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TOLERANCES OF INJECTION MOLDED PARTS AND EVALUATION IN CAQC SOFTWARE

Abstract: *As the technology of injection molding becomes more sophisticated, demand on moldings with tight tolerances rises. This becomes a big issue in the whole chain of molding lifetime, starting at the phase of product design. This paper deals with design philosophy and the problematic of molding tolerances. In the following section are causes of warpage described and the possibility of warpage analysis in CAE software. In the final section an approach of evaluating of geometric tolerances is described. Preparing a template for this evaluation is easy and can be used repeatedly for the molding with same geometry but analyzed with different conditions.*

Keywords: *CEA, injection molding*

1. INTRODUCTION

The times we live in are often known as the “Computer Age”. It could also be referred to as the “Plastics Age,” as the production of plastics has exceeded that of steel (by volume) since 1979. In fact, the volume of plastics produced has more than doubled in the last 20 years [1].

The mature plastics industry is a worldwide, multibillion-dollar industry in which a steady flow of new or improved plastic materials, new or improved production processes, and new or improved market demands has caused rapid and tremendous growth in the use of plastics. For over a century the World of Plastics product production, with over a billion products, continues to expand enormously with the passing of time. Manufacturers are introducing new products in record time. The ability to shrink time-to-market schedules continues to evolve through the more knowledgeable application and behavior or familiarity of the different plastic materials, processing techniques, and design approaches.

Warpage of the molded plastic parts is one of the most important problems occurring on final injection molded part. Warped parts may not be

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functional, visually acceptable or fit into assembly. Different shear rate profiles, cooling profiles and packing pressure history along the cross-section of part cause differences in orientation, density and these phenomena affect the shrinkage.

2. DESIGN PHILOSOPHY

Unlike metals, the properties of most plastics vary considerably within normal operating temperatures. A particular acrylonitrile butadiene styrene (ABS) whose tensile strength is 42 MPa at room temperature can drop to 20MPa 52°C [1]. Other properties are also affected. For example, brittleness increases as the temperature drops, etc. What does this mean to the design engineer? Basically, it means there will be more work to do. Various pertinent properties will need to be examined at both extremes of the service range. Furthermore, the design parameters must be explored more fully. It cannot be assumed that the product will survive the temperatures endured in cleaning, shipping, or storage unscathed.

It is important that the design engineer be cognizant of this when employing the data in an empirical fashion. Generous safety factors are customarily used. When greater precision is required, the proposed material may be independently tested under conditions more appropriate to the actual application [2]. When the anticipated market is sufficient, the resin manufacturer may be inclined to perform these tests at the company's expense. Otherwise, it will be the obligation of the product manufacturer to bear the cost. The general stiffness range of most plastics, combined with the general effort to use the thinnest possible wall thickness, means the geometry has a pronounced effect. Other than through comparison to similar constructions, the stiffness of the actual part is difficult to predict in a precise fashion. Although the traditional equations will produce approximate results, stiffness remains a question until the first part is molded. (Finite element analysis results are vulnerable to the many variables involved.) Fortunately, there are so many compound variations available within a given resin, it is usually possible to adjust stiffness within a reasonable range. This has been the saving grace of many an engineer. Also, many plastics engineers withhold the placement of ribbing until the first parts are tested. Even if the material maintained its properties throughout the product's temperature range and the data was perfectly reliable, the product's performance could still vary. That is because the plastics processes are subject to tooling quality and process parameter variations[1].

3. MOLDING TOLERANCES

Molding tolerance is a specified allowance on the deviation in parameters such as dimensions, weights, shapes or angles, compounding mixtures, etc. at standard or stated environmental conditions. To maximize control in setting tolerances, there is usually a minimum and maximum limit on thickness, based on the process to be used. Each resin has its own range that depends on its chemical structure and melt-processing characteristics (Fig. 1). Outside these ranges, melts are usually uncontrollable. Any dimensions and tolerances are theoretically possible, but they could result in requiring special processing equipment, which usually becomes expensive. There are, of course, products that require and use special equipment.

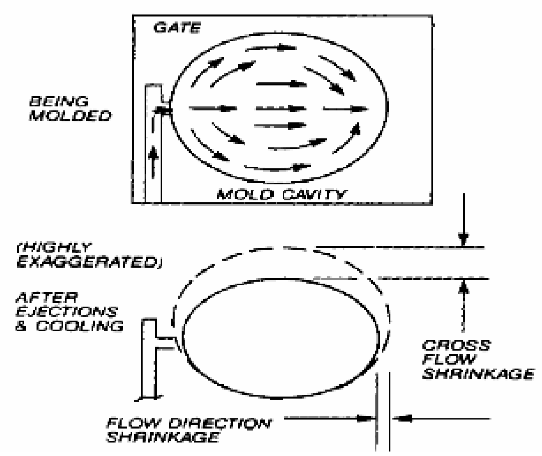

Fig. 1. Example of directional shrinkage in an injection molding that can be related to the isotropic performance of plastics during processing [2]

One factor in tolerances is shrinkage. Generally, shrinkage is the difference between the dimensions of a fabricated part at room temperature and the cooled part, checked usually 12 to 24 h after fabrication. Having an elapsed time is necessary for many plastics, particularly the commodity TPs, to allow parts to complete their inherent shrinkage behavior. The extent of this post-shrinkage can be near zero for certain plastics or may vary considerably. Shrinkage can also be dependent on such climatic conditions as temperature and humidity, under which the part will exist in service, as well as its conditions of storage.

Like metals, plastics generally expand when heated and contract when cooled. Usually, for a given temperature change TPs change more than metals. The coefficient of linear thermal expansion (CLTE) is the ratio between the change of a linear dimension to the original dimension of the material per unit change in temperature (per ISO EN standards Because this CLTE value usually has to be determined at the part's operating temperature to specify a plastic that will do the job. It is important to include in the designspecifications the operating temperature conditions. All the extremes in CLTEs can be provided by plastics, including graphite-filled compounds that could work in reverse. Upon heating, they contract rather than expand, and vice versa [2].

The CLTE is an important consideration if dissimilar materials such as one plastic to another or a plastic to metal and so forth are to be assembled. The CLTE is influenced by the type of plastic (liquid crystal, amorphous, etc.) and composite, particularly the glass-fiber content and its orientation. It is especially important if the temperature range includes a thermal transition such as T_g. Normally, all this activity with dimensional changes is available from material suppliers readily enough to let the designer apply a logical approach and understand what could happen.

The design of products has to take into account the dimensional changes that can occur during fabrication and its useful service life. With a mismatched CLTE, there could be destruction of plastics from factors such as cracking or buckling.

Tolerances and Designs

Computer programs developed since the 1980s have continued to make possible the modeling of complex interactions of the many processing factors. These include plastic properties and behaviors, geometry of the part, toolmaking quality applied to manufacturing dies or molds, and the processing conditions and fluctuations inherent in the equipment and materials.

Tolerance Allowances

Tolerance allowances are basically an intentional difference between material limits of mating parts. It is the minimum clearance (positive allowance) or maximum interference (negative allowance) between such parts.

Tolerances and Shrinkages

Two different forms of product shrinkage must be considered when designing to meet tolerances: the initial shrinkage that occurs while a part is cooling after fabrication, called the mold or tool shrinkage, and that which occurs after as many as 24 hours, called the after shrinkage or after-swell. Some plastics are extremely stable and others are very close to being stable so that once cooled, dimensions (and other factors) do not change. However, many plastics shrink and do not influence performance of the parts when in service.

In many cases low shrinkage may indicate more stability of the plastic part. Large, unpredictable shrinkages can make close tolerance designing almost impossible. However, in such situations, one can use a material where the shrinkage is controllable; there are many of these plastics in use. Various kinds of compounds with their additives and fillers are available from which to choose (consider graphite powder additive). If a part has to be postcured or annealed to relieve internal stresses, allowance must be made if the material shrinks during this secondary operation.

The transition from room temperature to a high processing temperature may decrease a plastic's density by up to 25%. Cooling causes possible volume shrinkage of up to 3 % and may cause surface distortions or voiding with internal frozen strains. As discussed in other sections of this book, this situation can be eliminated or reduced by choosing another material and/or a process control such as cooling under pressure.

Tolerances and Warpages

A fabricated part that warps is usually caused by the shrinkage behavior of plastic, which may be characteristic of the plastic but more probably a result of the way it was processed. Corrective action can be taken by controlling the fabricating process to eliminate or (if permitted) almost eliminate the warpage, which in turn permits meeting tolerance requirements.

4. DIMENSIONAL TOLERANCES

The specific dimensions that can be obtained on a molded product basically depend on the performance and control of the plastic material, the fabrication process, and in many cases, properly integrating the materials with the process. In turn, a number of variable characteristics exist with the material itself [3]. Unfortunately, many designers tend to consider dimensional tolerances on plastic products to be complex, unpredictable, and not susceptible to control. This is simply not true, though they can be complex. Plastics are no different in this respect than other materials. If steel, aluminum, and ceramics were to be made into complex shapes but no prior history on their behavior during processing existed, a period of trial and error would be required to ensure their meeting the required measurements. If relevant processing information or experience did exist, it would be possible for these metallic products to meet the requirements with the first part produced. This same situation exists with plastics. To be successful with this material requires experience with its melt behavior, melt-flow behavior during processing, and the process controls needed to ensure meeting the dimensions that can be achieved in a complete processing operation. Based on the plastic to be used and the equipment available for processing, certain combinations will make it possible to meet extremely tight tolerances, but others will perform with no tight tolerances or any degree of repeatability.

Fortunately, there are many different types of plastics that can provide all kinds of properties, including specific dimensional tolerances. It can thus be said that the real problem lies not with the different plastics or processes, but rather with the designer, who requires knowledge and experience to create products to meet the desired requirements. The designer with no knowledge or experience has to become familiar with the plastic-design concepts expressed throughout this book and work with capable people such as the suppliers of plastic materials.

Certain injection molding parts can be molded to extremely close tolerances of less than a 0.01 mm, or very close to 0.0%, particularly when TPs are filled with additives or TS compounds are used. To practically eliminate shrinkage and provide a very smooth surface, one should use a small amount of chemical blowing agent (< 0.5% by weight) and regular packing procedure. For conventional molding, tolerances can be met of ±5% for a part 0.5 mm thick, ± 1 % for 1.27 mm, ±0.5% for 25.4 mm), ±0.25% for 127 mm, etc [4]. Thermosets generally are more suitable than TPs for meeting the tightest tolerances.

Economical production requires that tolerances not be specified tighter than necessary. However, after a production target is met, one should mold "tighter" if possible for greater profit. Many plastics change dimensions after molding, principally because molecular orientations and molecules are not relaxed. To ease or eliminate the problem, one can change the processing cycle so that the plastic is "stress-relieved," even though this may extend the cycle time, and/or heat-treat per the resin supplier's suggestions.

4.1 Specification of molded product

Tight tolerances on dimensions should be specified only when absolutely necessary. Too many drawings show limits on sizes when other means of attaining the desired results would be more constructive. For example, if the outside dimensions of certain drill housing halves were to have a tolerance of ±0.008 cm , this would be a tight limit. Yet if half of the housing were to be on the minimum side and the other on the maximum side, there would be a resulting step that would be uncomfortable to the feel of the hand while gripping the drill. A realistic specification would call for the matching of halves so as to provide a smooth joint between them, with the highest step not exceeding 0.05 mm. The point is that limits should be specified in such a way that those responsible for the manufacture of a product will understand the goal that is to be attained. Thus, we may indicate "dimensions for gear centers," "holes as bearing openings for shafts," "guides for cams," etc. This type of designation would alert a moldmaker as well as the molder to the significance of the tolerances in some areas and the need for matching parts in other places and the clearance needed for assembly in still other locations.

Most of the engineering plastics faithfully reproduce the mold configuration, and when the processing parameters are appropriately controlled, they will repeat with excellent accuracy.

We see plastic gears and other precision parts made of acetal, nylon, polycarbonate, and Noryl with tooth contour and other precision areas made with a limit of 0.005 mm and in which the spacing of the teeth is uniform to meet the most exacting requirements.

The problem with any precise part is to recognize what steps are needed to reach the objective and to follow through every phase of the process in a thorough manner, to safeguard the end product. Different factors can cause a variation in shrinkage; indeed, the way processing parameters can influence dimensional variation is very important. Some materials perform better than others in that respect.

Generally, if we approach tolerances according to their purposes-(1) functional requirements, such as running fit, sliding fit, gear tooth contour, etc.; (2) assembly requirements-that is, to accommodate parts with their own tolerances; and (3) matching parts for appearance or utility-we should come up with feasible tolerances that will be reasonable and useful. This will be more productive than trying to apply tolerances strictly on a dimensional basis [1].

Tight tolerances should be indicated only when they are needed, carefully analyzed for their magnitude, and of proven usefulness. The designer should recognize that attaining extreme accuracy of dimensions is expensive and, in some cases, impossible to hold in processing. The adaptation of metal tolerances to plastics is not advisable. The reaction of plastics to moisture and heat, for example, is drastically different from that of metals, so that pilot testing under extreme use conditions is almost mandatory for establishing adequate tolerance requirements.

4.2 Using Geometric Tolerancing

By clearly showing design intent on the drawing that, in turn, is transferred to the mold manufacturer, geometric dimensioning and tolerancing can play an important role in the success of integrated manufacturing or computer-aided manufacturing.

The physical elements of mass-produced products must be described clearly, concisely, and precisely so they can be produced efficiently and profitably. Geometric dimensioning and tolerancing (GD & T) is one way to enhance this critical communication with minimal expense. GD & T is a system of symbols and internationally accepted notation that greatly increases the expressive power of the drafting language. The GD & T language system has evolved through the efforts of engineering, design, and manufacturing personnel familiarwith the added costs caused by inadequate drawings [3].

The current standard of dimensioning and tolerancing is ISO TC 10 and ISO/TC 213. The goal of the standard is to increase production efficiencies by enhancing one’s ability to express design intent and critical functional relationships on the drawing itself.

Drawings are essentially contracts governing the production of a manufactured product. Quite often, designers and manufacturers find that the old plus and minus or coordinate dimensioning system falls short of expressing the true limits of production variability. Therefore, functional design integrity at minimum cost cannot be ensured.

A datum is one component of the GD&T language that allows dimensional networks to be established in ways that make functional sense.

Datums enable designers to clearly express relationships between key elements of a product; to guide how a product should be aligned in manufacturing and set up at inspection; and to reflect on how a product will operate or be installed at assembly.

Datum referencing is just one of many aspects of GD&T that ensures more functional products while saving money. GD&T as a total language system is a practical and straightforward way to document functional design requirements. GD&T develops 100% interchangeable and 100% functional products at minimum cost, unlike the old plus or minus tolerancing language.

5. WARPAGE OF INJECTION MOLDED PARTS

Imbalance of shrinkage in any section of a part will produce a net force that could warp it. The stiffness of the part and the shrinkage imbalance level determine the warpage amount. If the part is too stiff to allow deflection, residual stresses will be created in the part that may cause problems later in its life [6].

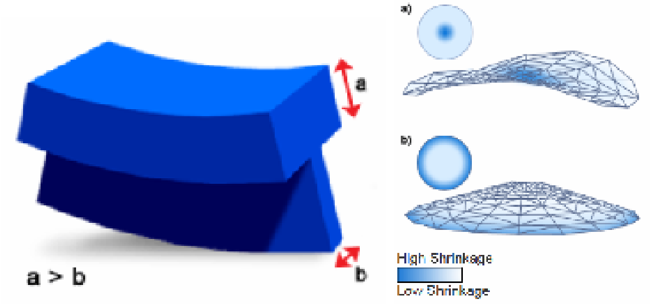

Fig. 2. Warping of molding due differential shrinkage [6]

If the shrinkage of a material is completely isotropic with respect to thickness, flow direction and distance, and packing pressure plastic parts will not warp. Asymmetric shrinkage and unequal contraction in the different directions cause warpage. When considering the contributors to warpage, it is convenient to identify shrinkage due to:

- Variation in shrinkage from region to region (differential shrinkage) Fig.2.
- Temperature differences from one side of the mold to the other (differential cooling) Fig.3.
- Variations in the magnitude of shrinkage in directions parallel and perpendicular to the material orientation direction (orientation effects) Fig.4.

The Fig.2 (left) shows a thin rib attached to a thick top. In general, the cooling rate of the top will be lower than that of the thin section. The top will have increased crystalline content and therefore, will shrink more and cause the warpage shown. Figure 2 (right) (a) shows saddle warping of a centrally gated disk with high shrinkage at the center. Conversely, if the shrinkage is higher around the outer part of the disk, the resulting warpage may cause the disk to dome, shown in (b).

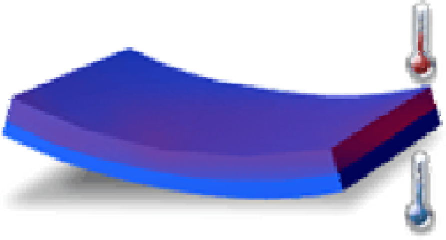

Fig. 3. Warping of molding due differential cooling [6]

Shrinkage due to differential temperature typically results in bowing of the component, as shown in the figure below. Usually this type of shrinkage is due to poor cooling system design. While the part is in the mold, temperature differences from one side of the mold to the other cause variations in shrinkage through the thickness of the component. In addition to this, any temperature differences at ejection will cause further warpage as both sides of the part cool to room temperature.

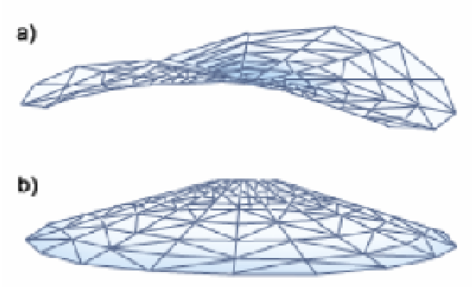

Fig. 4. Warping of molding due orientation effect [6]

Orientation causes variation in the magnitude of shrinkage in directions parallel and perpendicular to the material orientation direction[5]. This type of shrinkage can produce warpage similar to that of differential shrinkage. Figure (a) below shows the warpage when parallel shrinkage is greater than perpendicular shrinkage. On the other hand doming can be produced if the perpendicular shrinkage is higher than parallel shrinkage, see (b).

