ΔP and ΔT were obtained to be 9 (0.1mm) and 5°C, respectively.

*Experiment* 4: If, use content level of 25 wt% of composite materials, and everything else being equal, in experiment 3, So, the weight fraction of crumb rubber and recycled polyurethane foam mixture were 50 wt% and 50 wt%, respectively. Results obtained of softening point, penetration and viscosity values were found to be 62$^{o}$C, 41(0.1mm), and 11.0 dPas, respectively.

Table 1 Compares the softening point for finished products.

| Component | Softening point, $^{o}$C | Modification indexes |
|---|---|---|
| Composites (CR:PUF) | 59.5 | 129.35 |
| Processed PUF only | 56.0 | 121.74 |

Table 2 Compares the penetration for finished products.

| Component | Penetration, (dmm | Modification indexes |
|---|---|---|
| Composites (CR:PUF) | 43 | 50.59 |
| Processed PUF only | 50 | 58.82 |
| PUF: polyurethane foam; CR: Crumb rubber | | |

Table 3 Compares the storage stability for finished products.

| Component | ΔT, $^{o}$C | ΔP, 0.1mm |
|---|---|---|
| Composites (CR:PUF) | 4.7 | 2.0 |
| Processed PUF only | 1.0 | 1.0 |

Table 4 Compares the viscosity for finished products.

| Component | Viscosity, dPas at 180$^{o}$C |
|---|---|
| Composites (CR:PUF) | 4.83 |
| Processed PUF only | 2.07 |

Discussions

From tables it can be seen that the softening point temperature has been slightly improved for the two modifications compared with the value of 46 $^{o}$C for the virgin asphalt. Composite material made from extrusion of crumb rubber and recycled polyurethane foam have the best value. The penetration degree is also greatly improved, for example, the penetration was decreased from 85 (0.1mm) for the virgin asphalt to 50 (0.1mm) for the processed polyurethane foam alone at 15 wt%. Also the composite materials showed the best penetration value. Besides**,** the providing products having high storage stability for both processed recycled polyurethane form modified asphalt compared with the same content level of crumb rubber alone (one of the major asphalt-modifiers used nowadays) which has low storage stability. The improve in storage stability indicates that recycled polyurethane foam has been reacted with the compositions of asphalt matrix [1, 4, 13]. The viscosity of finished products are all increased compared with the value 0.45 dPa.s for the virgin asphalt., for example 15 wt% composites materials modified asphalt have a viscosity about 5 dPas at 180$^{o}$C compared with the same content level of crumb rubber alone modified asphalt which has a high viscosity, about 9.0 dPas. So, the pumping power, shear forces and energy consumption will be reduced [14].

## Conclusion

The results of this study shows, that the physical properties of the asphalt binder are increased by addition of singular and combined modifiers. These increases are more influence with the increase of content level of the modifiers. One objective of this study was to develop a new material combined from PUF and CR wastes which prepared during the extrusion process, which can efficiently and cost-effectively be used for asphalt modification. Finally, as a result and from an environmental and economic point of view, the use of both CR and PUF as secondary materials in road pavement would prevent from additional road construction cost in one hand and in other hand it would be a solution to decrease environmental pollution.

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# BADANIE PĘCZNIENIA HYDROŻELOWYCH OPATRUNKIÓW AKTYWNYCH ZMODYFIKOWANYCH KOLAGENEM

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## Streszczenie

Opatrunki hydrożelowe znajdują coraz częstsze zastosowanie w przypadku leczenia ran oparzeniowych czy pooperacyjnych. Ich modyfikacja przy pomocy substancji o właściwościach promujących regenerację tkanki skórnej przyspiesza proces gojenia uszkodzonych tkanek poprzez możliwość kontrolowania uwalniania substancji aktywnej, a także zapewnienie odpowiedniego nawilżenia środowiska gojenia się rany. W niniejszej pracy przedstawione zostaną hydrożele o właściwościach regeneracyjnych bazujące na poli(alkoholu winylowym) oraz agarze pochodzenia naturalnego, usieciowane przy pomocy tetraboranu sodu.

## Wstęp

Skóra jest jednym z największych narządów w organizmie człowieka i stanowi około 10% masy ciała. Działa jako bariera chroniąca przed utratą płynów ważnych dla utrzymania homeostazy organizmu, a także stanowi osłonę przed urazami mechanicznymi i termicznymi. Ponadto skóra izoluje głębiej położone tkanki i narządy od szkodliwych czynników zewnętrznych, takich jak substancje chemiczne, patogeny biologiczne i promieniowanie UV [1]. Ze względu na swoje funkcje skóra narażona jest na różnego rodzaju uszkodzenia prowadzące do powstawania ran, czasem nawet rozległe uszkodzenia skóry mogą zagrażać życiu. Rany oparzeniowe są doskonałym przykładem bardzo groźnych i szczególnie trudnych do leczenia urazów skóry [2]. Zwykle ludzka skóra charakteryzuje się dużą zdolnością do regeneracji po urazach poprzez następujące po sobie procesy fizjologiczne, takie jak: krzepnięcie i hemostaza, stan zapalny, proliferacja i przebudowa [3–5].

Materiały stosowane w leczeniu ran powinny wykazywać właściwości lecznicze zgodne z koncepcją TIME (ang. *Tissue, Infection, Moisture, Edge*), co oznacza, że zapewniają wilgotne środowisko gojenia, umożliwiają wymianę gazową, ochronę przed zakażeniem bakteryjnym, chronią brzegi rany i pomagają kontrolować infekcję [6]. Warunki takie spełniają hydrożele. Dzięki temu stanowią one jedne z najbardziej skutecznych i najczęściej stosowanych opatrunków.