Each of these types of shrinkage will contribute to the total warpage of the product. Moreover, process parameters such as melt temperature and holding pressure have an effect on the rate of shrinkage in the different directions [5, 6]. Thus, different melt temperature and holding pressure will affect the warpage amount of the part. Non-uniform shrinkage in different directions could be determined using the material pressure-volume-temperature (pVT) relation diagrams [4].

5.1 Warpage simulation in CAE

Warpage analysis of injection molded part is available in all major CAE simulation software for injection molding process [5]. Autodesk Simulation Moldflow Insight (ASMI) is capable to perform warpage with all three types of FEM mesh (midplane, Dual Domain, 3D) used in this product to simulate injection molding process. User of ASMI has two basic tools or approaches to evaluate results of warpage analysis: "best fit technique" and anchor planes.

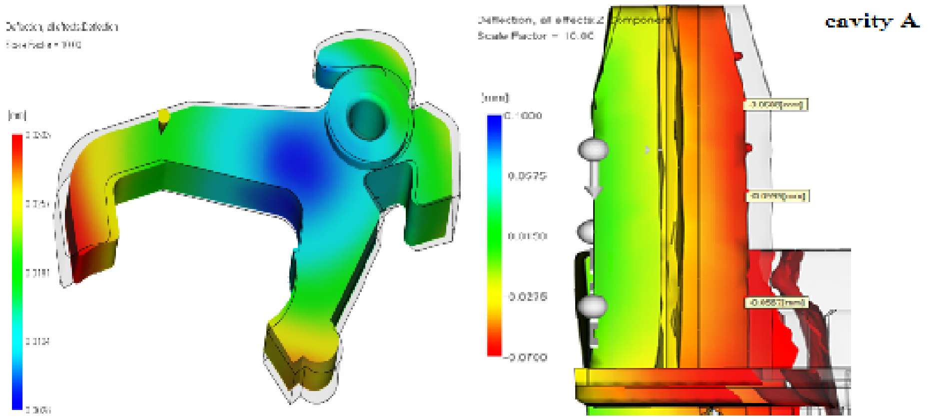

Fig. 5. Visualization of molding warpage (10x magnified)

Using of "best fit" technique for warpage visualization is preferable in early stages of product development, where is important to obtain visual behavior of molding warpage to identify problem areas. The designer can fast identify the changes in warpage when a change in design or molding condition is made [6]. When evaluating if the molding meets the dimension requirements specified in production drawing is using of "best fit" technique very problematic if not even impossible. In case when evaluating of specific dimension is necessary application of anchor planes.

Despite existence of these two tools for evaluation of warpage, when there is need for evaluation of geometric tolerances of molding, these tools are not suitable. For the user is practically impossible to measure distances between each of thousands nodes and then calculate the value to evaluate if the molding will meet desired geometric tolerance.

6. EVALUATING OF GEOMETRIC TOLERANCES

These limitations in the process of geometric tolerances evaluation, inspired us to use software from the CAQC family. Software that is used for evaluation of tolerances of 3D scanned models. It is generally known, that primary data output of 3D scan are data if form of cloud of points. Then the cloud of point is processed into STL data, eventually further to parametric model [7].

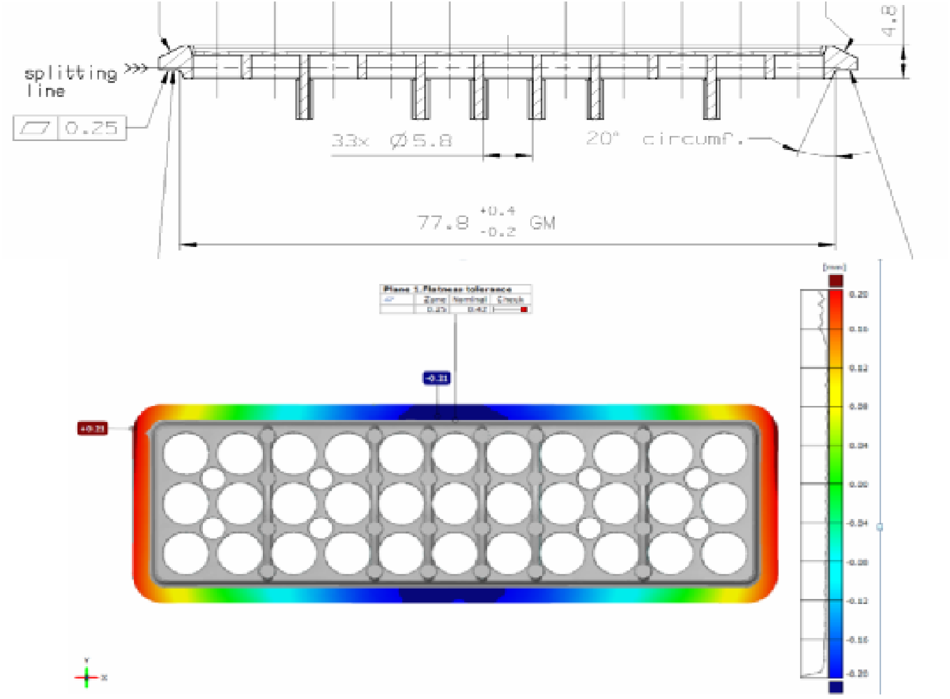

Fig. 6. Evaluation of flatness for example molding geometry

One of these type of software is GOM Inspect^{TM} (GI). This system is aimed on control and evaluation of dimensional accuracy and geometric tolerances of 3D scanned model. Data from 3D scanned model are compared with initial 3D CAD model used at manufacturing of real part. User defines desired control values and the software checks if the real part meets desired criteria. We combined ability of GI to evaluate 3D scanned model from STL data and the ability of ASMI to export geometry of warped model in STL format.

In the figure 6 is presented evaluation of flatness for example molding. In this case is obvious that the defined value of flatness 0,25 was not met and the molding is faulty. Other tolerances can be evaluated in this way. A template containing all dimensions and tolerances can be prepared for each model and applied for all next warpage analysis results of the same model (e.g. observer influence ofchanging molding conditions). Then the dimension and tolerances check in GI can be made fast at “one click”.

7. CONCLUSION

As the technology of injection molding becomes more sophisticated, demand on moldings with tight tolerances rises. This becomes a big issue in the whole chain of molding lifetime, starting at the phase of product design. Nowadays molding and mold designers can rely on strong tools in form of CAD and CAE systems. When correct and accurate input data are used in CAE injection molding analysis, results of warpage simulation is very accurate. Considering the complex geometry of nowadays molded product, evaluation of warpage results with “best fit” technique and anchor planes is problematic or even not possible. In this paper is presented approach of using GI software to enable evaluation of dimension and geometric tolerances from the result of CAE warpage analysis. Preparing a template for this evaluation is easy and can be used repeatedly for the molding with same geometry but analyzed with different conditions.

Acknowledgements

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VERIFICATION OF THE CAPABILITY OF THE PLASTIC MOULDED PIECE PRODUCTION PROCESS

Abstract: *The process capability is statistical measure of inherent variability of the process for the respective characteristics. Up to present the process capability has not been agreed on. At times the standard deviation or the range of quality indicator or their multiple based on inherent variability are considered to be the measure of capability. At times it is a combined value of the component induced by the inherent variability and component induced by the inconsiderable and determinable causes. The contribution deals with the problems of influence of added regranulate into base material on dimensional accuracy of molded parts. Influence of regranulate on dimensional accuracy of molded plastic parts of material Celanex ®2004–2 PBT was evaluated by Shewharth control chart for arithmetic average and index competence of process.*

Key words: *polymer composites, regranulate, dimensional accuracy, Shewharth control chart*

INTRODUCTION

Very significant factor determining the quality of products is the quality of processes in which the products were produced. The quality of the processes can be assessed through their capability – the ability to meet the criteria determined in advance. Knowledge on the process capability is significant for the following:

- customer possessing thus the proof whether the product was produced under stable conditions assuring observance of the prescribed quality criteria,
- maker as it allows them to select the appropriate process for the production of particular product, to estimate the risk of occurrence of the discrepant products, to plan preventive and corrective precautions and to assess their efficiency.

1. ANALYSIS OF PROCESS CAPABILITY

Statistical techniques can be very useful in the entire production cycle: in pre-production activities, in modelling of process variability, in analysis of this variability with regards to requirements or specifications and can be helpful also

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in the process of its reduction. This general activity is referred to as the analysis of process capability.

The process capability correlates with the output uniformity. Variability usually acts in the process by the uniformity measure. Two views of the variability are known:

- natural or inherent variability at specified time, i.e. instant variability,
- variability in time.

The data analysis of the process capability can be applied especially in the following spheres:

- prognosis of the process measure during its progress within the scope of tolerance limits,
- selection or modification of the process,
- determination of interval width in statistical regulation of the process,
- specification of the requirements for new equipment performance,
- selection of suppliers,
- planning of succession of production processes in case the interactive influence of the processes upon the tolerances exist,
- reduction of variability in the process.

The analysis of the process capability mainly the four following techniques are applied: histograms or other diagrams of distribution of frequencies, capability indices, regulation diagrams, and proposals of experiments.

1.1 Indices of the Process Capability

Initially, the assessment of the process capability applied histograms. However, the requirement of the managers from practice was to express the facts shown in histogram by certain number (by the indicator). Those were the foundations laid for creation of the process capability indices (PCI).

The task of the process capability indices is to simply express the relation between target values *T*, specific limits *LSL, USL*, and actual process expressed by mean value μ and standard deviation σ of the measured values of the selected character of the process quality. Target value T is required mean value of the quality character which must be achieved or which must be approached. Lower and upper tolerance limits *LSL* and *USL* represent the limits determined for the particular quality character with respect to the required variability and with the aim to assure the required functionality of the product, semi-product, etc.

Capability indices have developed in the course of several tenths of years and they can be divided into three generations:

- Structure of *indices of the first generation* C_p, C_{pk}, C_{pL}, C_{pU} stems from the conventional approach towards quality control according to which the products produced within the range of required tolerance are identical and the products

produced off the tolerance range are discrepant. Such indices applied the most frequently assess thus the potential and actual ability of the process to provide permanently the products, and the values of the selected quality character, which correspond to tolerance limits.
- *Indices of the second generation* C_{pm}, C^*_{pm} are based on a concept of the Taguchi loss function. They quantify the process capability from the point of view of variability of the quality character around its target value. In the late 80s of the 20th century, when the application of indices got spread, their drawbacks emerged as well including sensitivity to preconditions of use such as normality, independence of monitoring, and process stability.
- *Index of the third generation* C_{pmk} using the positive properties of the previous indices represents combination of indices C_{pk} and C_{pm}. The last index is C_{jpk}, which can be applied also in case of the skewed distribution. These indices react with higher sensitivity to random variability causes and lack the drawbacks typical for the indices of previous generations.

Determination of the process capability cannot be referred to only as the calculation of capability indices. It is suitable to proceed according to five steps as follows:

- quality character selection,
- measurement system analysis,
- premise tests,
- calculation of the capability indices,
- test of index significance.

1.1.1 Process Capability Index Cp

Process capability index C_P is a measure of potential ability of the process to assure the monitored quality character to be lying within the scope of tolerance limits. It is calculated according to the following relation:

$$C_P = \frac{USL - LSL}{6.\sigma} \tag{1}$$

The C_P values are interpreted as follows:

- if $C_P < 0.66$ the capability is not extensively observed (width of $USL - LSL < 4\sigma$),
- if $C_P < 1$ the process capability is not observed,
- if $C_P \geq 1.33$ good observance of the process capability and the achieved mean value occurs in distance of 4σ from tolerance limits,
- if $C_P > 1.66$ very good observance of the process capability,
- if $C_P > 2$ extremely good observance of the process capability which can be caused by unduly tolerant requirements of a customer or by unsuitable determination of tolerance limits.

1.1.2 Process Capability Index C_{pk}

Capability index C_{pk}, contrary to index C_p, takes into consideration both variability and placement of the values of the monitored character within the tolerance zone. Thus it characterizes the actual process capability to respect the prescribed tolerance limits. At present this index ranks among the most frequently applied characteristics of the production process capability. It is calculated according to the following relation:

$$C_{pk} = min\left\{\frac{USL-\mu}{3\sigma}, \frac{\mu-LSL}{3\sigma}\right\} = min\{C_{pL}, C_{pU}\} \qquad (2)$$

Tolerance zone ranging from *LSL* up to *USL* is distributed into two parts by the value of the average. If the centre of distribution of the measured values occurs in the centre of tolerance zone, the width of these parts is identical as well as the values of indices C_p and C_{pk}. In case of discrepancy the values of index C_{pk} are lower, which means that is tougher contrary to index C_p. Disadvantage of this index rests in the fact that if μ recedes from T and σ remains unchanged, C_{pk} deteriorates. But if deviation μ is from T compensated by the change of σ, the index C_{pk} does not intercept the variation of T, which is shown in Figure 1. Another negative of this index is that if target value T does not occur in the centre of tolerance zone, it cannot intercept its deviation from the actual mean value of the process.

The C_{pk} values are interpreted as follows:

- if $C_{pk} < 0$ the process is centred off the tolerance limits,
- if $C_{pk} = 0$ the process is centred on one of the tolerance limits,
- if $C_{pk} < 1$ it is the case of ineffective production process – the process incapable of following the prescribed values,
- if $C_{pk} \leq 1.25$ the production process is capable for standard products,
- if $C_{pk} \leq 1.45$ the newly introduced or well-run production process of the products related to safety is the capable one,
- if $C_{pk} \leq 1.6$ the newly introduced process of the products related to safety is the capable one.

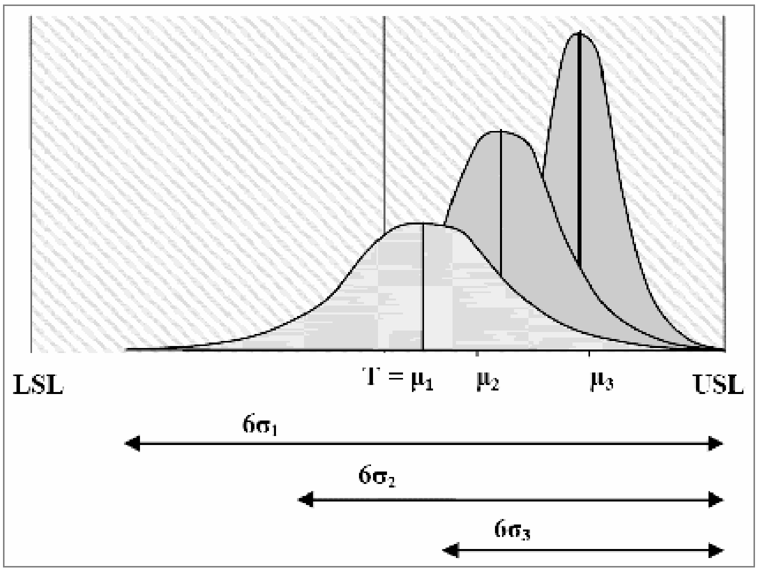

Fig. 1. Three processes $C_{pk} = 1$ with diverse variabilities and mean values

1.1.3 Capability Index C_{pL}

Capability index C_{pL} is applied if only lower tolerance limit *LSL* is defined, i.e. if in control of the production process the significance is laid on not reaching the value lower than *LSL*, i.e. avoided should be "under - stepping" of the limit. The magnitude of the deviation in upward direction is unimportant.
It is calculated according to the following relation:

$$C_{pL} = \frac{\mu - LSL}{3\sigma} \tag{3}$$

1.1.4 Capability Index C_{pU}

Capability index C_{pU} is applied only if the upper tolerance limit *USL* is defined, i.e. if in control of the production process the significance is laid on not exceeding the value higher than *USL*, i.e. avoided should be "over - stepping" of the limit. The magnitude of the deviation in downward direction is unimportant.
It is calculated according to the following relation:

$$C_{pU} = \frac{USL - \mu}{3\sigma} \tag{4}$$

Interpretation of the values of indices C_{pL} and C_{pU} is identical with the one in case of C_{pk}.

1.1.5 Capability Index C_{pm}

Capability index C_{pm}, so - called the Taguchi capability index eliminates some drawbacks of indices C_p and C_{pk} and keeps the positive features.
It is calculated according to the following relation:

$$C_{pm} = \frac{USL - LSL}{6\sqrt{\sigma^2 + (\mu - T)^2}} \qquad (5)$$

The expression $\sigma^2 + (\mu - T)^2$ represents the measure of the average quadratic loss caused by breaching the conditions of the quality production. If the standard deviation is increased and/or mean value recedes from the target value, the denominator of the index increases as well and the C_{pm} value decreases. The advantage of this index is the ability to record even the changes of the mean value which are in case of the C_{pk} index "compensated" by the standard deviation change. This index is used for two-sided tolerances and the target value occurring in the centre of tolerance zone.

1.1.6 Capability Index C^*_{pm}

Capability index C^*_{pm} represents generalization of index C_{pk}. It is applied in case if the target value does not occur in the centre of tolerance zone or only if a single tolerance limit is defined.

It is calculated according to the following relation:

$$C^*_{pm} = min\left\{\frac{T - LSL}{3\sqrt{\sigma^2 + (\mu - T)^2}}, \frac{USL - T}{3\sqrt{\sigma^2 + (\mu - T)^2}}\right\} \qquad (6)$$

In case that the mean value of the monitored quality character μ equals to the target value T and at the same time it represents the centre of the tolerance zone the indices of capability C_{pk}, C_{pm} and C^*_{pm} equal. The disadvantage of indices C_{pm} and C^*_{pm} is that if their calculated values signalize the process incapability, they do not provide information on its causes.

1.1.7 Capability Index C_{pmk}

Capability index C_{pmk} was created by integration of a numerator of index C_{pk} and of a denominator of index C_{pm}.

It is calculated according to the following relation:

$$C_{pmk} = \left\{\frac{\mu - LSL}{3\sqrt{\sigma^2 + (\mu - T)^2}}, \frac{USL - \mu}{3\sqrt{\sigma^2 + (\mu - T)^2}}\right\} \qquad (7)$$

Its advantage is higher sensitivity to variability around the target value. This index compares the distance between the mean value of the monitored quality character and closer tolerance limit with half of variability around the target value. In case of two-sided symmetrical tolerance the following relation is applicable:

$$C_{pmk} = \frac{C_{pk} \cdot C_{pm}}{C_p} \qquad (8)$$

1.1.8 Capability Indices for the Quality Character with Distribution Different from the Normal One

In case that distribution of the monitored quality character is not normal, the assessment of the process capability can be performed by means of the indices using the quantities of distribution different from the normal one. Consequently, the following is applicable:

$$C_{pp} = min\left\{\frac{\mu - LSL}{\mu - x_{0.00135}}, \frac{USL - \mu}{x_{0.99865} - \mu}\right\} \qquad (9)$$

$$C_{pT} = min\left\{\frac{T - LSL}{T - x_{0.00135}}, \frac{USL - T}{x_{0.99865} - T}\right\} \qquad (10)$$

with

- $x_{0.00135}$ is 0.135% quantile corresponding to distribution of the monitored quality character,
- $x_{0.99865}$ is 99.865% quantile corresponding to distribution of the monitored quality character.

With regards to the demand of extensive range of the set (n = 740), which is rarely at disposal for the calculation of the mentioned quantiles, these can be replaced by a minimal or maximal value of the set the range of which could be significantly restricted (n = 100).

2. EXPERIMENTAL PROCEDURE

2.1 Materials for experiments and methods

Process capability was evaluated on plastic molding parts made from TICONA Celanex ®2004–2 PBT material with specific amount of primary regranulate: 0%, 20%, 40%, 70% and 100% of regranulate. Material PBT (Polybutylene Terephthalate) is a crystalline, high molecular weight polymer that has an excellent balance of properties. PBT provides excellent dimensional properties and stability versus moisture (better than nylon from a molding and performance standpoint) and good heat resistance. PBT material is often used for injection moldings, which can be found in automotive, electronics, electrical or mechanical engineering.

Mixing of tested material to reach established amount of regranulate was performed in gravimetric mixing machine type WSB-4. The samples for experiments were produced by injection molding in four cavity injection mold on machine type Battenfeld 80 t. Defective samples were excluded and all test specimens used in the experiments did not reveal any deficiencies (Fig.2).

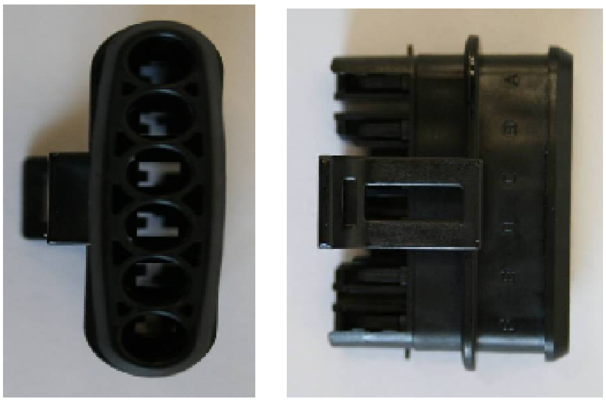

Fig. 2. Testing molded part

Dimension control was performed on 30 moldings from each tested material according to percentage of added regranulate and from all cavities on prescribed dimensions – Fig. 3.

$$DIM1 \rightarrow 11{,}00^{+0.10}_{-0.10}\,mm \qquad DIM2 \rightarrow 30{,}50^{+0.10}_{-0.10}\,mm$$

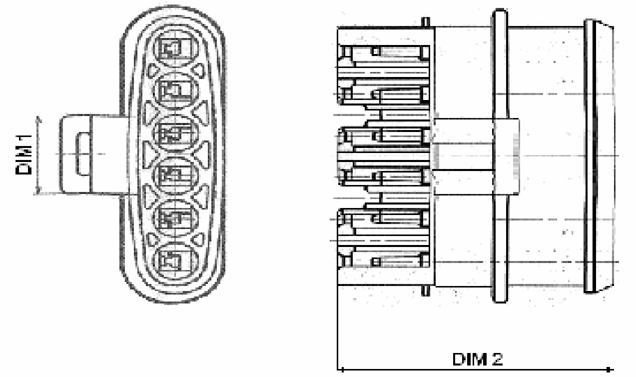

Fig. 3. Measured dimensions of molded part

2.2 Experimental results

Figure 4 and Figure 5 illustrates the influence of the regranulate on the change of measured prescribed dimension for cavity 1 and on Figure 6 and Figure 7 for cavity 2 by Shewhart control charts.

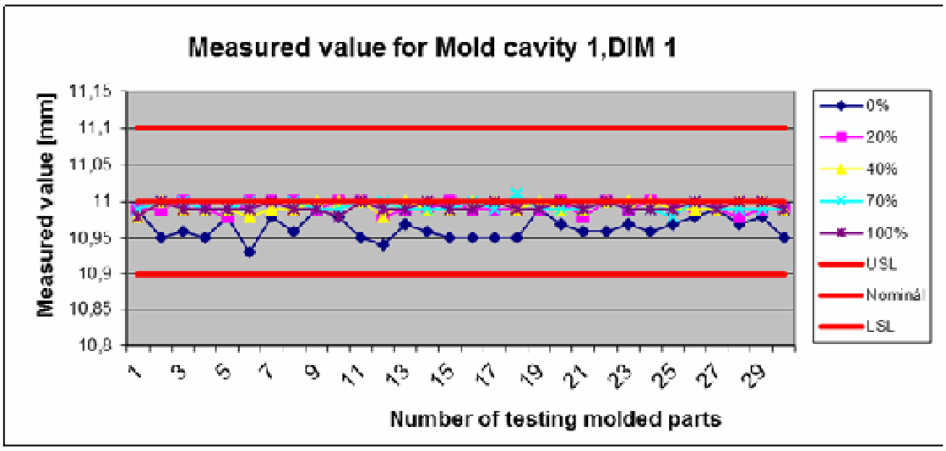

Fig. 4. Shewharth control chart of measured value with different material mixture

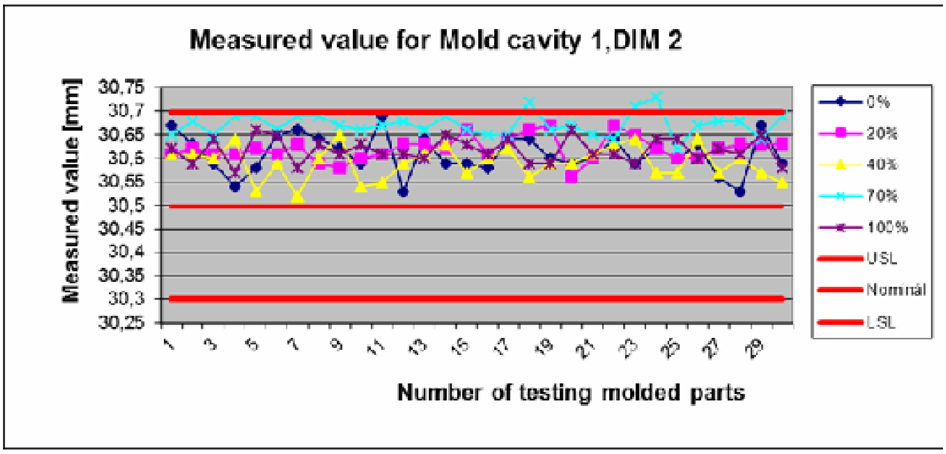

Fig. 5. Shewharth control chart of measured value with different material mixture

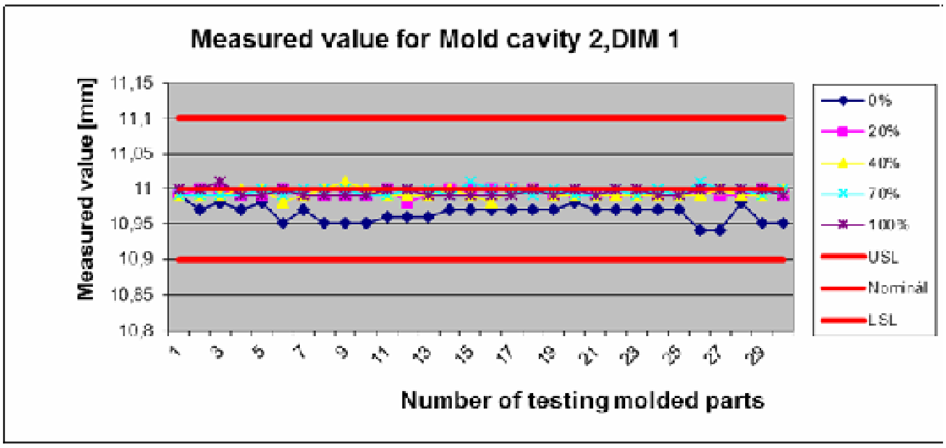

Fig. 6. Shewharth control chart of measured value with different material mixture

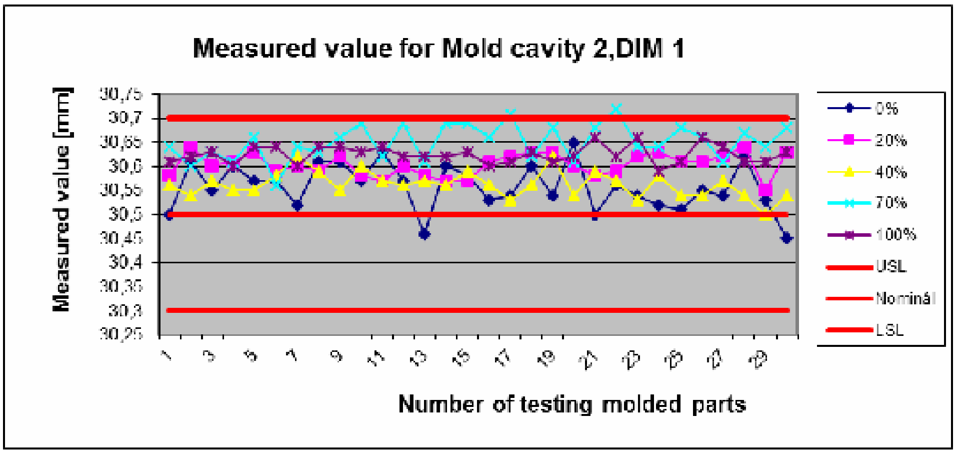

Fig. 7. Shewharth control chart of measured value with different material mixture

Process capability was made for each molding according to Table 1 Table 2 shows process capability index C_p according to tested material, individual cavity of mold and measured dimensions (DIM1 and DIM2).

Table 1. Capability process of testing material

Material: PBT (0% regranulate), DIM 1, Mold cavity 1		
	Number of testing molded parts =	30
DIM1: 11 ± 0,1 mm		
„μ“	**Average =**	10.965
„σ“	**Sigma =**	0.01613
	Minimum measured value =	10.930
	Maximum measured value =	10.990
Cp = T / 6 σ	**Cp =**	**2.066**
Cp > 1,3- Good process capability		
CpU = (USL - Average) / 3 σ	CpU =	2.796
CpL = (Average - LSL) / 3σ	CpL =	1.336
	Cpk =	**1.336**

Table 2. Process Capability Index Cp of molded parts

Material PBT with % regranulate	**Mold cavity 1**		**Mold cavity 2**		**Mold cavity 3**		**Mold cavity 4**	
	DIM1	**DIM2**	**DIM1**	**DIM2**	**DIM1**	**DIM2**	**DIM1**	**DIM2**
0%	2.066	1.634	2.661	1.375	1.995	1.773	2.373	1.619
20%	5.017	2.648	6.097	2.798	4.886	3.232	6.555	2.212
40%	5.044	1.941	5.118	2.493	5.118	2.096	4.397	3.531
70%	5.421	2.736	5.364	1.809	4.892	2.592	4.464	2.352
100%	5.715	2.648	5.824	3.636	5.715	2.495	6.097	3.286

CONCLUSION

Based on the inspection of dimensional check we came to the following conclusions:

- Measured values at all checked moldings and at all amount of added granulate were at defined dimension DIM 1 within the allowable tolerance. The dimension DIM 2 was within the allowable tolerance with an exception of molding containing 70% regranulate, where in the cavities 1, 2, 3 were five measurement values outside the tolerance range.

- The most accurate measured values were obtained at 20% and at 40% of the regranulate.
- Process capability for dimension DIM 1 was just 2 or bit above for all cavities and all types of material. This result shows excessively good process capability. Process capability for dimension DIM 2 was only in some cases above 2. Material with 40% (in cavity 1) and 70% (in cavity 2) of regranulate showed Cp= 1,6-2,0, what is also good process capability.
- Lowes Cp value was observed with base material in cavities 2 and 4, where Cp= 1,33 – 1,6, what is sufficient process capability.

Quality is becoming a key factor in customer decisions when choosing between multiple products or suppliers. Therefore, quality is the key factor of commercial success and strengthening market position. Based on the results of the dimensional checks, we can propose to add 40% of regranulate to raw material to the base material. A higher content of regranulate would require adapting the injection parameters for this production.

These conclusions, however, may not be applied to other properties of the molding, because verification of material properties (mechanical, physical) was not the aim of this contribution. To adapt this conclusion to production, several following test must be performed to verify other properties of tested material. Mechanical test and following ageing test can show, if this amount of regranulate fulfils request for this product.

Acknowledgements

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SELECTED ISSUES OF POLYMER COMPOSITE TECHNOLOGY AND TENSILE STRENGTH

Abstract: *The aim of this paper is to determine the effect of arrangement of fibreglass fabric plies in a polymer composite on their tensile strength. Based on the experimental results, the real effect of plies arrangement and their most favourable configuration with respect to strength is determined. The experiments were performed on 4 types of handmade composites which had different fibre orientations and thicknesses due to suitable technology. In this article the technology of hand making composites was described. The first three of the composites had three plies of fabric. The plies arrangement in composite I was unchanged, in Composite II the central ply had the 45^o orientation, while in Composite III the outside ply (tangential to the adhesive layer) was oriented at $45.^o$ In contrast, Composite IV consisted of five plies with unchanged arrangement. Composite plates were cut into smaller specimens. After stabilizing, the adhesive joints were subjected to tensile strength tests. It was noted that plies arrangement in composite materials and affects the tensile strength of these composites*

Key words: *polymer composites, plies orientation, tensile strength*

INTRODUCTION

Structural composites constitute a wide and diverse group of composite materials. Composites materials are mainly used in the production of aircraft, sports equipment, and different types of boats, tanks as well as pipelines and their fittings and also bearings and tubular structures [1, 2, 3]. A great variety of constituent material types, shape and dimensions of the reinforcement material as well as technologies are used in composite production [4]. In spite of the diversity all structural composites share one property, namely high strength achieved through careful selection of components [5]. The use of composite materials requires knowledge of properties prediction methods, which can be characterised by various degrees of accuracy due to difficulties in forming a composite model successfully representing a real composite. In addition, strict adherence to such a model in production is impossible. Therefore, proper

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combination of components is a fundamental condition for obtaining desired composite properties [6].

Products made of materials such as fibreglass-reinforced polymers play a significant role in industry [7]. These components include fillers and polymer matrix. The filler material can be made fibres, fabric, paper and others [8,9,10]. The polymer matrix can be made of various type of resins, such as epoxy resins, polyester resins, phenol-formaldehyde resins or maleic resins [11-15]. The variety of resin and filler types provides an opportunity to fabricate diverse composite materials [11]. Most of them are designed for particular purposes depending on technical and operational aspects of a given composite [14].

The character of used to strengthen glass greatly affects the strength of the obtained polyester laminate both because of the different possibilities of the fibers, their content in the laminate and method of forming, and the porosity of the product. However the manufacturing of laminates can be expensive because of the high labour requirement in the manual lay-up of plies [11]. In practice this rarely occurs axial stretching, and most often it is bending. By bending the beam on two supports, which runs the force is compression, and opposing — tension. It is therefore appropriate to adjust the ownership of materials. In table 1 summarizes the mechanical properties of non-reinforced resin polyester laminate obtained from fabric, test parallel to the direction of the position of the fibres [15].

Table 1. *Selected mechanical properties of non-reinforced resin and laminate [15]*

Material	**Strenght [MPa]**	
	Tensile strength	**Compressive strength**
Non-reinforced polyester resin	20-80	about 150
Laminates obtained from fabric, test parallel to the direction of the position of the fibres	about 200	about 210
The difference in the strength of the laminate and resin	120-180	60

As is evident from the data provided in table 1 polyester resin is relatively resistant on the compression, and the bad — for stretching. Laminate of fabric is much better resistant for stretching. And the laminate with high resin content is also good on the compressive and is bed resistant on tensile. So it is not indifferent, on which side of the bending cross section will be the strengthening material. The example of bending laminates samples consisting of two layers of mats and one layer of fabric is shown in Fig. 1.

This sample supports distance was 4 centimeters, the thickness of the laminate polyester - 2 millimeters, the contents of the glass — 36% w/w. Bending strength obtained for a sample of the compression side mat was 322 MPa, while the reverse side — only 120 MPa. The difference of bending strength (R_g) in both of these cases, for the same samples was significant.

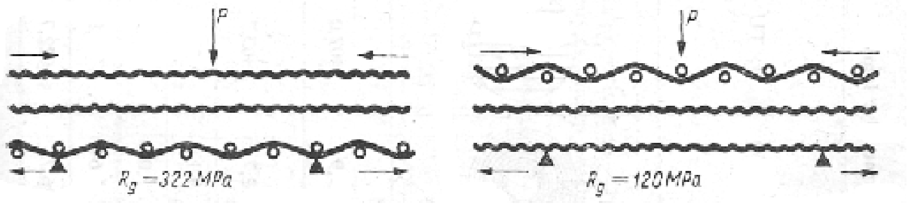


Fig. 1. The schema of bending laminates samples consisting of two layers of mats and one layer of fabric [15]

This paper investigates the effect of arrangement of individual plies of fibreglass fabric in a composite material on the tensile strength of polymer composites. On the basis of the analysis of the studies specified the actual impact of the arrangement of layers and the best of their arrangement affect strength of these composites. The one of main purpose is presents the some technological aspect of making the composite.

1. EXPERIMENTAL PROCEDURE

1.1 Material preparation

For the purpose of the study, we fabricated four polymer composites made of two constituent materials. The reinforcement material was plain weave fibreglass fabric 200g/m^2 (Fig. 2), while the matrix material was POLIMAL 1094 polyester resin [16]. The schematic of plain weave fibreglass fabric was presented in Fig. 3.