Duża łatwość modyfikacji jest możliwa za sprawą wysoko porowatej struktury materiałów hydrożelowych, które są zdolne do uwalniania bardzo małych cząsteczek, a także dużych biomakromolekuł [7]. Szerokie zastosowanie zawdzięczają miękkości, elastyczności i utrzymaniu wilgoci, co sprzyja tworzeniu optymalnego środowiska gojenia ran [8]. Prof. Winter w 1962 roku udowodnił, że naprawa uszkodzonych tkanek następuje w środowisku wilgotnym ponad dwukrotnie szybciej, niż w środowisku suchym [9].

Hydrożele wykonane z poli(alkoholu winylowego) (PVA) mają szerokie zastosowanie jako opatrunki od co najmniej 30 lat. Wykazują dużą przejrzystość, odporność mechaniczną, biodegradowalność, biokompatybilność i zapewniają wilgotne środowisko podczas gojenia ran [10]. Ponadto PVA jest materiałem rozpuszczalnym w wodzie i jest zatwierdzony przez FDA do zastosowań medycznych [11]. Materiał ten stanowi również dobrą bazę do modyfikacji związkami o działaniu regeneracyjnym jak na przykład kolagen, którego pozytywny wpływ na regenerację tkanki skórnej został potwierdzony wieloma badaniami histopatologicznymi [12].

### Wykonanie i modyfikacja hydrożeli

W celu syntezy opatrunków hydrożelowych wykorzystano PVA (Mowiol 4-88, Sigma-Aldrich, Niemcy, stopień hydrolizy = 86,7-88,7 mol%, Mw = 31 000 g/mol), Agar E406 (Biomus, Lublin, Polska, Mw = 120 000 g/mol [13]), kolagen (Noble Health, Radom, Polska). Jako środek sieciujący wykorzystano dziesięciowodny tetraboran sodowy (borax) (TechlandLab, Tarnobrzeg, Polska, Mc = 381,44 g/mol) [14].

W celu uzyskania kilku rodzajów hydrożeli, przygotowano różniące się składem roztwory za pomocą mieszadła magnetycznego z funkcją grzania firmy ChemLand (Stargard Szczeciński, Polska). Skład procentowy każdego hydrożelu oraz przedstawiono w **Tabeli 1**.

**Tabela 1.** Skład procentowy hydrożeli [%]

| Symbol | Woda | Agar | PVA | Borax | Kolagen |
|---|---|---|---|---|---|
| **H1** | 97,2 | 1,6 | - | 1,2 | - |
| **H2** | 97,2 | 1,2 | 0,4 | 1,2 | - |
| **H1K** | 96,6 | 1,6 | - | 1,2 | 0,6 |
| **H2K** | 96,6 | 1,2 | 0,4 | 1,2 | 0,6 |

Pierwszym etapem syntezy było odważenie odpowiedniej ilości wszystkich substratów. Początkowo w kolbach umieszczono po 97,2g wody destylowanej oraz określoną ilość agaru. Mieszadło ustawiono na 800 RPM i temperaturę w zakresie 90 – 100°C. Po rozpuszczeniu agaru dodawano kolejne składniki, a czynność powtarzano do całkowitego wymieszania i rozpuszczenia wszystkich substratów, przy czym kolagen dołączono do roztworu po jego wcześniejszym ochłodzeniu do temperatury ok. 50°C. Cały proces trwał godzinę. W celu dokładnego połączenia wszystkich elementów, roztwór mieszano jeszcze 20 min. Gotowe mieszaniny wylano na szalki, a następnie wymrażano w temperaturze -10°C przez 18 godzin, w celu fizycznego usieciowania hydrożelu. **Rys. 1.** przedstawia uzyskany hydrożel H1K oraz H2K.

**Rys. 1.** Hydrożel H1K (lewa strona) oraz H2K (prawa strona)

## Metodyka badań

### *Pomiar pęcznienia w wodzie destylowanej (W)*

Przed przystąpieniem do badania, wszystkie rodzaje hydrożeli zostały suszonew suszarce w temperaturze 37°C przez 24h. Następnie, z wysuszonych hydrożeli wycięto wykrojnikiem, po trzy próbki w kształcie walca i zważono ich masy. Każdą z próbek umieszczono w 5 ml wody destylowanej i po określonym czasie ponownie zważono. Zmiany masy wyznaczano za pomocą wagi WAS 110/X firmy RADWAG. Pomiary mas zostały wykonane po 5, 15, 30, 45, 60, 300 i 1215 min. Następnie z otrzymanych wartości W dla każdego typu hydrożelu wyznaczono krzywą pęcznienia W=f(t). Pęcznienie W wyliczono z zależności (1), gdzie: W- chłonność wody [%], $M_1$- masa początkowa [g], $M_2$- masa po określonym czasie [g].

$$W = \frac{M_2 - M_1}{M_1} \times 100\% \qquad (1)\ [15]$$

### *Pęcznienie równowagowe (W∞) i stała kinetyki pęcznienia (K)*

Wartość *W∞* wyznaczono z równania (2), gdzie: $W_{\downarrow(}$ - pęcznienie równowagowe, *t* – czas [min], *W* – stopień pęcznienia [%], *K* – stała kinetyki pęcznienia [1/(%·min)].

$$t/W = 1/(K[W_{\downarrow(}]^{\uparrow 2}) + t/W_{\downarrow(} \qquad (2)\ [15]$$

Następnie wykonano wykresy o równaniu (3), z których wyznaczo parametry prostej (4):

$$\frac{t}{W} = f(t) \qquad (3)\ [15]$$

$$y = ax + b$$ (4) [15]