Fig. 2. Fibreglass fabric 200g/m^2

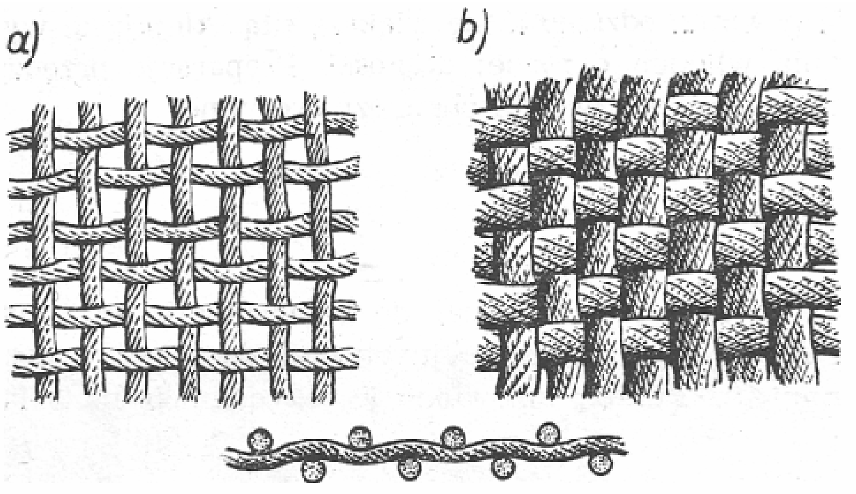


Fig. 3. Plain weave scheme of: a) rare woven, b) dense woven [15]

In plain weave, each warp thread is interwoven and intersects with each weft thread and thus the fabric is tightly bound and rigid.

The first three of the composites had three plies of fabric. The plies arrangement in Composite I was unchanged, in Composite II the central ply had the 45° orientation, while in Composite III the outside ply (tangential to the adhesive layer) was oriented at 45.° In contrast, Composite IV consisted of five plies with unchanged arrangement (Table 2 and Fig. 4).

Table 2. *Characteristics of the tested polymer composites*

Item no.	**Name of material**	**Plies arrangement**
1	Composite (I): plain weave fibreglass fabric 200g/m^2, Matrix - polyester, 3 plies	0°/0°/0°
2	Composite (II): plain weave fibreglass fabric 200g/m^2, Matrix - polyester, 3 plies	0°/45°/0°
3	Composite (III): plain weave fibreglass fabric 200g/m^2, Matrix - polyester, 3 plies	45°/0°/0°
4	Composite (IV): plain weave fibreglass fabric 200g/m^2, Matrix - polyester, 5 plies	0°/0°/0°/0°/0°

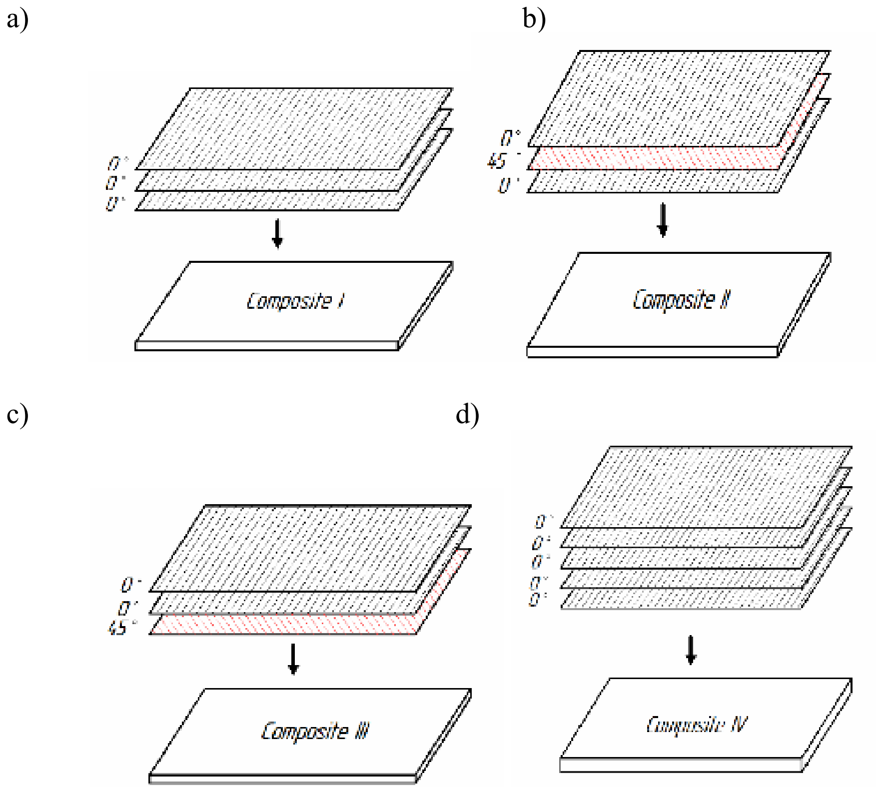


Fig. 4. The composites: a) Composite I, b) Composite II, c) Composite III, d) Composite IV

1.2 Technology of making composites

1.2.1 Mould design and preparation

First, it was necessary to design a mould where a composite material was to be fabricated. The mould was made of multi-chamber polycarbonate with the dimensions 60 x 60. This popular material is widely used in the roofing and roof glazing of sports, industrial and commercial buildings, as it is very light and easy to process. Prior to creating a composite material, the mould was suitably prepared. First, the entire surface of the mould was degreased with acetone to remove dirt which accumulated during mould fabrication and other activities. Next, it was thoroughly coated with an anti-adhesive agent, Polsiform. After atomizing, the agent generated a thin layer of silicon oil on the surface of the mould. Besides having anti-adhesive proprties, the silicon oil has no negative effect on the processing and casues no defects in the finished product.

Prior to fabricating each composite material, cut-to-dimension fibreglass fabric and polyester resin (POLIMAL 1094, produced by Organika Sarzyna, Poland [17]) were mixed with Metox-50 curing agent. The resin and curing agent were thoroughly mixed in a ratio of 100:10. Particular care was taken to prevent introducing too many air bubbles into the mixture during this process.

Polimal 1094 is orthophthalic structural resin (Fig. 5), medium-flexible, accelerated, low emission of styrene and a colored indicator of cure. It is used in the production of glass laminates with a thickness of 5 mm. Good curing requires the ambient temperature above 18°C and low humidity. It is accelerated resin having a relatively short and stable shelf life gel time.

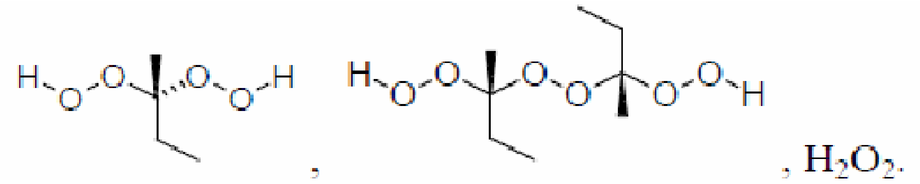


Fig. 5. Structure of Polimal 1094 resin [18]

Metox-50 is a peroxide initiator for copolymerization of unsaturated polyester resins and vinyl ester. This hardener contains methylethylketone peroxide and it is 20% solution in dimethylphthalate. It is used mainly with cobalt accelerators at environment. Due to the reduced the water content is recommended for curing gelcoats, polymer concrete and some polyester varnishes.

1.2.2 Making of the composite materials

After protecting the entire mould surface from adhesion, its inside was coated with a thin layer of polyester resin, and the first ply of fibreglass fabric was laid out depending on the type of a composite to be made (Table 2). Next, another ply of resin was applied with a brush (Fig. 6a). To supersaturate the fabric with the resin and to remove air bells from the space between fibres, the whole material was subjected to rolling (Fig. 6b). This operation was repeated for two successive plies, with the fibreglass fabric laid out in accordance with the desired composite layup design.

In the course of the process, particular care was taken to spread the resin over the entire surface of the fabric as thoroughly as possible, ensuring that it is distributed evenly. The obtained composite material is shown in Fig. 6c.

The microscopic views of prepared composites were presented in Figs. 7-10. The photographs were made using the stereoscopic microscope NIKON SMZ 1500.

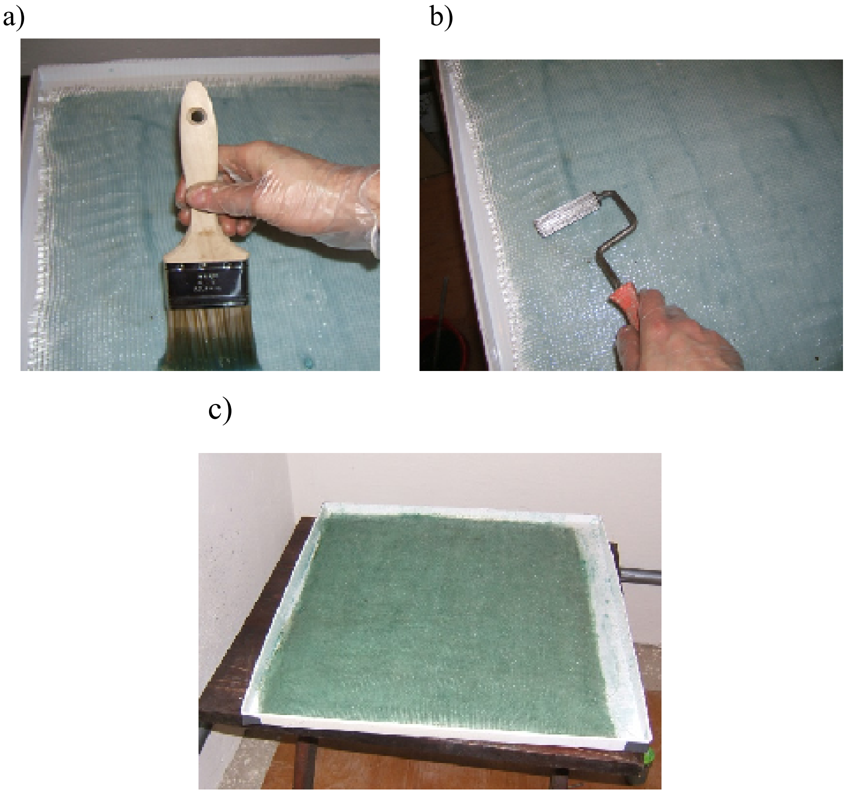


Fig. 6. Making of a composite material: a) application of resin to sucessive layers of fibreglass fabric using a brush, b) resin impregnation using a roller, c) composite material

In Fig. 7 and Fig. 10 the microscopic photographs presented the plies which have 0^{o} orientation, but the different the amount of plies. It can be noticed that the composite IV (5 plies) is more compact structure than the composite I (3 plies). In microscopic view of composite II (Fig. 8) the $0^{o}/45^{o}/0^{o}$ plies arrangement was noticed. In Fig. 8b it can be noticed the first (0°) and the second plies (45°). In Fig. 9 the first plie of 45^{o} orientation is observable.

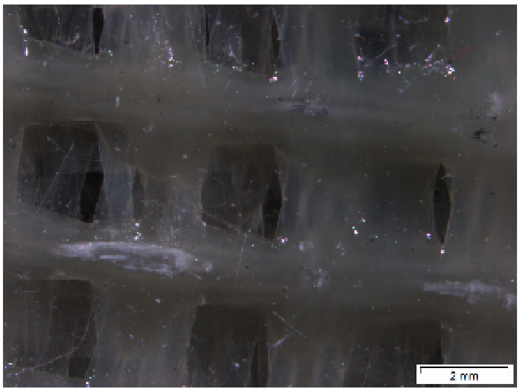


Fig.7 Surface view of composite I: 0°/0°/0° plies arrangement

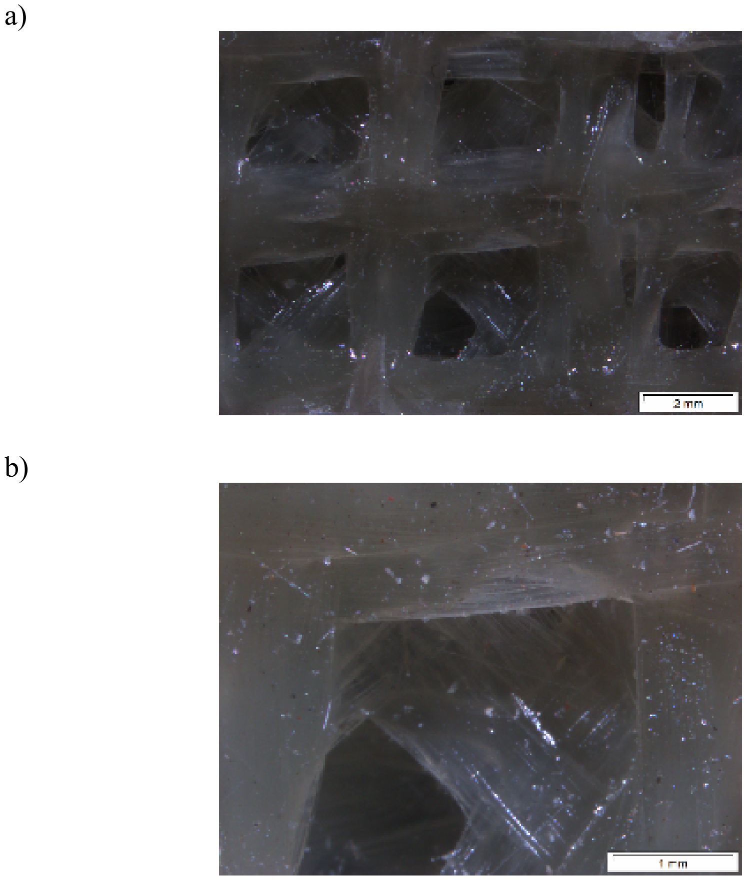
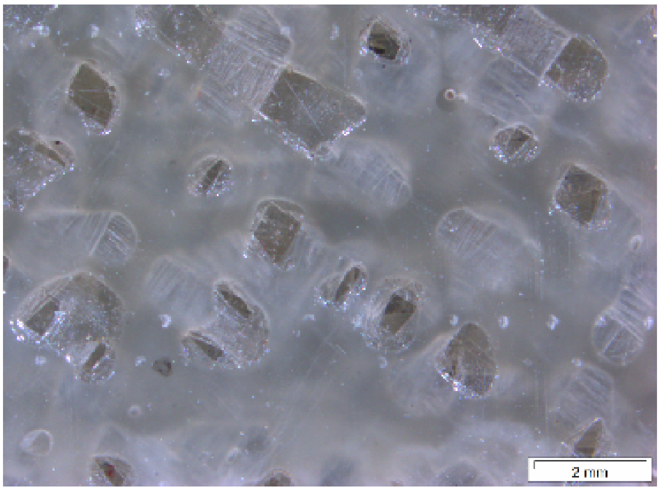


Fig. 8 a, b) Surface view of composite II: 0°/45°/0° plies arrangement a)



b)

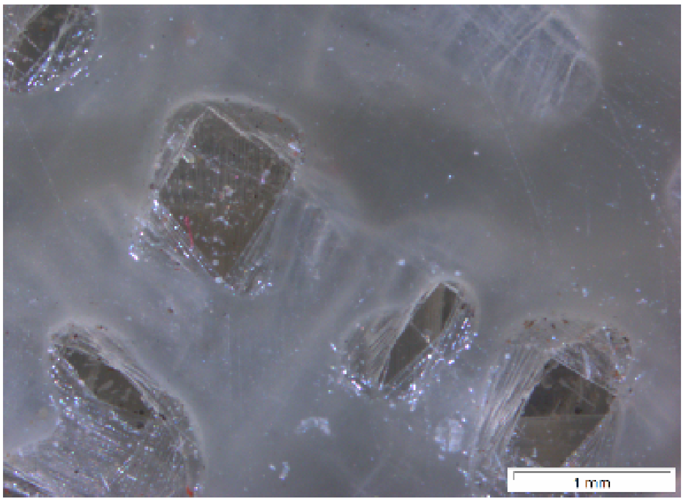
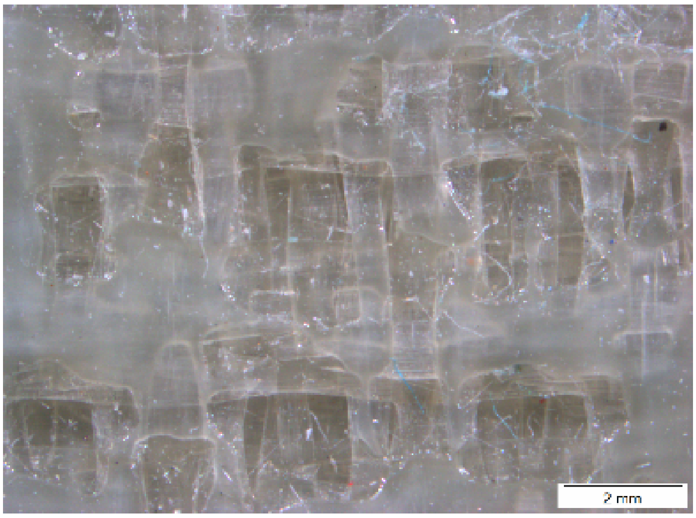


Fig. 9 a, b) Surface view of composite III: 45°/0°/0° plies arrangement a)



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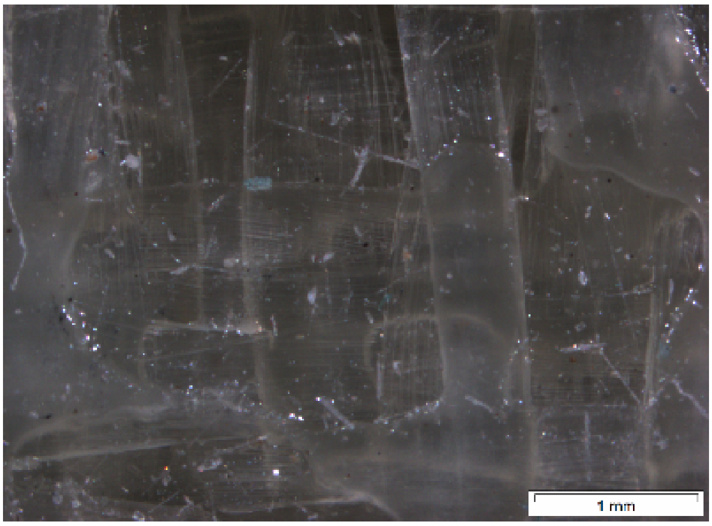

Fig. 10. a, b) Surface view of composite IV: 0°/0°/0°/0°/0° plies arrangement

It can be noticed that the composite IV (5 plies - Fig. 10) is more compact structure than the composite I (3 plies – Figs. 6-9).