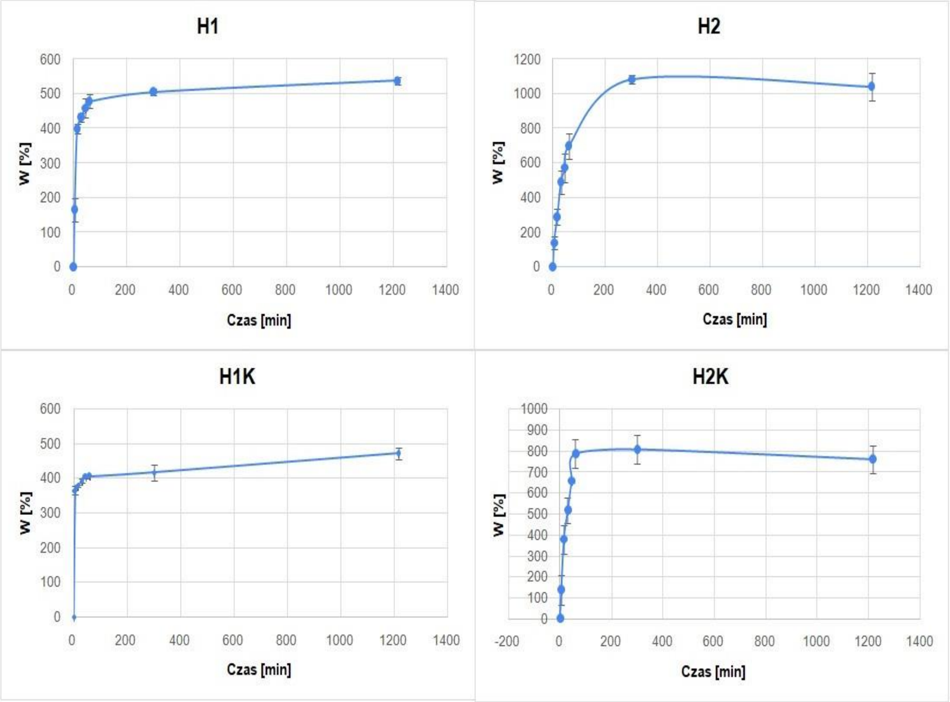
Z równań (5) i (6) wyznaczono parametry $W_{\downarrow}($ oraz $K$ :

$$W_{\downarrow}(= 1/a$$ ) [15]

$$K = 1/(b \, [\![ \, [\![ W ]\!] \, _{\downarrow}( ]\!] \, ^{\uparrow}2 \; )$$ (6) [15]

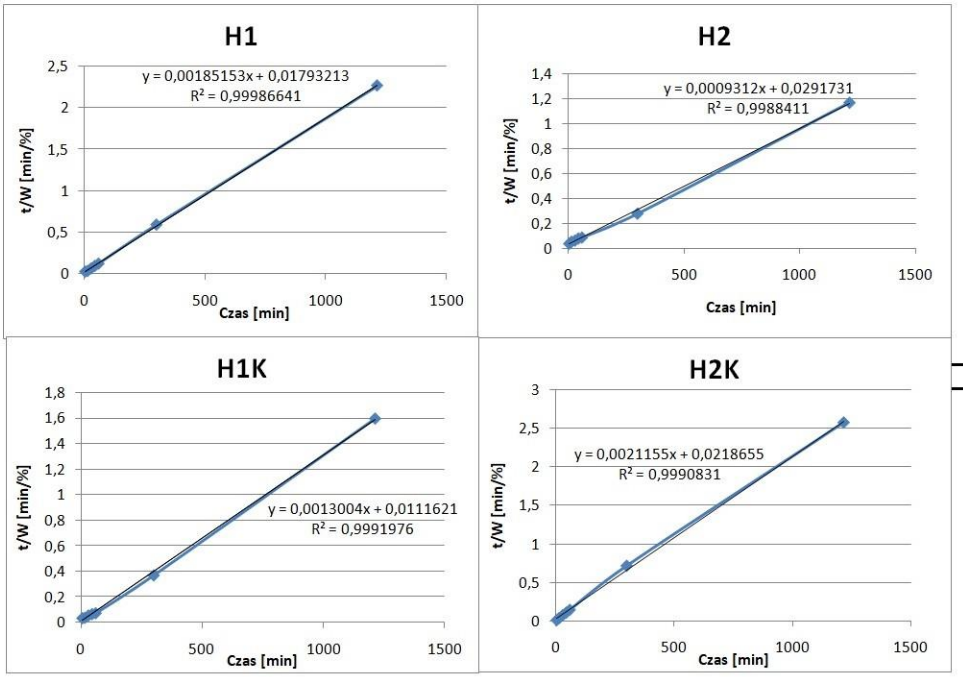
## Wyniki badań

Otrzymane próbki (H1, H2, H1K, H2K) poddano badaniu pęcznienia w wodzie destylowanej, które pozwala określić jaką ilość medium jest w stanie pochłonąć hydrożel, a także czas potrzebny do ustabilizowania się krzywej pęcznienia. Wykresy pęcznienia przedstawiono na **Rys. 2**. Dla wszystkich próbek etap najszybszego pochłaniania występuje przez pierwsze 60 min badania. Po tym czasie wartości pęcznienia zaczynają się stabilizować. Można również zauważyć, że dla próbek bez dodatku PVA (H1, H1K) trend wykresów jest rosnący – najwyższe pęczeniania występowały po 1215 min pomiaru: 536 ± 11% (H1) oraz 471 ± 17% (H1K). Dodatek 0,4% PVA spowodował zmianę charakterystyki pęcznienia hydrożeli. W przypadku próbek H2 oraz H2K najwyższe pęcznienia wynosiły kolejno: 1081 ± 26% oraz 806 ± 49% po 300 min, po czym zaczęły spadać.