1.2.3. Cutting and preparation of samples

The four prepared composite materials were left to cure for 4 days. After that period, each composite was removed from the mould, cut and numbered. Each sample was assigned its own unique Roman numeral (I through IV) to indicate the number of a composite material and its serial number. The samples were cut by a FNU-50E milling machine. The cut composites were used four blade cutter mill with skew cuts in the working part of the CVD diamond coating for the assay JRT0600 a diameter of 6 mm. The cut was implemented with the following technological parameters: RPM 9000 min $^{-1}$ and a feed of 1000 mm/min. Individual samples were numbered was to facilitate experimental tests and detection of defects.

1.3. Description of polymer composite samples

The experiments were performed on samples produced in compliance with the above procedure. Each sample had a length of 100 mm and a width of 25 mm (Fig. 11). Their thickness varied depending of the number of plies. Composites I, II, III had a thickness of 2 mm, while Composite IV had a thickness of 3 mm.

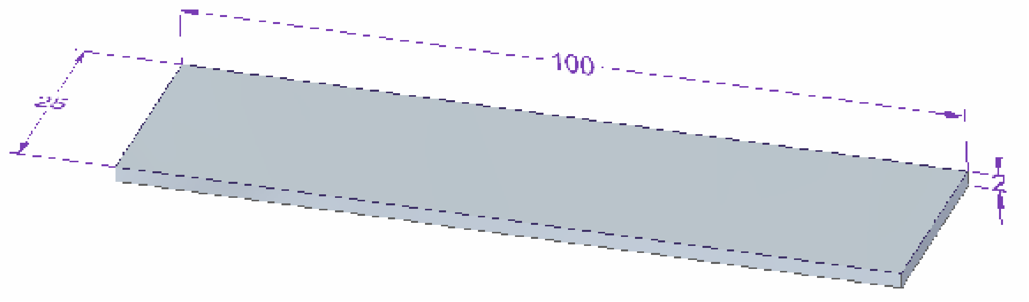

Fig. 11. Dimensions of the samples (Composites I, II, III) after cutting

After a 10 day-long stabilizing period, the samples were subjected to strength tests on a Zwick/Roell 150 testing machine (Fig. 12), in compliance with the standard DIN EN ISO 527-1. The rate at which shear tests were carried out was 5 mm/min and the rate of tensile module was 1 mm/min. The following strength test results were analyzed: E- tensile modulus in MPa, $R_{p\ 0.2}$ – elongation limit at disproportionate extension of 0.2% and R_m – tensile strength in MPa.

Fig. 12. View of Zwick/Roell 150 testing machine

2. EXPERIMENTAL RESULTS

The results of tensile strength test of the polymer composite samples are illustrated in Figs. 13-15.

The highest value of tensile modulus (Fig. 13) for Composite III ($0^o/0^o/45^o$) was obtained, while the lowest value of tensile modulus for Composite IV (5 plies $0^o/0^o/0^o/0^o/0^o$). The highest tensile strength (Fig. 14) and elongation (Fig. 15) are characteristic for Composite IV, which was the higher the thickness from the tested composite samples. The lowest tensile strength was noted in case of Composite II ($0^o/45^o/0^o$). In this composite central ply has the 45^o orientation. Composite II ($0^o/45^o/0^o$) has the lowest values of strength parameters among the tested composites, which contain three plies.

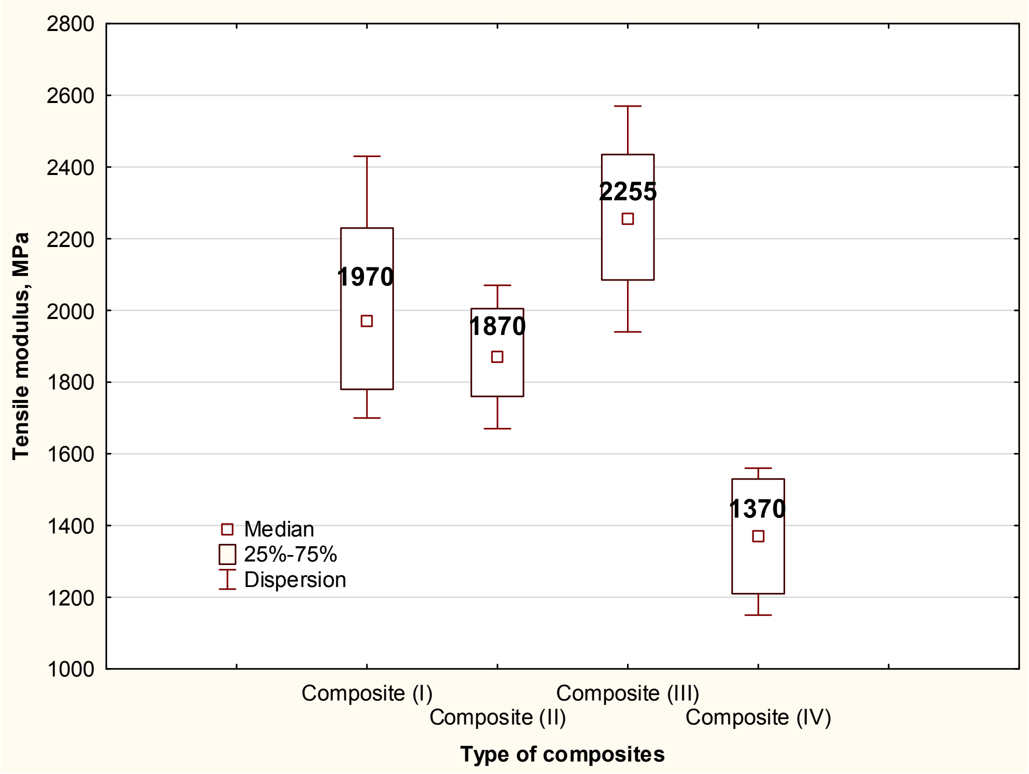

Fig. 13. Tensile modulus of the tested composites samples

3. SUMMARY AND CONCLUSIONS

The paper investigated the effect of plies arrangement in a hand-made composite material on the tensile strength of this composite. The significance of this problem is particularly true these days owing to a wide use of composite materials to design structures with required specific strength. To investigate the effect of plies arrangement on the strength of fibreglass fabric, 4 composite materials were fabricated, each having a different plies arrangement and thickness.

Concluding, plies arrangement is of vital importance and should be taken into account when designing composite materials. Nonetheless, this problem has not been exhaustively investigated in this paper. It can be studied further using samples which differ from those used in this study (e.g. samples with $45^{o}/0^{o}/45^{o}$ plies arrangement).

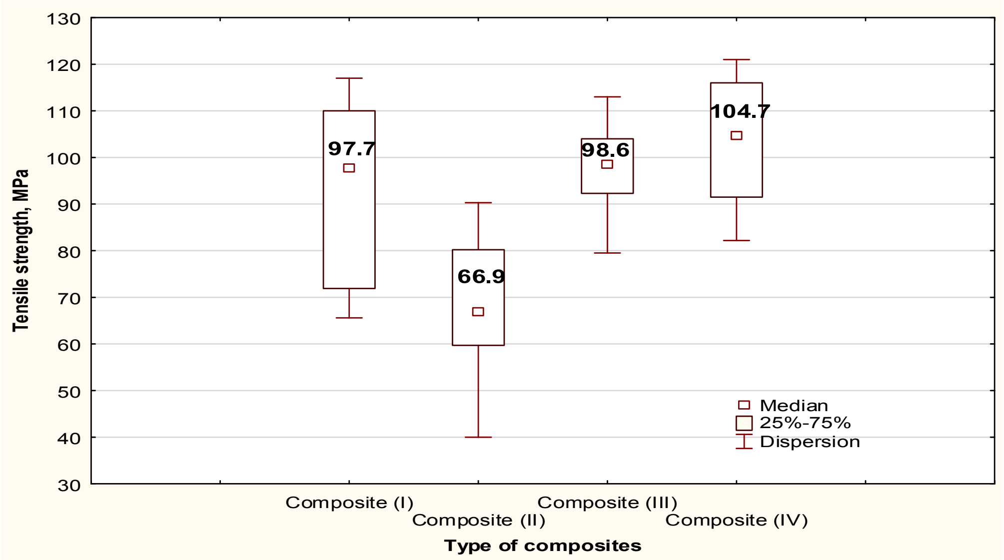

Fig. 14. Tensile strength of the tested composites samples

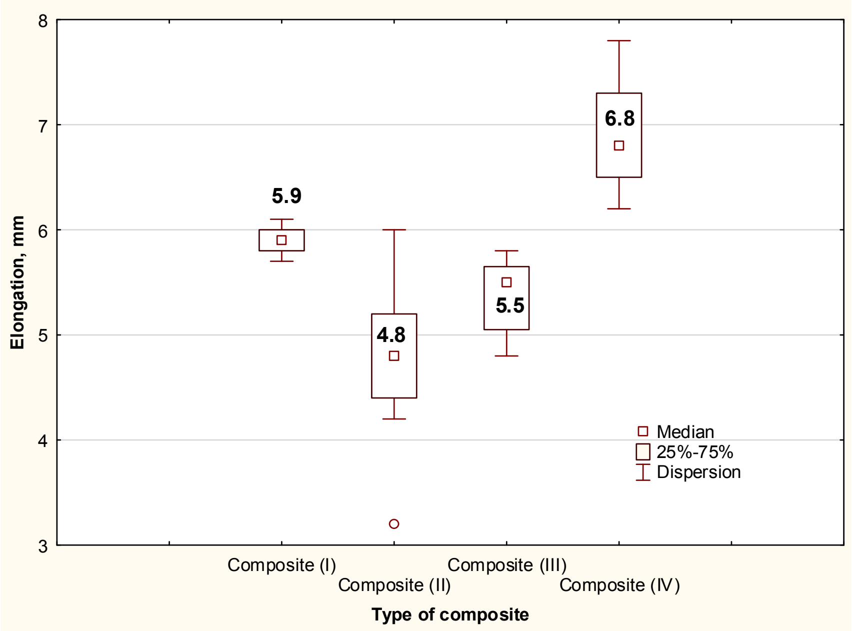

Fig. 15. Elongation of the tested composites samples

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MODIFICATION OF POLYOLEFINES WITH ORGANIC FILLERS

Abstract: *This article presents test results on mechanical, thermal and processing properties of a polymer blend obtained by modifying a high-density polyethylene (HDPE). The applied fillers were two types of Neuburg Siliceous Earth: Silitin Z86 and Silitin V88 in the form of powder.*

The tested samples contained from 10% to 60% of filler, and the results were compared to the unmodified polymer material. The polymer blend was prepared in the process of twin-screw extrusion, conducted at the rotational speed of screw of 120 rev./min, during which pellets were obtained, which were then used to perform the injection process.

Key words*: organic filler, polymer blend, modification*

1. INTRODUCTION

The main characteristic of polymeric materials is the ability to control their properties and adapting them to the specific requirements by modification. Special attention should be focused on physical modification with modifiers: organic, not organic and others [1-3].

Literature studies in recent years indicate a rapidly growing interest in both research centers and in industry, in polymer blends containing fillers of natural origin.

Technical use of such polymer blends forces wider research of the possibility of modifying, with the use of fillers, the mechanical, electrical, thermodynamic, or rheological properties. However, enhancement of all these properties should not be expected. A universal filler, with comprehensive influence, does not exist. Almost always an actual improvement in one or more properties results in the deterioration of others [1].

The aim of the presented test was determining the effect of adding a powdered filler from renewable sources on the Young modulus, hardness, heat distortion and Vicat softening temperature, as well as the longitudinal and transverse shrinkage of the filled polymer (HDPE), depending on the mass content of the filler.

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2. EXPERIMENTAL

2.1 Test stand

Experiments were performed using the ZSK18 MEGAlab twin-screw direct extruder manufactured by Coperion Werner and Pfleiderer GmbH (Stuttgart, Germany). The machine has cylindrical screws with an L/D ratio of 24 and an extrusion head with a 3mm diameter cylindrical nozzle. The plastic and the filler are fed into the plasticizing unit with a screw feeder. The extruder is part of a technological line for extrusion with cold pelletizing. The line comprises a water-cooling bath and the SP 30 Pure pelletizer from Pell-Tec GmbH (Stuttgart, Germany).

Test pieces were produced in compliance with the ISO 294-1:2002 standard using the Krauss Maffei 50-55CX injection molding machine (Munich, Germany) provided with a two-cavity injection mold. The machine has a screw with an 18-mm diameter and a clamping force of 500 000N, while its maximum injection pressure is 250MPa.

Other devices used in the tests included a testing machine and a Shore hardness tester. Tensile strength tests for produced composite injection molds were performed using a standard testing machine from Zwick Roell (Ulm, Germany), Z010 AllroundLine. The Z010 testing machine can be operated at the maximum tensile force of up to 10kN and a tensile rate of up to 2000mm/min. Hardness was measured by the Shore method using a hardness tester from Heinrich Bareiss Prüfgerätebau GmbH (Oberdischingen, Germany). The hardness tester has a unique digital system for processing gauge head data into digital signal; it also has a lighted read-out of the Shore scale and automatic recognition of the connected gauge head with hardness scale selection.

The measurements of heat distortion temperature (HDT) and Vicat softening temperature (VST) were made using the Instron-manufactured CEAST HV3 (Darmstadt, Germany) provided with three work stations.

2.2 Materials

The tests were conducted using high-density polyethylene, Hostalen GD 7255, manufactured by Olren Polyolefines (Plock, Poland) and mainly used for injection molding. The polymer has high density, good fluidity, high rigidity and its processing temperature ranges from 180 °C to 220 °C. Basic properties of this polymer are listed in Table 1.

Table 1. Basic properties of the tested polymer as given by the manufacturer

Property	Unit	Value
Density	kg/m^3	987
Melt flow rate (190 °C; 2.16 kg)	g/10 min	4
Melt flow rate (230 °C; 5.0 kg)	g/10 min	11
Tensile modulus	MPa	1180
Tensile stress at yield	MPa	27
Tensile strain at yield	%	8
Charpy notched impact strength (23°C, Notch A)	kJ/m^2	10
Ball indentation hardness, (H 132/30)	MPa	52
Shore hardness	°Sh D	60
Vicat softening temperature B50 (50°C/h, 50N)	°C	70

The applied fillers were two types of untreated Neuburg Siliceous Earth: Silitin Z86 and Silitin V88. Their basic properties are listed in Table 2. According to the manufacturer, NSE exhibits specific properties: high mixing ease and rate; minimal tendency for sedimentation, high surface activity, low compressibility, high abrasion resistance and a very high specific surface area.

Table 2. Selected properties of the untreated types of NSE

Property	Unit	Neuburg Siliceous Earth	
		Silitin Z86	Silitin V88
Density	kg/m^3	2600	
Electrical conductivity	80 µS/cm	80	
Melting point	°C	1600	
PH	-	6-8	
Particle size	µm	2-9	4-18
Specific surface area	m^2/g	11	8
Oil absorbtion	g /100g	55	47
Refractive index	-	1.55	

Silitin has numerous applications in polymer processing e.g. it is used for producing rubber parts, automotive parts, machinery components, cable coatings, coatings of electrical appliances; it is also used for producing sports and industrial flooring, polymer casts and paint coatings.

2.3 Tested parameters

Given the objective of the study, we devised a set of key parameters describing the processing, thermal and granulometric properties of the tested material. The parameters were divided into four groups.

Resulting parameters:

- heat distortion temperature HDT, ^{o}C;
- Vicat softening temperature, ^{o}C;
- standard density ρ_n, kg/m^3;
- bulk density ρ_r, kg/m^3;
- longitudinal shrinkage S_w and transverse shrinkage S_p, %;
- angle of natural slip α, deg.

Variables:

- filler type: Silitin Z86 and Silitin V88;
- filler content: ζ = 10; 20; 30; 40; 50 and 60%.

Constant parameters:

- rotational speed of the extruder screws ν = 120 rev/min:
- circumferential speed of the pelletizer cutters v = 15 m/min;
- geometry of the plasticizing unit and extrusion head, tools and injection mold, water-cooling bath and pelletizer;
- temperature of the injection mold 19^{o}C:
- temperature along the plasticizing unit of the extruder: 130, 140, 150, 160, 170 and 180^{o}C;
- polymer pressure in the extrusion head 8 bar;
- temperature along the plasticizing unit of the injection molding machine: 180, 200 and 220^{o}C;
- injection pressure: 1050 bar; holding pressure: 600 bar; holding time: 6s, injection cycle time: 35s; cooling time: 20s; time interval between cutting extruded sections t = 30s;
- Vicat load 10N;
- oil bath heating rate 120 K/h.

Disturbing parameters:

- electric voltage: 219 – 241 V,

- relative air humidity: 55 – 65 %,
- ambient temperature: 20 – 24°C.

The results of the investigated direct twin-screw extrusion and injection molding processes revealed that the disturbing parameters have a negligible effect on the results of the measurements.

2.4 METHODS

Prior to starting the extruder, a blend of high-density polyethylene and the desired content of NSE filler was made. The blend of NSE and polymer was mixed mechanically. To modify the surface of inactive high-density polyethylene, the polymer compound was directly mixed with 0.4 wt% carbofunctional silane with the trade name aminopropylotriethoxysilane [4]. This was followed by extrusion with cold pelletizing. The extrusion process was continued until the plasticizing unit of the extruder became empty. When the plasticizing unit was empty, another dose of the prepared polymer blend with a different filler content was fed into the extruder's hopper. Another stage of the research involved the injection molding of produced polymer blends in order to obtain test pieces for measuring heat distortion temperature, softening temperature as well as longitudinal and transverse shrinkage.

The heat distortion temperature was measured in compliance with ISO 75-1:2013-06 while the Vicat softening temperature was determined in compliance with ISO 306:2014-02.