**Rys. 2.** Wykres zależności pęcznienia od czasu dla hydrożeli H1, H2, H1K oraz H2K

**Rys. 3.** Przedstawia wykresy prostych dla próbek H1, H2, H1K oraz H2K wraz z równaniami, z których następnie wyliczono pęcznienia równowagowe oraz stałe kinetyki pęcznienia (**Tabela 2).**



**Rys. 3.** Wykresy zależności t/W = f(t) dla próbek H1, H2, H1K oraz H2K

**Tabela 2.** Zestawienie parametrów a, b równań liniowych oraz wartości *K* i $W_\infty$

| **Symbol** | ***a*** | ***b*** | ***K[1/(%·min)]*** | ***W∞[%]*** |
|---|---|---|---|---|
| **H1** | 0,001851 | 0,017932 | 0,000191 | 539,96 |
| **H2** | 0,000931 | 0,029173 | 0,000029 | 1073,88 |
| **H1K** | 0,002115 | 0,021865 | 0,000204 | 472,59 |
| **H2K** | 0,001300 | 0,011162 | 0,000151 | 768,99 |

Na podstawie **Tabeli 2** można stwierdzić, że najwyższe wartości pęcznienia równowagowego uzyskano dla hydrożeli z dodatkiem 0,4% PVA: 1073,88% (H2) oraz 768,99% (H2K). Dla próbek bez dodatku PVA (H1, H1K) wartości pęcznienia równowagowego wynosiły kolejno: 539,96% oraz 472,59%. Na tej podstawie można stwierdzic, że dodatek PVA powoduje istotny wzrost pęcznienia badanych próbek, co może być spowodowane występowaniem w jego łańuchach hydrofilowych grup hydroksylowych (ok. 90%) oraz octowych (ok. 10%). W przypadku wyznaczonych stałych kinetycznych dodatek PVA powoduje natomiast spadek wartości K, co jest zjawiskiem korzystnym, ponieważ stała K świadczy o szybkości pochłaniania medium. Im niższe są stałe K, tym przez dłuższy czas opatrunek zachowuje zdolność pochłaniania wysięku z rany. Zauważyć można również, że próbki zmodyfikowane kolagenem cechują się niższymi wartościami pęcznienia równowagowego niż próbki niezmodyfikowane oraz wyższymi stałymi K: 0,000204 1/(%·min) dla H1K oraz 0,000151 1/(%·min) dla H2K. Można więc wnioskować, że będą one wykazywać niższą zdolność do pochłaniania wysięku i krótszy czas działania w stosunku do hydrożeli niezmodyfikowanych (H1, H2).

## Wnioski

Opatrunki hydrożelowe, ze względu na swoje unikalne własności i brak negatywnego oddziaływania z organizmem, znalazły szerokie zastosowanie w medycynie, a szczególnie w leczeniu ran. Najczęściej są to rany pooperacyjne lub oparzeniowe, z których bardzo często sączy się wysięk. Przeprowadzone badania pęcznienia wykazały, że udało się uzyskać hydrożele na bazie PVA, agaru, boraxu i kolagenu, które posiadają zdolność do pochłaniania wysięku. Pomimo słabszych parametrów pęcznienia dla próbek zmodyfikowanych kolagenem udowodniono, że problem ten można rozwiązać poprzez dodatek odpowiedniej ilości PVA, który polepsza chłonność oraz wydłuża czas wchłaniania medium. Z tego powodu kolagen w dalszym ciągu wydaje się obiecującym modyfikatorem, zwłaszcza biorąc pod uwagę jego wysoką biokompatybilność i wysoką zdolność do regenracji uszkodzeń tkanki skórnej.

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# EVALUATION OF THE PROCESSING PROPERTIES OF "BIOPOL" WITH DIFFERENT MOLECULAR WEIGHTS

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## 1. Introduction

Polymer materials can be used in various applications in our everyday life. The advantages of polymers, compared to glass, metal or wood, are the low price and good performance properties [1].

Unfortunately most plastics donot have ability to degrade in natural environment. The environmental degradation time for traditional plastics such as polystyrene (PS) or polyethylene (PE) ranges from 500to 1000 years. Biodegradable polymers are prone to degradation in the natural conditions within six months to two years. Another disadvantage of conventional polymers is the fact that they are obtained from depletion petroleum reserves [2, 3, 5].

In response to problems associated with plastic waste and its effect on the environment, there has been considerable interest in the development and production of an alternative, biodegradable plastics. Bioplastics are a form of plastics derived from renewable biomass sources, for example corn starch, pea starchor another plants [2, 3, 5]

Polyhydroxyalkanoates - PHA andpoly(lactic acid) - PLA have a higher demand over other bioplastics. PHA, unlike PLA, is biodegradable in seawater, which is very important and desirableproperty from the environmental point of view. Some products, e.g. packaging, may eventually end up in the sea, regardless of where they are used. Plastic pollution of the seas is a very well known global problemrequiring the fastest possible development of new biodegradable polymeric materials that meet the appropriate mechanical requirements[3, 4, 5, 6].

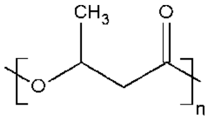
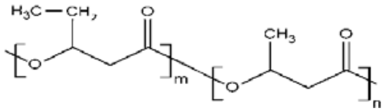
The aim of the study was to evaluate the processing properties of a biofield polymer (PHA) with different molecular weights and different PHV content.