The measurement of longitudinal and transverse shrinkage was made in compliance with the ISO 294-4:2005 standard.

3. RESULTS AND DISCUSSION

3.1 Young's moduls

With changing the content of untreated Neuburg siliceous earth in the test specimen, we first observe a decrease and then an increase in Young's modulus (Figure 1). The addition of a small amount (10%) of the filler leads to decreasing the Young's modulus of the produced composite by 68MPa for Silitin Z86 and by 77MPa for Silitin V88, which corresponds to a decrease by 9.44% and 10.69% in the initial value. On increasing the NSE content in the tested composite by up to 60%, the Young 's modulus increases by 15MPa and 26MPa compared to that of the unfilled polymer. This is probably caused by the fact that high-density polyethylene is a linear polymer with no branching, where partial spatial ordering of chains is possible [5]. This has a positive effect on Young's modulus because it enables better spatial ordering of chains and close proximity of macromolecules, which leads to formation of strong bonds between chains [6]. Lower values of Young's modulus are observed for bigger particles of Silitin V88, smaller specific surface area and, in effect, smaller difference in interfacial surface energy.

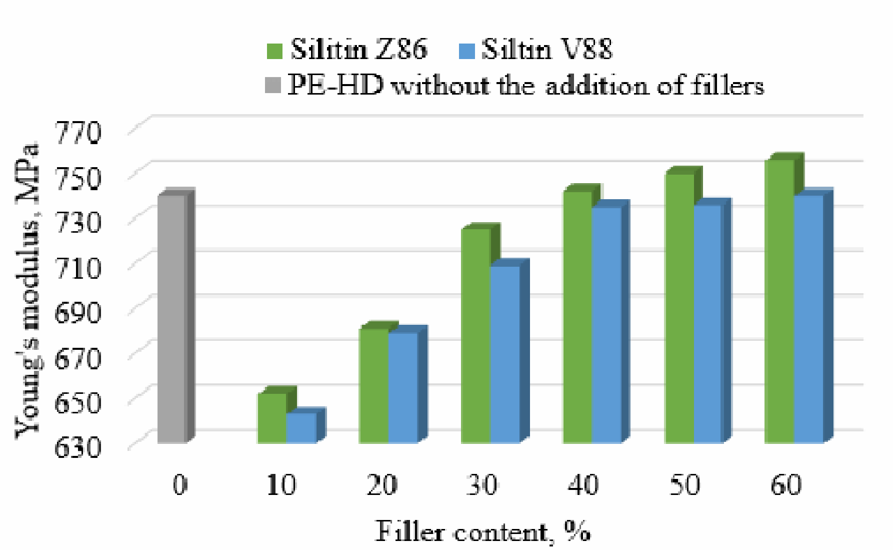

Fig. 1. Young's modulus versus filler content for NSE-filled polymer composites produced at rotational speed 120 rev/min: Silitin Z86, Silitin V88

3.2 Hardness

The investigation of the effect of filler content on hardness of the produced injection molds was performed by Shore-D hardness scale measurements. The results are illustrated in Figure 2 as a relationship between Shore-D hardness and different filler contents.

When added to high-density polyethylene, even in a small amount, Silitin Z86 and Silitin V88 cause an increase in hardness of the produced composite. A further increase in the filler's content in the composite also leads to a small increase in hardness. The increase in hardness can be attributed to the lamellar structure of kaolinite which is further reinforced by silica pellets. The produced molds have the highest hardness when the content of both filler types is the highest. This phenomenon was previously observed and described in the literature [7-8]. The highest increase in hardness can be observed for Silitin V88 and it amounts to

7.75%, which corresponds to an increase in hardness by 4.65°Sh D. This can be caused by the presence of hard quartz pellets, the size of which is bigger than that of Silitin V88.

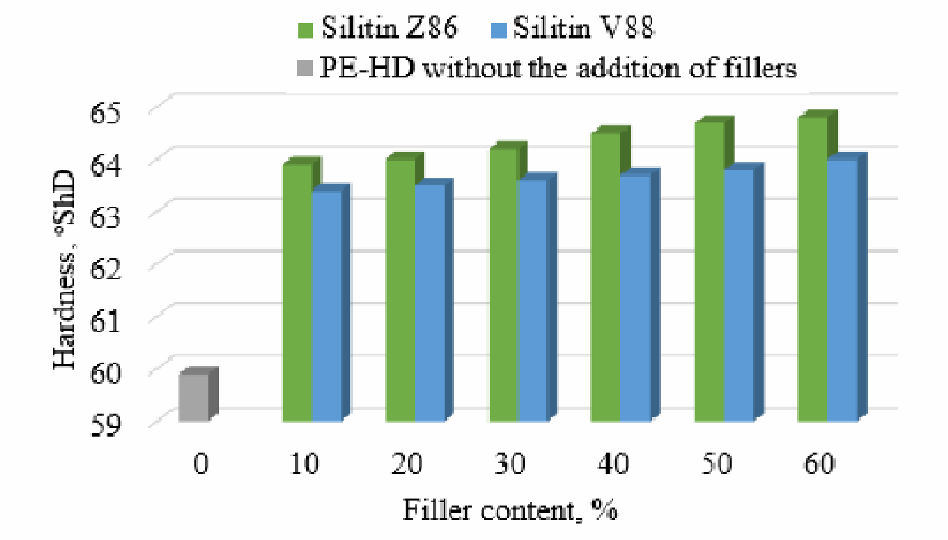

Fig. 2. Hardness of injection molds versus filler content for NSE-filled polymer composites produced at rotational speed 120 rev/min: Silitin Z86, Silitin V88

3.3 Heat distortion temperture and vicat softening temperature

The heat distortion temperature and Vicat softening temperature of the molded parts are shown in Figures 3 and 4. The relationship between HDT and filler type and content is shown in Fig. 3. The heat distortion temperature of the tested injection molded parts increases with increasing the content of both filler types and then starts to decrease. The highest heat distortion temperature of filled molded parts is observed at 10 wt% Silitin Z86. The maximum values of HDT are: 57.6°C for Silitin Z86 and 52.3 for Silitin V88, which corresponds to an increase by 28% and 16.22% in the initial value. The high contents of the mineral fillers lead to a decrease in the heat distortion temperature. The drop in HDT probably results from a wide range of variations in particle size of the fillers added to the polymer. The particle size of Silitin Z86 ranges from 2 μm to 9μm, so it is almost two times smaller than that of Silitin V88, which can have a significant effect on the interface between the HDPE matrix and the filler particle surface. As a result of the contact between particles in different layers, slipping between particles occurs. The forces necessary for forcing the slipping depend on the diameter of particles. The particles then form the irregularities of the layers which are in contact. The slipping of the layers can be greatly facilitated by adding to the liquid fillers with a wide range of particle diameter, i.e. Silitin V88 (Table 2). Smaller particles act as a" lubricant" to facilitate slipping. The studies on epoxy blends filled with silica revealed that the addition of a fine-grained filler to the polymer filled with coarse-grained silica leads to a significant reduction in viscosity despite increasing the filler content [9]. This is confirmed by the results of other studies [10-11].

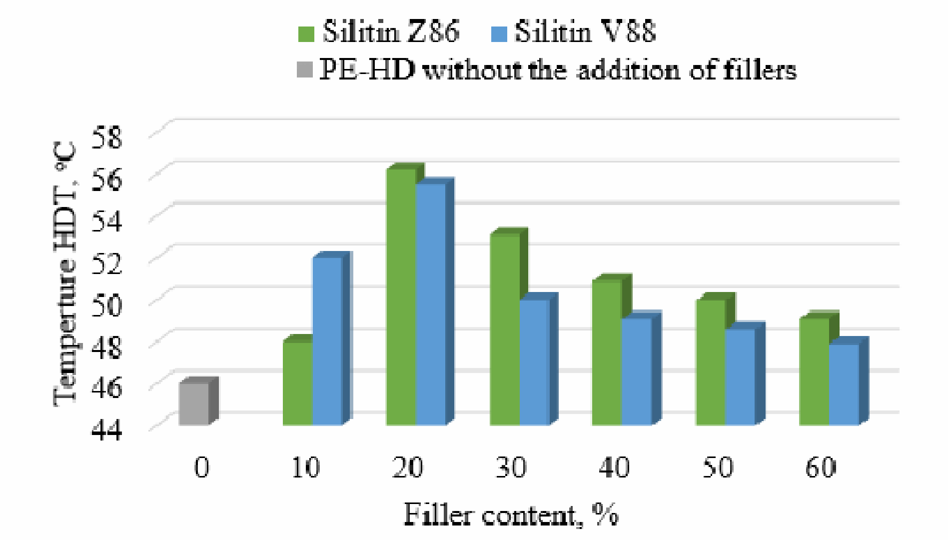

Fig. 3. Heat distortion temperature versus filler content: Silitin Z86, Silitin V88

Figure 4 illustrates the relationship between Vicat softening temperature (VST) and filler content in injection molded parts made of both unfilled and NSE-filled (10-60 wt%) high-density polyethylene. The Vicat softening temperature of HDPE filled with Silitin Z86 and Silitin V88 decreases with increasing the NSE content. Compared to the VST of unfilled polymer, the addition of 60 wt% Silitin Z86 leads to a decrease in the Vicat softening temperature almost by 2.2%, while the addition of the same amount of Silitin V88 causes a decrease in VST by 1.37%. Such a VST curve of polymer blends can probably result from inadequate distribution of filler particles [12]. Fillers can form agglomerates where interactions between filler particles are scarce. Loose clusters of filler particles easily degrade, as long-term exposure to high temperature results in a gradual degradation of the polymer, which leads to its softening.

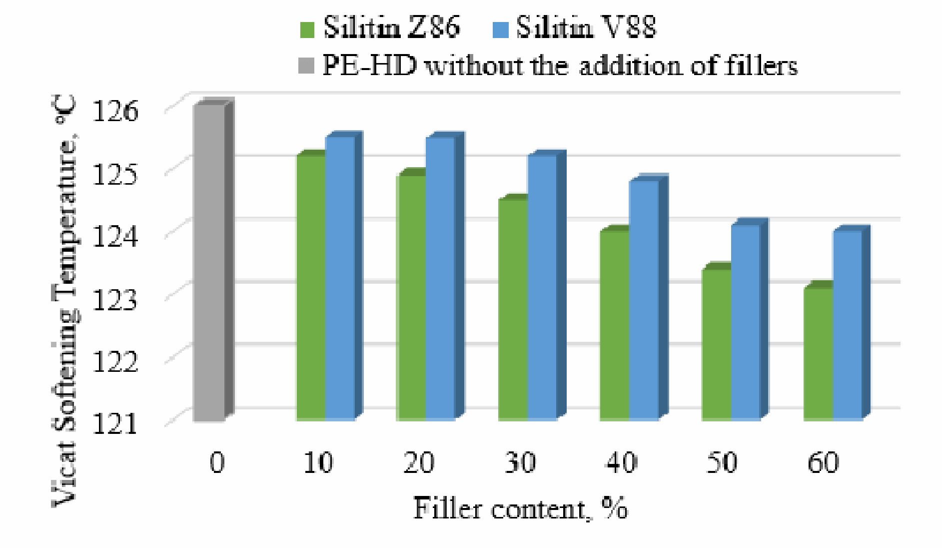

Fig. 4. Vicat softening temperature versus filler content: Silitin Z86, Silitin V88

3.4 Longitudinal and transverse shrinkage

The results of longitudinal and transverse shrinkage of hybrid injection molded pieces with different mineral powder filler contents are illustrated in Figures 5 and 6. The longitudinal shrinkage of the primary high-density polyethylene is 2.54%. The addition of 10 wt% Silitin Z86 leads to an increase in the longitudinal shrinkage of the hybrid molded parts up to 2.58%, which is almost by 1.57%. With a further increase in this filler's content, the processing shrinkage decreases. A similar trend can be observed for Silitin V88; the highest value of longitudinal shrinkage is 2.61% and can be observed for the 10 wt% Silitin V88.

Analyzing the results of transverse shrinkage, it can be observed that the content and type of applied filler also affect the processing shrinkage. The addition of a higher filler content to the polymer has a positive effect as it leads to a reduced injection shrinkage. The reduced transverse shrinkage can result from a lower effectiveness of heterogeneous nucleation, and hence from a lower uniformity of crystallization.

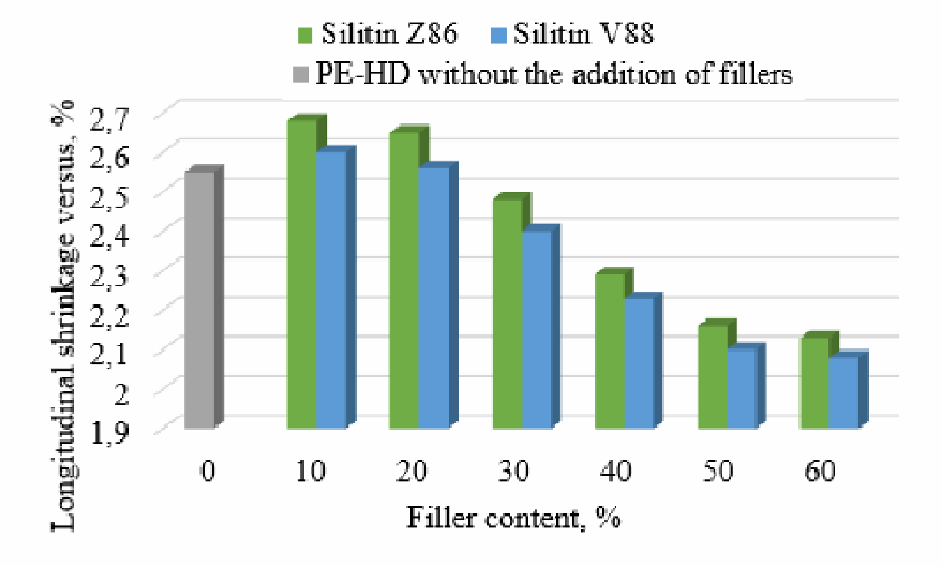

Fig. 5. Longitudinal shrinkage versus filler content: Silitin Z86, Silitin V88

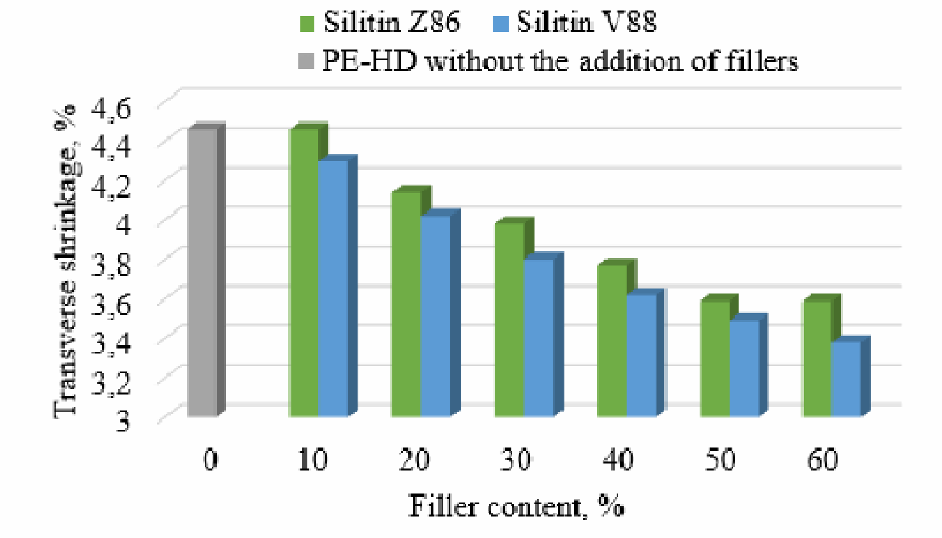

Fig. 6 Transverse shrinkage versus filler content: Silitin Z86, Silitin V88

The application of powder fillers leads to reduced transverse and longitudinal shrinkage, and its stabilization 13-14). The observed increase in longitudinal shrinkage at 10 wt% filler can be explained by a higher degree of crystallinity of the polymer, as fine-grained particles of the filler become nucleates initiating formation of crystallites.

4. CONCLUSIONS

The results of a polyethylene composite filled with untreated Neuburg Siliceous Earth demonstrate that its mechanical properties are not uniform: Young's modulus and tensile strength of the composite first decrease and then increase with increasing the filler's content.

Injection molds with different NSE contents have a higher hardness than the unfilled polymer. The highest hardness was observed for the specimens with 60 wt% of the tested filler types.

The results clearly demonstrate that the addition of different contents of NSE to high-density polyethylene affects heat distortion temperature, which leads to a higher range of operating temperature of products with such additives. Nonetheless, the addition of mineral fillers has a negative effect on Vicat softening temperature leading to reduced thermal resistance of produced modified materials.

The results of longitudinal and transverse shrinkage reveal that higher contents of the applied fillers cause a decrease in the processing shrinkage of the injection molded parts. Increasing the filler content in the polymer to a certain value clearly results in reducing the values of longitudinal and transverse shrinkage, and hence in a higher dimensional accuracy of the molded pieces, which leads to their much higher production quality and operating properties.

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THE EFFECT OF ADDITION OF UNTREATED NEUBURG SILICEOUS EARTH ON THE SELECTED PROPERTIES OF INJECTION MOLDED COMPOSITES

Abstract: *This paper reports the results of research on the mechanical properties of HDPE-matrix composite filled with two types of Neuburg Siliceous Earth (NSE). The HDPE/NSE composites are prepared by twin-screw direct extrusion, with the filler content ranging between 0wt% and 60wt%. Thereby prepared molded pieces are subjected to tests in order to determine their mechanical properties - tensile strength and strain at break. Granulated products are examined regarding their granulometric properties, i.e. the angle of natural slip as well as the standard and bulk density, depending on the content of the tested fillers. In addition, the paper reports the results of melt flow rate.*

Keywords: *polymer composites, granulometric properties, processing properties, mechanical properties, mineral filler*

1. INTRODUCTION

Injection molding is nowadays the most important polymer processing method, mainly because of its short duration, a wide range of operational opportunities it offers, and high precision of produced molded pieces regardless of the material used. This process is employed to manufacture a vast majority of complex-shaped parts which must meet high dimensional accuracy requirements [1]. Currently, about a third of thermoplastics used in the polymer processing industry are subjected to injection molding, and a half of manufactured machines and devices are used for injection molding [1]. Given the emphasis on reducing production costs along with a growing demand for materials with specified new properties, polymers are more and more often subjected to modification [2, 3]. Polymers with varying properties are produced by physical or chemical modification, reactive processing, the addition of fillers or auxiliary agents [2, 4, 5, 6]. For this reason, the composite injection molding process is preceded by extrusion to produce extrudate made of primary polymers and composite granulated products which are then used to manufacture composite molded pieces [7]. The making of polymer compounds is an interdisciplinary problem. When selecting a filler and its content, one must take account of various factors and parameters from the field of chemistry, physical chemistry of polymers,

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mechanical engineering, rheology, materials engineering, and even the design of processing machines [2, 3 ,8]. The selection of a suitable filler and its content enables shaping properties of composite materials as desired. Polymer compounds are usually used in order to improve properties such as impact strength, hardness, grindability, tensile or bending strength, chemical resistance, temperature stability, flammability, thermal and electrical conductivity, etc. [2, 3, 4, 9]. Besides the filler's type and content, the properties of produced composites are also significantly affected by the degree of polymer dispersion together with the polymer's structure, characteristics of adhesion phenomena, the applied processing technology, etc. [4, 10, 11].

The study aims to examine the processing and granulometric properties of polymer blends with a HDPE matrix filled with two types of untreated Neuburg Siliceous Earth (NSE), as well as to analyze the results of tensile test, such as tensile strength and strain at break.

2. TEST STANDS

The study was conducted in the laboratory of the Institute of Production Technology (Institut für Produktionstechnik) of the West Saxon University of Applied Sciences in Zwickau (Westsächsische Hochschule Zwickau). First of all, the composites of polyethylene containing 30 wt% of NSE were prepared using co-rotating twin-screw extruder from Coperion Werner and Pfleiderer GmbH. In a further step, the composites have been pelletized (cold cut) with strand pelletizer type SP 30 Pure from Pell-Tech GmbH. Ready-made pellets were injection molded with a Krauss Maffei KM 50-55CX injection molding machine. The injection molded test pieces were stretched with the use of Roell Z010 AllroundLine strength testing machine. The measurements of melt flow rate were conducted using the 4105.100 plastome-ter from Zwick/Roell (Ulm, Germany). The measurements of standard density were performed using a density bottle. The measurements of bulk density and natural slip angle of the granulated product were made using a funnel with valve that was mounted on a measuring frame at the desired height.

3. MATERIALS

In this study, 3 different groups of pellets were used. The first one was made of bare polymer, and the others were composites of polymer and two types of NSE. The polymer used is high-density polyethylene (HDPE) under the trade name Hostalen GD 7255, manufactured by Basell Orlen Polyolefins. Selected information about Hostalen GD 7255 was summarized in table 1.

Fillers used in this study are two different types of the Neuburg Siliceous Earth, manufactured by Hoffman Mineral. NSE, extracted near Neuburg (Germany), is a natural combination of corpuscular, crypto-crystaline and amorphous silica and lamellar kaolinite, a loose mixture inseparable by physical methods. As a result of natural formation, the silica portion exhibits a round grain shape and consists of aggregated, crypto-crystalline primary particles of about 200 nm diameter covered by amorphous silica opal-like [12].

The detailed information about the composition and properties of all types of NSE are presented in table 2 and table 3.

Table 1. Selected properties of HDPE Hostalen GD 7255

Property	Unit	Value
Normal density	kg/m^3	955
Melt flow index (190 °C / 2.16 kg)	g/10min	4
Melt flow index (190 °C / 5.00 kg)	g/10min	11
Shore hardness	°ShD	60
Ball indentation hardness (H 132/30)	MPa	52
Vicat softening point (B50, 50°/h, 50N)	°C	70

Table 2. Properties of NSE [13]

Property	Unit	Sillitin Z86	Sillitin V88
Density	kg/m^3	2600	2600
Electrical conductivity	µS/cm	80	80
Melting point	^{o}C	1600	1600
pH Value	-	6-8	6-8
Particle size	µm	2-9	4-18
Specific surface area	m^2/g	11	8
Oil absorption	g /100g	55	47
Refractive index	-	1,55	1,55

Table 3. Composition of NSE [13]

Mineral composition [%]	Sillitin Z86	Sillitin V88
Cryptocrystalline silica	60	70
Amorphous silica	10	8
Kaolinite	25	17
Other minerals	5	5

4. RESEARCH METHODOLOGY

The examined composites were prepared in co-rotation twin-screw extrusion process. Extruder tank was filled with HDPE pellets mixed with a proper NSE type in a suitable amount, that varied within the range of 10 to 60 wt%. Temperatures in the individual heating sections of the extruder and the extrusion head were constant (130, 140, 150, 160, 170, 180 and 180 °C). The rotational speed of the screws was 120 rpm. Extruded strands were pelletized after being cooled in water. Composite pellets were injection molded to produce samples for a static tensile test. The parameters of the injection molding process were set as follows: temperature along plasticizing system 180, 200 and 220 °C, temperature of the injection mold 19 °C, injection pressure 1050 bar, cooling time 20 s, injection cycle time 35 s. The obtained composite specimens were put under tensile test, MFR measurement, and granulometric tests.

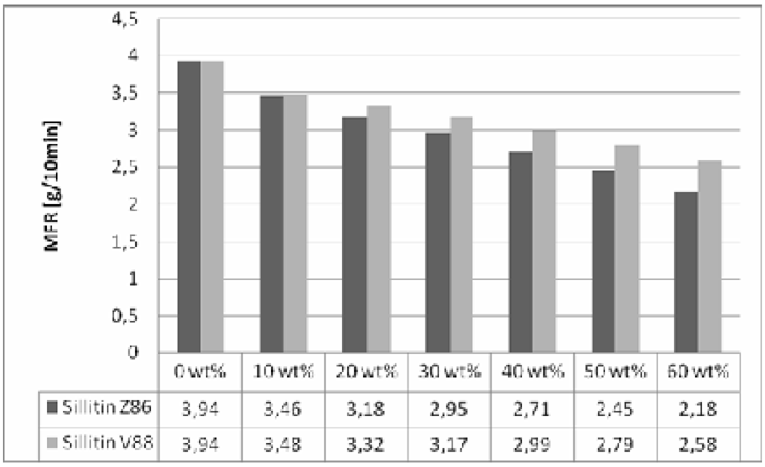
We received six resulting parameters, which were melt flow rate (MFR, g/10min), standard density (ρ_n, kg/m^3), bulk density (ρ_r, kg/m^3), angle of natural slip (α, deg), tensile strength (σ_z, MPa) and strain at break (ε_r, %).

The measurement of melt flow rate defining the processing properties of thermoplastics was made in compliance with the ISO 1133-1:2011 standard. The measurements of standard density were performed according to the procedure de-scribed in the ISO 3923-1:2010 standard, and bulk density in ISO 60:1998. The angle of normal slip was measured in compliance with the procedure defined in ISO 6186:2001. Static tensile test was corresponding with ISO 527-1.

5. RESULTS

The results of the tests were plotted on graphs (Fig. 1 – 6) showing the relationship between the selected processing, granulometric and mechanical properties versus the filler type and filler content, which varies over the range of 10 to 60 wt%. The composites were also compared with bare polymer.

The results of the mass flow rate (MFR) of bare polyethylene and composites with two types of untreated Neuburg Siliceous Earth are presented in figure 1. The addition of Silitin Z86 and Silitin V88 for high-density polyethylene leads to a decrease in melt flow rate in the entire tested range of filler content. Interestingly, the addition of 10 wt% of both filler types yields similar results ranging between 3.46 and 3.48g/10min. The highest difference in melt flow rate in the entire tested range of filler content was observed for the Silitin Z86 specimens where MFR decreases from 3.94g/10min (HDPE) to 2.18g/10min at the highest filler content, that is by 44.67%. When adding Silitin V88 to HDPE, the MFR decreased to 2.58g/10min for the same tested range of the filler content, which amounts to a decrease by 34.52%.



	0 wt%	10 wt%	20 wt%	30 wt%	40 wt%	50 wt%	60 wt%
■ Sillitin Z86	3,94	3,46	3,18	2,95	2,71	2,45	2,18
■ Sillitin V88	3,94	3,48	3,32	3,17	2,99	2,79	2,58

Fig. 1. The relationship between MFR and filler content and type

A potential cause of the MFR drop for high-density polyethylene can be an increase in the blend's viscosity under the tested conditions. Interactions between the polymer and the surface of filler particles as well as the phenomena occurring on both surfaces have a significant effect on the rheological behavior of the disperse system, including its viscosity [14, 15]. It is observed that the viscous flow resistances increase following the addition of the fillers. This can be explained by the occurrence of adhesive forces which make the liquid molecules cling to the surface of the solid, which leads to an increase in viscous energy dissipation in the liquid [16, 17].

The diagram illustrating the relationship between standard density and filler type and content shown in Fig. 2 reveals that the standard density tends to increase with an increase in Silitin Z86 and Silitin V88 contents. It should be emphasized that the standard density of the tested high-density polyethylene is 987 kg/m^3, while the density of the tested fillers is 2600 kg/m3. The increase in standard density in the entire tested range of Silitin Z86 content is 1323kg/m3, which is 34% of the initial value. The standard density of the granulated product containing Silitin V88 increases to 1282 kg/m^3 for 60 wt% filler, which is 29.8% of the initial value.

The relationship between bulk density and filler type and content is shown in Fig. 3. The bulk density increases regardless of the applied type of untreated Neuburg Siliceous Earth. The highest bulk density of the granulated product, 26.36%, is observed at 60 wt% Silitin Z86 and Silitin V88, and it corresponds to an increase by 140kg/m3.

The results confirm that the standard and bulk densities of the tested granulated products increase with increasing the filler content in the polymer. This regularity is correct and well known as both the bulk and standard density of the applied fillers is much higher than the density of the polymer; therefore, the higher the filler content in the polymer is, the higher the density of the granulated product.

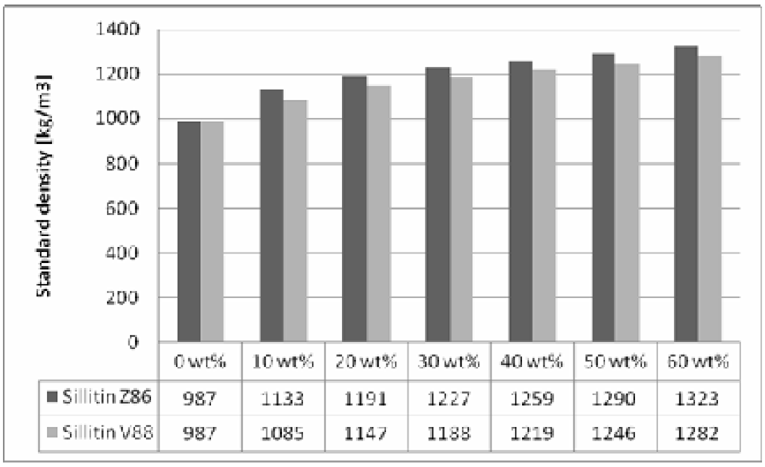


Fig. 2. The relationship between standard density and filler content and type

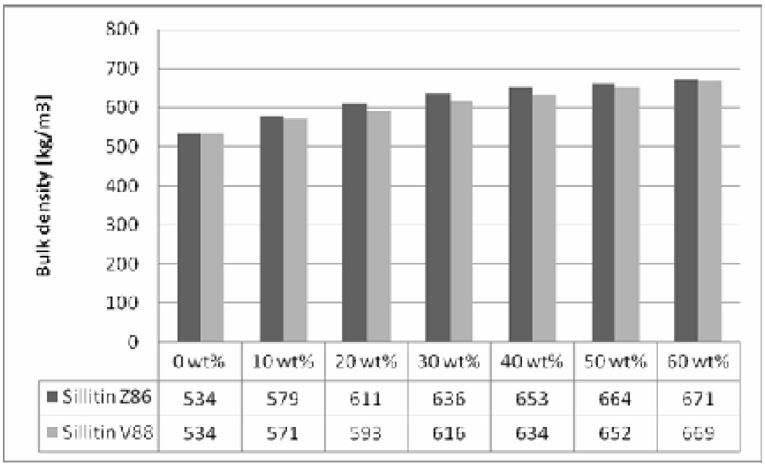
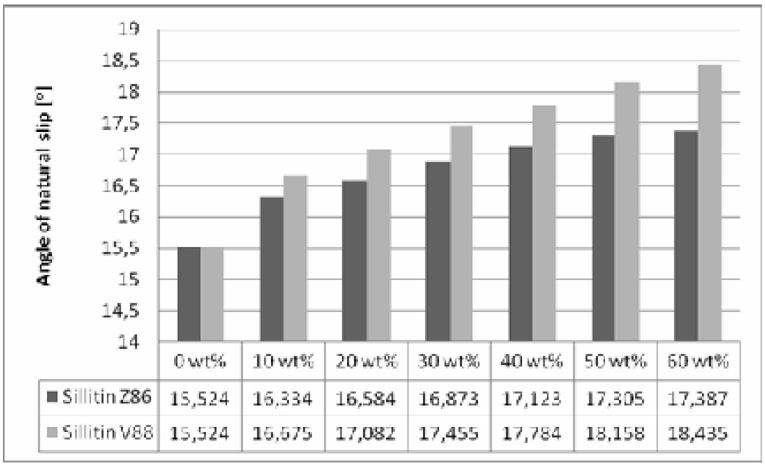


Fig. 3. The relationship between bulk density and filler content and type

The results of natural slip angle are shown in Fig. 4. Following the addition of the powder fillers to HDPE (regardless of their content), the angle of natural slip increases. The highest increase in this parameter is observed for Silitin V88. The addition of 60 wt% Silitin V88 causes an increase in the normal slip angle by almost 18.8%, whereas the addi-tion of the same content of Silitin

Z86 leads to an increase in the normal slip angle by 12% compared to the initial value.



	0 wt%	10 wt%	20 wt%	30 wt%	40 wt%	50 wt%	60 wt%
■ Sillitin Z86	15,524	16,334	16,584	16,873	17,123	17,305	17,387
■ Sillitin V88	15,524	16,675	17,082	17,455	17,784	18,158	18,435

Fig. 4. The relationship between angle of natural slip and filler content and type

It can be suspected that this results from an increase in frictional resistance on the outside of the granulated product. The value of natural slip angle is also affected by the particle mobility depending on the cohesion forces between individual particles, as well as the above-mentioned frictional resistance generated due to particle displacement [18].

Polyethylene composites with Neuburg siliceous earth Silitin Z86 and Silitin V88 ex-hibit a lower tensile strength compared to that of unfilled polymer (Fig. 5) in the entire range of variability in filler content. Irrespective of the NSE kind, the addition of even a small content of the filler (10%) leads to a decrease in tensile strength, ranging from 6.2% for Silitin Z86 to 10.0% for Silitin V88 compared to the initial value. One can observe that a further increase in the filler's content in the composite leads to an increase in tensile strength. A higher increase in the tensile strength of produced injection molds is observed for Silitin Z86.

The consolidation mechanisms of composites with powder fillers are strictly connected with such properties as particle size, specific surface and the degree of particle dispersion in the matrix, as well as the properties of adhesion promoters which cause the coupling of filler particles and matrix material due to chemical bonds [4]. The observed drop in the tensile strength of both filler types can result from a wide range of particle sizes (Table 2). The mechanism of consolidating polymers with particles is connected with cavitation and the tension of spaces formed in a direction of the acting force [19, 20]. A detailed description of this mechanism is given in [21]. It is taken that the promoter effect occurs for particle size lower than 5 µm, otherwise the formed pockets will be too large, and can hence be the place promoting crack initiation [13]. Composite strength can be reduced even due to a small amount of oversized particles [3, 4], what is easily noticeable after introduction of 10 wt% of the filler to the polymer matrix. Further increasing of the filler content cause slight increase of the tensile streangth but it remains significantly lower that the tensile strength of the bare polymer.

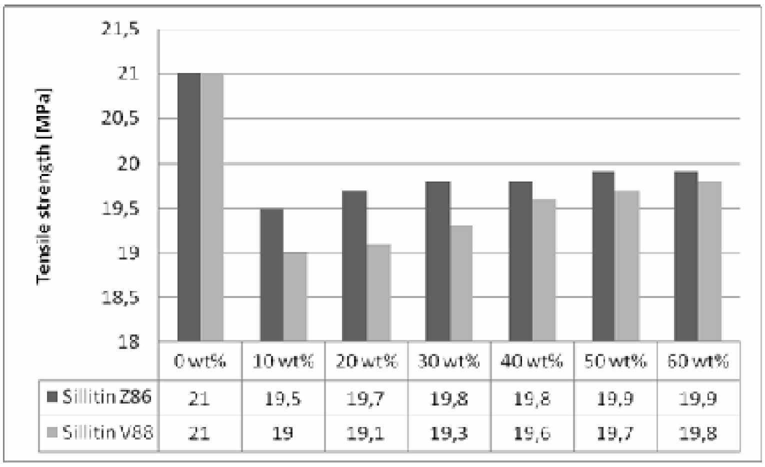


Fig. 5. The relationship between tensile strength and filler content and type

The examined injection molds have a smaller strain at break compared to that of the unfilled polymer (Figure 5). Polyethylene composites filled with NSE, Silitin Z86 and Silitin V88, reveal a very high decrease in strain at break, by 574MPa and 564MPa, respectively, which is 97.6% and 95.6% of the strain at break for the unfilled polymer.