## 2. “Biopol”: properties and application

On an industrial scale, a principle producer of PHA is Monsanto. This company produces homopolymer –poly(3-hydroxybutyrate) (PHB) and copolymer poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) with different PHV content (3 – 25% PHV). PHB and PHBV are producedunder the trade name “Biopol®”.Another trade name for PHA produced by Monsanto is “Biopol$^{TM}$”. The acrylic polymer is also known under the trade name “Biopol”. The same trade name can refer to two chemically different polymers. Therefore, caution is advised [7 ,9].

In the late 1980s, PHA was commercially developed by Imperial Chemical Industries (ICI) and was sold under the trade name “Biopol®”. In 1990, the agricultural and pharmaceutical businesses of ICI, including “Biopol®”, were spun off as Zeneca Ltd. In 1996, Monsanto has bought Zeneca’s “Biopol®” [7, 9]. **Table 1** shows the chemical structure of mentioned polymers [7, 8].

Table 4.Chemical structure of “Biopol” [3, 4]

| **Name** | **Symbol** | **Structure** |
|---|---|---|
| **poly(3-hydroxybutyrate)** | PHB |  |
| **poly(3-hydroxybutyrate-co-3-hydroxyvalerate)** | PHBV |  |

“Biopol” is produced from renewable resources. These polymers are produced by the fermentation of a carbohydrates (currently glucose) by naturally occuring microorganism - *Alcaligenes eutrophus* - species of bacteria, which occurs widely in soil and water. “Biopol” is produced as a backup material due to a deficiency of nutrients such as nitrogen, phosphorus, potassium, oxygen or in the presence of excess carbon. PHAs are stored as intracellular inclusions. The isolation and preservation of these granules can be obtained through solvent extraction[8, 10].

The molecular mass of PHAs depends up on the type of growth conditions. It may range from$2\times10^3$to $4\times10^6$g/mol or even higher, what allows to use “Biopol” in wide field of applications [11]. Furthermore, it has similar material properties to conventional thermoplastics, e.g. polypropylene (PP) (**Table 2**) due to its polyester structure (**Table 1**) [10].

Table 2. Basic data of “Biopol” compared to polypropylene[10]

| **Parameter** | **“Biopol”** | **PP** |
|---|---|---|
| **Melting Point [°C]** | 136 - 162 | 160 – 168 |
| **MFR [g/10 mins]** | 5 – 8 (170 C/5kg) | 0,3 – 40 (230 C/2,16 kg) |
| **Youngs Modulus [GPa]** | 0,4 – 1,0 | 1,4 – 1,8 |
| **Tensile Strength [MPa]** | 20 - 31 | 25 – 35 |
| **Elongation at break [%]** | 8 - 42 | 400 - 900 |

Physical properties vary depending on the PHV contents of the polymers. LowPHV content increases tensile strength and stiffness, but lowers impact resistance. Polymers with higher PHV contenthave greater impact resistance and lower tensile strengths. They are also more flexible [10].

Biopol homopolymer - PHB is highly crystalline polymer with a melting point (180°C) only a few degrees lower than the degradation temperature. The crystallinity ranges from 55 to 80%. The melting point of the copolymers decreases with increasing PHV content [7, 10].

PHAs produced by Monsanto are fully biodegradable and compostable. Biopolymers produced by Monsanto decompose under the influence of microorganisms (bacteria, fungi, algae, protozoa) and environmental factors (temperature, sunlight, oxygen content, moisture) to harmless inorganic compounds (water and carbon dioxide or water, carbon dioxide and methane) and biomass [7, 10]

The rate of degradation depends onthe range of environmental (in particular on the microbial activity) and material parameters (molecular weight, crystallinity) [7].

“Biopol” resin can be processed using conventional techniques, such as extrusion and injection. The processing requires careful temperature control - material should be processed at the lowest possible temperature and residence time in the machine kept at a minimum. If the machine is stopped for a short time (5 -15 minutes) “Biopol” degradates immediately [7]. However, the polymer exhibits good oxygen, moisture and aroma barrier properties. Monsanto's PHAs are used in particular in the production of packing films [9].

Moreover,PHAs are used as disposable items, in the construction industry, in agricultural applications or in the production of electronic devices, such as mobile phone casings, for CD or in medical applications (for drug delivery, in tissue engineering) [7, 9, 10].

## 3. Materials and methods

“Biopol” (white powder, Monsanto Company Inc.) samples with a different PHV content (3,8 - 24%). were tested in this study. Melt flow rate examination was performed using polymers with different molecular weights (297 000 - 646 000g/mol). **Fig.1** shows the appearance of the tested samples.

The melt flow rate (MFR) test was performed using a Zwick&Roell MFlow load plastometer (**Fig. 2)** in accordance with the PN-EN ISO 1133-1: 2011 standard (method B, load: 2,16 kg, pre-heating time: 300s). Results were processed using TestExpert software. Prior to testing, the samples were dried for 4 hours in an oven at 70 ° C.

**Fig. 1.** Appearance of the tested samples (packed powder)

**Fig. 2.** Load plastometer (Zwick&RoellMFlow)

## 4. Results and discussion

**Table3** presents the results of the MFR measurements including information about molecular weights of tested polymers, PHV contents and set temperatures (load 2,16 kg).

Table 3.MFR data for "Biopol" with different molecular weight (Mw) and PHV content

| Sample | PHV content [%] | Mw [g/mol] | Temperature [°C] | MFR [g/10 min] |
|---|---|---|---|---|
| PHB/24PHV | 24 | 297 000 | 130 | 9,67 ± 0,71 |
| PHB/20.1PHV | 20,1 | 397 000 | 140 | 3,34 ± 0,20 |
| PHB/19.1PHV | 19,1 | 643 000 | 145 | 2,82 ± 0,14 |
| PHB/15.6PHV | 15,6 | 646 000 | 155 | 2,15 ± 0,22 |
| PHB/10.8PHV | 10,8 | 335 000 | 165 | 3,84 ± 0,11 |
| PHB/3.8PHV | 3,8 | 611 000 | 175 | 3,12 ± 0,03 |

The melt flow rate of the copolymers decreases with increasing molecular weight of the polymer. This was probably due to the increasing viscosity with increasing molecular weight of the polymer. For the sample PHB/24PHV with a molecular weight 297 000 g/mol, the MFR value was the highest and reached 9,67± 0,71 g/10 min. The lowest value of the mass flow rate index can be observed for a sample PHB/15.6PHV with a molecular weight of 646 000 g/mol (2,15 g/10 min).

The melt flow rate depends also on the PHV content. For all the PHB/PHV samples containing up to 20,1% PHV MFR results were very similar (2,15 ± 0,22 - 3,84 ± 0,11 g/10min). However, MFR value significantly increased for PHB/24PHV blend (9,67 ± 0,71 g/10min). Beside of MFR values, addition of PHV has a strong impact on the processing temperatures of PHB/PHV blends. PHB/3.8PHV samples with the lowest content of PHV were characterized by the highest melting temperature (175 °C), while PHB/24PHV blends could be processed at 130°C. It can be related to high degree of crystallinity of neat PHB that strongly affects the melting temperature of PHB/PHV polymers. Addition of PHV decreases the crystallinity of the polymer and can also have an impact on the morphology of crystal structures. Referring to **Table 3** it can be concluded that rheological properties of PHB/PHV blends can be controlled in a wide range and designed by the addition of suitable amount of PHV. These properties allow for application of mentioned polymers in many different fields, e.g. from packaging industry to drug delivery systems.

Low molecular weight PHV/PHB samples can be used for extrusion process (low values of the melt flow index). High molecular weight samples can be used for injection process (high values of the melt flow index).

According to literature data, MFR For PLA, another biodegradable polymer, higher values of the melt flow index can be observed (29,38 g/10 min, 210°C, 2,16 kg). The melt flow index for polystyrene (PS), traditional polymer, and "Biopol" polymer with a molecular weight 646 000 g/mol has a similar value ("Biopol"- 2,15 g/10 min, 155°C, 2,16 kg; PS - 2,5 g/10 min, 200°C, 5,0 kg).

## 5. Conclusions

Based on the information and results presented in this work the following conclusions may be drawn:

- MFR of "Biopol" depends more on molecular weight of the polymer than the amount of PHV present in the main chain and decreases with increasing molecular weight of the polymer.
- MFR for PHB/PHV samples with different molecular weight and PHV content is in the range of2,15 ± 0,22 - 9,67 ± 0,71 g/10 min, so "Biopol" can be processed using different conventional techniques.
- Biopol with higher Mw and lower amount of PHV demands the highest temperature of processing, what can be related to the degree of crystallinity of polymer
- PHB/PHV blends can be applicated in a wide range of industrial fields due to the possibility to control the rheological properties of PHV/PHB blends by the addition of appropriate amount of PHV.

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# APPLICATION OF POLYAMINOGUANIDINES IN POLYMER TECHNOLOGY

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Polyaminoguanidines are polyfunctional compounds. Currently, it is known about their use for modifying rubbers, processing wood, and for water purification.

Among the polymer composite materials, reinforced ones occupy a large proportion. Reinforcement of plastics and rubbers with fibers makes it possible to create composites with enhanced mechanical, thermophysical and antifriction properties. When reinforcing, an important task is to ensure high bond strength at the "polymer-reinforcing material" interface. Among the reinforced plastics, a prominent place is occupied by basalt plastics, which are used as structural materials in aircraft, automobile and instrument making.

In the robot, the adhesion strength at the interface of composites based on polypropylene and basalt fibers, finished with polyaminoguanidine salts, was investigated. The contact angle of wetting of the sized fibers with the polypropylene melt was determined by the drop method, and the adhesion strength was determined by the direct method. It was found that when dressing basalt fibers with PAG-carbonate, the adhesive strength in the "polypropylene-basalt fiber" system increases by 2.5 times.

The effect of polyguanidine salts on the properties of tire regenerate was also studied. The modification of the crushed crumb was carried out under thermal, chemical and mechanical action in the presence of regeneration activators, softeners and polyaminoguanidine salts in order to destroy the vulcanization network and obtain new bonds.

When using salts of polyaguanidine with stearic and carboxylic acids to obtain a regenerate, an improvement in the technological characteristics of the plastic compound (Mooney viscosity) and a decrease in the content of non-expanded particles were found.

The study of the properties of the regenerate itself was carried out on test mixtures of standard composition. The results obtained showed that in the presence of polyguanidine salts, the level of physical and mechanical characteristics of the regenerate increases.

The production of the modified regenerate and the analysis of its physical and chemical characteristics were carried out in the conditions of LLC "Sumy Plant RTI"

Thus, polyguanidine salts can be recommended for obtaining new properties of plastics and rubber products.

# SYNTHESIS OF PHENOL-FORMALDEHYDE RESIN-BASED ORGANIC AEROGELS AND THEIR POTENTIAL APPLICATION

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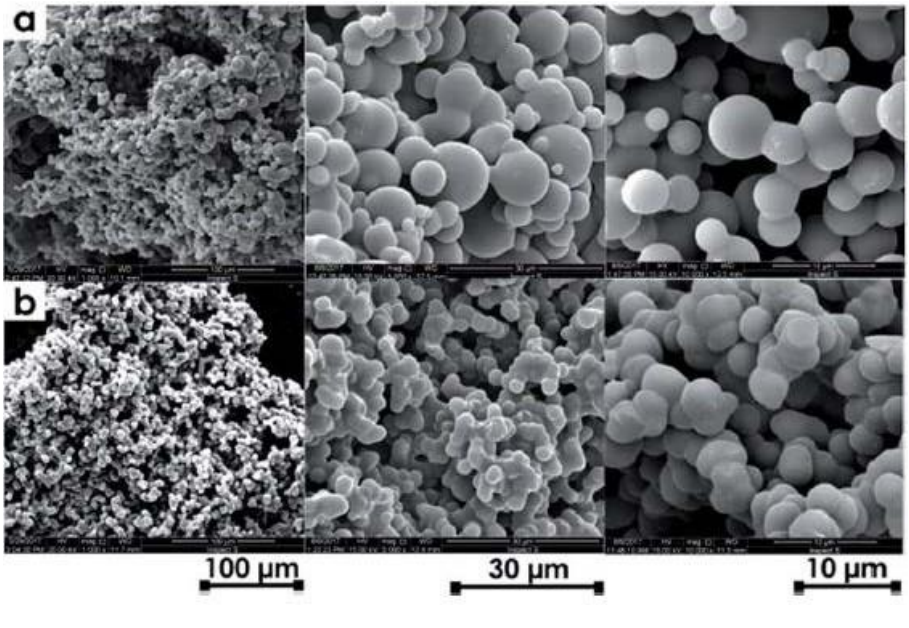
## GRAPHICAL ABSTRACT



## ABSTRACT

This study presents the example of phenol-formaldehyde (PhF) resin-based organic aerogels (AGs) applied for environmental remediation, removal of organic molecules and heavy metal ion sorption from water sources. Two AGs containing modifed resins were obtained as a product of polymerizatin reaction. PhF resins with different molar ratios of both components, together with bisphenol A diglycidyl ether, with the different

concentrations were used for the copolymerization of the monomers [1]. Concentration of used monomers and experimental conditions used for their formation affects the nanoporous structures of AGs. Despite the fact that PhF organic AGs, show lower sorption capacity compared to some other aero-like sorbents, our samples are still promising to be used for removing of some organic pollutants and heavy metal ions from wastewater, considering the multifunctionality, low-cost, fast sorption rate and excellent recyclability. The obtained data showed that organic AGs exhibited porous and functionalized structures resulting in efficient Cu(II), Mn(II) and Fe(III) ions removal from water sources. AGs were also characterized by fairly good sorption properties towards organic solvents and dyes. Combined complex permittivity and ac electrical conductivity measurements sense (broadband dielectric spectroscopy – BDS) structural changes, indicating that AGs can be also promising sensors for the interaction of fluids interpenetrating their porous system. We have demonstrated the first example of PhF-based aerogels used in the removal of oils, as well as organics and heavy metal ions removal from wastewater. BDS results indicate that the huge internal grains cause that surface area of AGs exhibit increased efficiency of collecting undesirable atoms or molecules by transferring them through the porous system by fluids or air. AGs may also be used as sensors of such entities by simply recording changes, of some orders of magnitude, in both the capacitance and electric conductivity.

## ACKNOWLEDGEMENTS

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# RESEARCH OF THE POSSIBILITY OF OBTAINING POLYMERIC MATERIALS FROM WASTE OF THE FISHING INDUSTRY

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More than 40% of the polymers produced in the world are packaging materials - non-durable products that are subject to disposal after use. Although in developed European countries the share of recycled polymer waste reaches (65-95)%, the volume of non-recyclable waste as a whole remains very significant. In particular, in Ukraine, 50% of 11 million tons of municipal solid waste is accounted for annually by polymers, of which no more than one third is subject to disposal. The rest of the polymer waste accumulates, at best, in solid waste landfills, and often in the environment. The extremely slow degradation of the vast majority of packaging and other polymers in vivo has already created a serious environmental problem.

Another problem associated with the production and use of polymers is the impending commodity crisis, which, according to some estimates, will become quite tangible in the coming decades. The raw materials for polymeric materials are mainly products of processing of fossil hydrocarbons, the explored deposits of which are depleted. At the same time, the share of renewable plant materials in modern polymer production is no more than 1%. The foregoing determines the relevance and prospects of research aimed at creating new polymeric materials based on renewable raw materials that can rapidly decompose in natural conditions after the end of their use. In this regard, we focused on waste products from the fishing industry – scales and skins of *Abramis brama* and *Rutilus*. Compared with other types of collagen-containing raw materials, fish scales and skin are of limited demand. Therefore, the number of publications and patents devoted to the utilization of this raw material in order to obtain products for various purposes has increased recently. There is information about the manufacture of dishes, packaging, construction and protective materials using fish scales.

We have carried out studies to determine the possibility of conditions for processing the scales and skin of the above-mentioned fish into ecological biodegradable polymer materials. The combination of ichthyocollagen with polysaccharides (chitosan, agar-agar) and plasticizers produced materials filled with dispersed hydroxyapatite particles (fig. 1) with varying degrees of elasticity. In this case, the filler was formed during the processing of the scales from the mineral compounds present in it.

The results obtained indicate the possibility of creating composite materials with a controlled degree of filling and elasticity, which can be used, for example, for the manufacture of containers and packaging materials for food products.

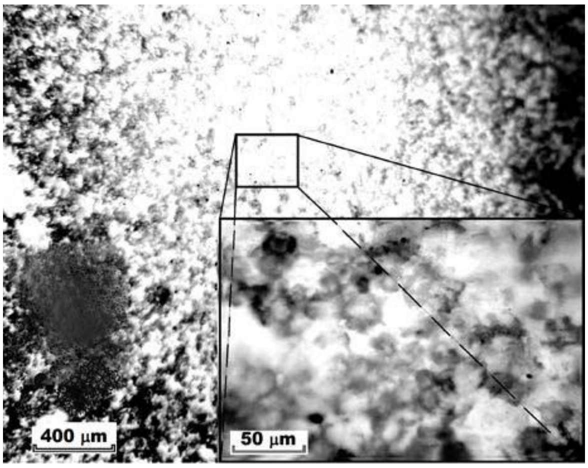

Figure 1 Micrograph of a filled composite material based on products of processing fish scales and skins

# A PINCH OF SULFUR TO POLYMERIC STRUCTURES

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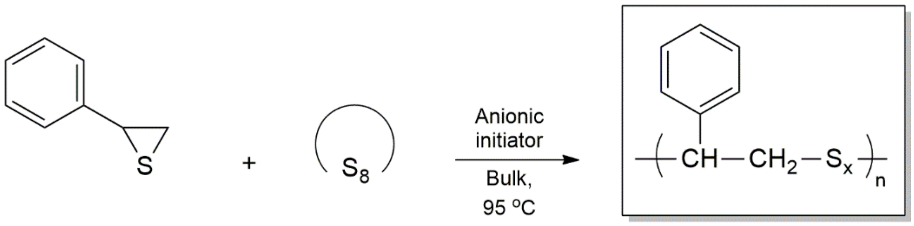
The preparation of polymeric materials with novel structures and simultaneously interesting and preferably smart properties has a big priority in modern polymer chemistry. Incorporation of some elements of the *p*-block such as sulfur, boron or prominently phosphorous into the carbon mainchain permits the formation of more exotic structures that should be of importance for polymer synthesis development [1].

The ability of thiiranes (episulfides) to undergo ring-opening polymerization in the presence of nucleophilic (anionic) initiators allows the preparation of chemically stable polysulfide homopolymers. The placement of a large quantity of sulfur atoms in the polysulfide mainchain may be achieved by the copolymerization of thiiranes with elemental sulfur ($S_8$) [2-3].



1 2 3

The propensity of styrene sulfide (2-phenylthiirane) **1** to undergo the anionic homo- and copolymerization with elemental sulfur ($S_8$) **2** to obtain chemically stable polysulfides **3** will be discussed**.** Raman spectroscopy results will be presented to characterize the chemical structure of the copolymers and to demonstrate that a true copolymerization process had been acquired. Thermal properties of the polysulfides and their application potential as a curing agents/coagents for rubber will also be mentioned.

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# PROPERTIES AND APPLICATIONS OF POLYMERIC SULFUR OBTAINED BY PLASMOLYSIS OF SULPHUR OR HYDROGEN SULFIDE

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A new method for obtaining polymeric sulfur by treatment of a melt of rhombic modification of sulfur or hydrogen sulfide in ultrahigh-frequency nonequilibrium plasma has been developed. It consists in the dissociation of sulfur-conteining molecules, which is fed into the plasma-chemical reactor in the form of melt or vapor, or hydrogen sulfide with the generation of atomic sulfur, which during cooling forms macromolecules. Depending on the cooling rate of the plasmolysis products of sulfur-containing compounds, it is possible to purposefully obtain a polymer with a molecular weight of $10^4$ to $10^6$ with a narrow molecular weight distribution. The polymer content in the obtained product increases with increasing cooling rate of plasmolysis products. When increasing the cooling rate above 80 K / s, the polymer content is greater than 90%. Depending on the molecular weight and conditions of formation of macromolecules, the structure and physicochemical properties of polymeric sulfur differ significantly.

Products with a molecular weight $(25...170)\cdot10^3$ are characterized by high values of crystallinity (over 90%) and thermal stability (70… 75%). The glassing-temperature of such products is equal to 337 ... 340 K. The singlet spectrum of the EPR indicates the formation of a polyconjugated system with a high concentration of unpaired electrons. As the molecular weight of the product increases, the degree of crystallinity, thermal stability and glassing-temperature naturally decrease.

Stabilizers are used to increase the stability of polymer sulfur in time. They are introduced directly into the plasma, for example, alkans or alkens, or into an aqueous medium, which is used to hardening the products of plasmolysis (alcohols, surfactants, quinones, etc.).

The use of polymeric sulfur as a vulcanizer makes it possible to obtain rubber, which is characterized by a relative elongation from 765 to 970%, with a residual deformation after rupture does not exceed 26%. This rubber has less hardness and much higher elasticity.

Unlike rhombic sulfur, which is commonly used to vulcanize rubbers, polymer sulfur does not fade on the surface of the product. Due to this, the polymer sulfur obtained by the plasma-chemical method should be used to obtain responsible rubber products in particular for the aviation, space, military industry, etc.

It is established that the obtained polymeric sulfur is resistant to ionizing radiation and is characterized by a high value of linear attenuation. Therefore, the use of such sulfur is promising in the production of radiation-resistant materials and in technologies for protection against ionizing radiation.

The addition of polymer sulfur to cement compositions reduces the duration of hardening, provides higher mechanical compressive strength, reduces water absorption and increases frost resistance of products.

## CONTENT

Наукове видання

*Тези доповідей*

X Українсько-польської наукової конференції

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