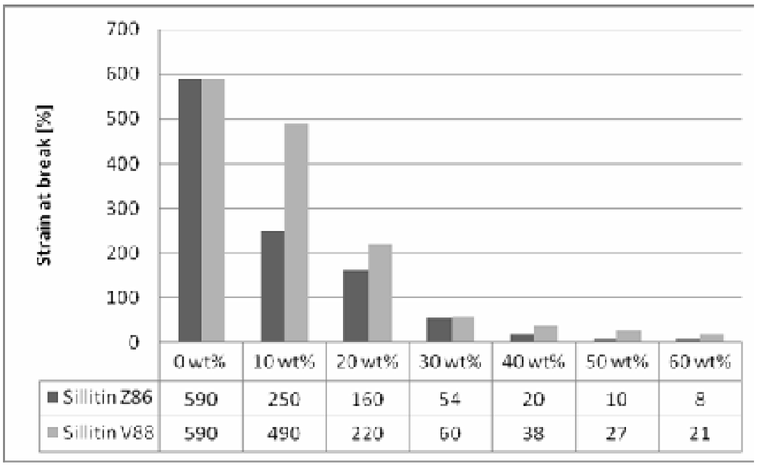


Fig. 6. The relationship between strain at break and filler content and type

The addition of high contents of the mineral fillers leads to reduced composite elasticity described by tensile strain at break. High contents of the fillers lead to a rapid drop in the maximum strains, which can result from the accumulation of large amounts of imprecisely mixed mineral particles on the section of the specimen and low interaction between the filler particles and the polymer matrix, as well as the nature of polymer reinforcement with dispersed particles [19, 21]. This effect can be also caused by bad adsorption on the surface of the filler and low filler pellets wettability by the melted polymer. The wettability of fillers and their dispergation in the polymer matrix depend, among others, on the polymer's surface energy and its polar and dispersive components, as well as on dipole moment and polarizability. The value of surface energy can be changed by the addition of surface-active substances. Introduced in the polymer composite, these substances adsorb on the interface and decrease the surface tension of the fillers, playing the role of structural plasticizers [22].

6. CONCLUSION

The reinforcing effect of a filler on a polymer matrix is conditioned by many factors, yet among the most significant ones are the size and shape of grains and the type of adhesive forces. These factors determine the force acting between the matrix material and the dispersed phase.

The results of melt flow rate of high-density polyethylene filled with two types of untreated NSE demonstrate that the processing properties of the tested polymer blends decrease; the MFR drops already at a low filler content in the polymer. This drop notwithstanding, the MFR is enough high to process the tested polymer blends by standard polymer processing methods.

The results clearly demonstrate that the addition of different contents of NSE to high-density polyethylene affects heat distortion temperature, which leads to a higher range of operating temperature of products with such additives. Nonetheless, the addition of mineral fillers has a negative effect on Vicat softening temperature leading to reduced thermal resistance of produced modified materials.

As for granulometric properties, it has been observed that the angle of natural slip as well as the standard and bulk density increase depending on the content of the tested fillers. It can therefore be claimed that the granulated product will lead to more effective filling of the plasticizing unit of processing machines, which can results in higher efficiency compared to the processing of an unfilled granulated product.

The results of a polyethylene composite filled with untreated Neuburg Siliceous Earth demonstrate that its mechanical properties are not uniform: Young's modulus and tensile strength of the composite first decrease and then increase with increasing the filler's content. The examined injection molds have a smaller strain at break compared to that of the unfilled polymer.

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THE EFFECT OF GAS TYPE ON CHOSEN PROPERTIES OF MOLDED PIECES AND PROCESS PARAMETERS OF MUCELL® INJECTION MOLDING ON THE BASE OF NUMERICAL SIMULATIONS

Abstract: *In this work the effect of the gas type (nitrogen, carbon dioxide) used in supercritical state on the parameters of MuCell® injection molding process and mechanical properties of molded part on the base of numerical simulation was evaluated. The used in research material was Grilon AG-25 HM polyamide 66 with glass fiber (25 wt%), for which the foaming simulations with 9 vol% of porosity were made. The process parameters were optimized using the Taguchi method by means orthogonal tables. The ranges of input parameters were based on material data-base. Numerical simulations of MuCell® microcellular injection molding process were performed using Autodesk Moldflow Insight 2013. The simulations results of MuCell® injection molding process were used in microstructural analysis, taking into account the complex structure for the composite. Calculations were carried out for the model of sample used in uniaxial tensile test. The mechanical properties prediction of composite structures for two types of gases was performed. For this purpose, the calculations by means Digimat commercial code were conducted. The material data were introduced for each phase of the composite and calculations were made using the Mori-Tanaka analytical model.*

Keywords*: microcellular composites, numerical simulations, optimization, injection moulding, Mori-Tanaka homogenization method*

INTRODUCTION

The foaming injection molding process is a technology that allows to obtain products with a cellular structure. This method consists of injecting a foamed polymer into the mold, which is preceded by dispensing foaming gas to the melt polymer in the plastifying unit or directly into the cavity through a specially head, designed for this process [1].

Pores expand occurs as a result of the presence of a blowing agent in the polymer. These are substances gas or foam-creative, which can be divided into physical and chemical types. The first group is determined by abbreviation - PBA (Physical Blowing Agent) and occur in several forms as: gas dispensed under pressure, microspheres consisting of a foaming agent surrounded by a

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polymer coating and volatile liquids undergoing boiling during processing. An example of this type of blowing agent is: carbon dioxide, nitrogen, hydrocarbons, and water [2]. The second group of materials which causes the pores production, are chemical substances, abbreviated - CBA (Chemical Blowing Agent). These materials due to chemical processes are often added at elevated temperature directly, or as the result of degradation of organic and inorganic compounds. They emit then gases involved in generation of a porous structure. It should be noted that these materials can be characterized by endo- or exothermic degradation type, which may result in uneven distribution of melt temperature and may eve added n disrupt the formation of pores [3-5]. These materials are added mainly in the form of a solid granular or powder polymer, which are then processed in a plasticizing unit and injection molded into the cavity. Representative of these type foaming agents are: sodium bicarbonate, mixtures of organic acids or hydrocarbons and azodicarbonamide [6, 7]. The advantage of using chemical blowing agents is the ability to carry out the foaming process in standard injection molding machines.

The main method of the cellular injection molding process was designed and developed under the trade name MuCell®. During this process the foaming gas (carbon dioxide or nitrogen) is added under a pressure as volatile supercritical fluids (SCF) into the melt polymer [8]. The presence of the blowing agent in a supercritical state makes it easier to inject the melt polymer, due to the low compressibility. Nitrogen reaches the supercritical state at the conditions of temperature of -147°C and a pressure of 3.4 MPa, and the carbon dioxide temperature of 31.1°C and a pressure of 7.22 MPa. The use of carbon dioxide results in a reduction of injected polymer viscosity, which allows the to manufacture parts with complex shapes (Fig. 1.). On the other hand, pore formation is carried out intensely using nitrogen. In the MuCell® injection molding process is not necessary to use the packing phase, due to the pressure of expanding gases in the pores (Fig. 2.). This fact results in generation of a large amount of micropores, as well as a reduction in the cycle time for injection moulding process [9, 10].

The degree of gas dissolution in the melt polymer depends on the condition of blowing agent, temperature and shear rate. In turn, the density of obtained porous structure is dependent on the injection speed. Higher injection speeds results in a more intense, short-lived reduction of pressure in the form, leading to the maintenance of a dense, porous microstructure. With the increase of pore diameter the injection temperature is larger due to the increase of gas expansion in the pores. In turn, increasing injection volume leads to reverse phenomenon - the decrease of pore diameter, due to the fact that the greater amount of material in the cavity reduces the possibilities for enlarging microcell structure. Increasing the mold temperature and injection time, results in enlarging the pores. It should be noted that at too high temperature of the molten polymer, the gas can easily escape, due to the easier diffusion at elevated temperature conditions. In the case of increasing the amount of the introduced cells, it can often be observed a gas diffusion between the cells, which results in decreasing of cell size on the wall. Using of this type of process a homogeneous, porous structure with a variable number of pores (in the range 10^7 - 10^{15} pores/ 1cm^3 of polymer and pore sizes from 0.1 - 10 μm) can be obtained [13, 14, 15].

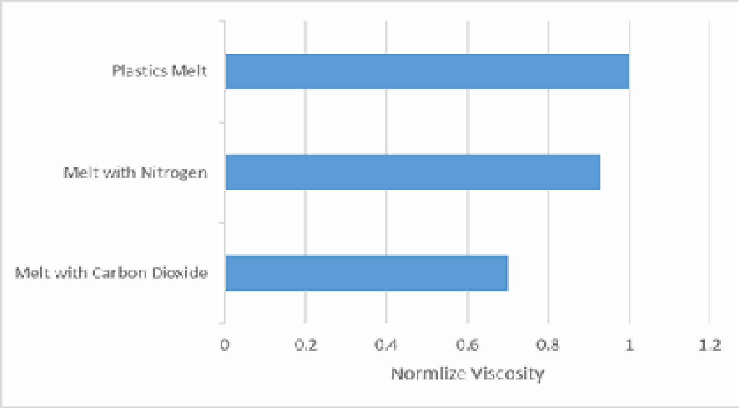


Fig. 1. Influence of gas type on melt viscosity for PA [11]

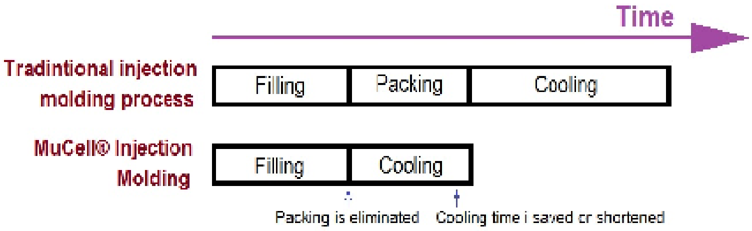


Fig. 2. Comparison between MuCell® injection molding process cycle and traditional injection molding process [12]

The main factor behind the increasingly wider use of this type of technology is a significant reduction in the specific gravity of the molded detail. Qualitative and quantitative state of the resulting structure depends on numerous factors such as, for example: the processing parameters, the type of blowing agent, polymer and filler(in the case of occurrence). Details formed by this technology are characterized by: reduced weight, lack of subsidence and deformation, lower shrinkage and a reduction in wall thickness. Furthermore, the benefits of using this technology is the optimization of the injection process. Noticeable is: the reduction of the viscosity of the plasticized composition, a shorter cycle time, easier distribution of the fibrous fillers and lower value of clamp force. The injection pressure may be in the technology even lower by 60% compared to standard injection molding method. It should also pay attention to the disadvantage of the above process - eg. receiving matt surface detail and higher costs of injection molding machines dedicated to this process [1, 8, 9, 16].

AIM OF STUDY

The growing number of manufactured products with microcellular structure involves the need to perform numerical analyzes of the processing processes, including an injection molding process and simulate the behavior of these devices during the operation. The correctness of the results of numerical simulations largely depends on the accuracy of estimated material properties, which methodology of determining is generally known. In addition to conducting accurate numerical strength analysis of composite materials important issue is the definition of a heterogeneous composite structure, resulting from the different phases of the composite and the specific nature of manufacturing technology.

The aim of this study was to evaluate the effect of foaming gas type (nitrogen, carbon dioxide) used in supercritical state on the parameters of the MuCell® microcellular injection molding process and mechanical properties of molded part by means computer simulation. The algorithm of test procedure is shown in Figure 3. The used material was polyamide 66 with glass fiber (25 wt% - Grilon AG-25 HM with 9 vol% of porosity. Simulations of MuCell® injection molding process and microstructural analysis taking into account the complex structure of the composite was carried out on the base of model sample used in uniaxial tensile test.

NUMERICAL ANALYSIS OF MUCELL® INJECTION MOLDING PROCESS

For many years it has been possible to perform a numerical analysis of MuCell® microcellular injection molding process using specialized commercial codes. During calculations of this process, among others, the phenomenon of solubility, gas diffusion and polymer-gas mixture viscosity are taken into account [17]. The solubility of the gas is usually defined by the equation:

$$k=k_1 e^{\frac{k_2}{T}} \tag{1}$$

where:
k – solubility coefficient,
T - temperature,
k_1, k_2 - constant coefficients.
If $k_2 = 0$, the solubility coefficient k has value equal to constant k_1.

Gas diffusion equation determines the state in which, after injection to a cavity mold, a gas dissolved in plastic diffuses into the plastic material, followed by nucleation and micropores growth:

$$D=d_1 e\left(\frac{d_2}{T}\right) \qquad (2)$$

where:
D - diffusion coefficient,
T - temperature,
d_1, d_2 - constant coefficients.

If $d_2 = 0$, the diffusion coefficient D will have a constant value equal to d_1.

Fig. 3. The diagram of research procedure

The viscosity model for polymer-gas mixture made by microcellular foaming technology is usually defined by the equation:

$$\eta=\eta_r\,(1-\varphi)^{v_1}\,\exp(v_2c+v_3c^2) \qquad (3)$$

where:
η - the viscosity of gas-polymer mixture,
η_r - the polymer viscosity,

φ - volume fraction of gas bubbles,
c - the gas initial concentration,
v_1, v_2, v_3 - constant factors.

Properties of supercritical fluids used in the simulation are summarized in the Table 1.

Table 1. The properties of foaming gas using in simulations

Gas type	Molecular weight of the gas	Surface tension [N/mm]	Viscosity coefficients for gas			Solubility coefficients for gas		Diffusion coefficient for gas	
			v_1	v_2	v_3	k_1	k_2	d_1	d_2
CO_2	44	5e-005	1	-17.135	186.95	1.5361e-009	1.9829e+005	8.741e-008	-2830.5
N_2	28	5e-005	1	-58.381	3520	1.3489e-009	1.7089e+005	3.819e-007	-2830.5

Numerical simulations of the MuCell® injection molding process for polyamide 66 - glass fiber composite comprise steps of: preparing a model and discretization using finite element (FE) in Dual Domain technology, introduction of initial and boundary conditions, carrying out numerical calculations and interpretation of simulation results. The molded piece was designed by means of NX8 (Fig. 4.).

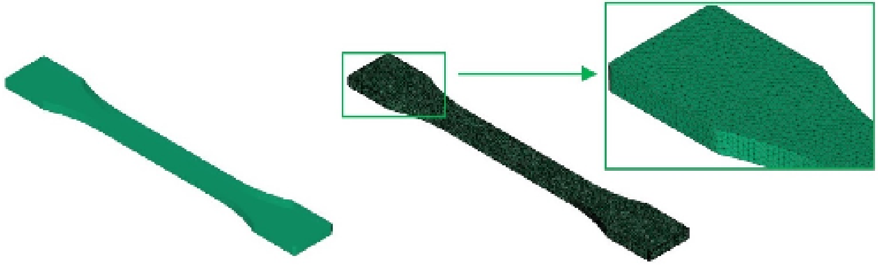


Fig. 4. The molded piece (specimen): a) geometrical model, b) model discretized by approx. 100 000 of thin shell, triangular FE

Numerical simulations of MuCell® microcellular injection molding process were performed using Autodesk Moldflow Insight 2013 (AMI 2013). Simulations were performed for Grilon AG-25 HM polyamide 66 - filled with 25% of glass fibers, (MFR = 117 g/10min). The terms to carry out the analysis for such a complex composite structure is an access to possibly full range of material properties. In order to perform numerical simulations the mathematical model of the polymer viscosity curve was assumed. Among the well-known mathematical models the 7-parameter Cross-WLF model is commonly used, which provides a relatively accurate mathematical description of polymer processing properties. Figure 5 shows the viscosity curves for the Grilon AG-25 HM composite, determined for different temperatures.

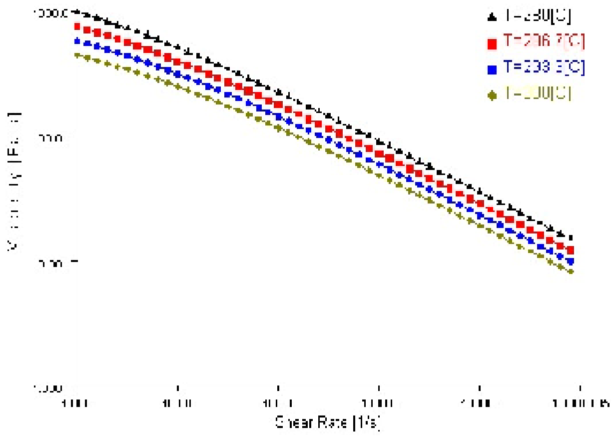


Fig. 5. Viscosity curves for Grilon AG-25 HM

The chosen process parameters allowed to get the ability to manufacture this molded piece by obtaining the maximum potential benefits of this process. The predicted injection parameters are shown in the Table 2.

Table 2. The processing parameters used in the numerical simulation of MuCell® microcellular injection molding process for different types of foaming gas

Parameter	Unit	Value
Mold temperature	^{o}C	90
Melt temperature	^{o}C	290
Injection time	s	1
Cooling time	s	20
Volume filled at start of foaming	%	91
Number of cells per volume	cm^{-3}	$2*10^{5}$
The amount of gas dissolved in the plastic	%	0,7
The initial pore diameter	mm	0,01
Type of gas	-	CO_2, N_2

Two numerical simulations were carried out using the same processing parameters but for two different gases type. A significant differences in results were received (Tab. 3.). This may indicate the importance of proper use of gas and its impact on the process parameters. Lower value of maximum injection pressure and the clamping force can confirm the results correctness. Using of carbon dioxide gas results in reduction of polymer viscosity, which allows to manufacture products with more complicated shapes. In turn, it confirms that the foaming of the polymer takes place more intensively by using nitrogen, what is shown in lowering weight of the part.

Table 3. Results of numerical analysis for two types of gas

Parameters	Unit	N_2	CO_2
Maximum injection pressure	MPa	4.12	3.66
Maximum clamp force	tonne	0.387	0.345
Total weight	g	9.46	9.82

THE OPTIMIZATION OF MUCELL® INJECTION MOLDING PROCESS PARAMETERS

The next step of the research was to optimize the MuCell® numerical analysis for two types of gas using design of experiments procedures (DOE). The process parameters were optimized using the Taguchi method by means orthogonal tables [18]. The ranges of input parameters were based on material data-base of Autodesk Moldflow Insight 2013 commercial code. The control factors were: mold temperature, melt temperature and the injection time. A detailed list of optimization parameter are presented in Tab. 4.

Table 4. Details of optimization parameters

Input parameter - mold temperature (three levels of variation)	70°C, 90°C, 110°C
Input parameter - melt temperature (three levels of variation)	270°C, 290°C, 310°C
Input parameter - injection time (three levels of variation)	0.8s , 1s , 1.2s
The method of experiment planning	Taguchi
Number of experiments for each type of gas	15
Output parameter	Maximum clamp force

As a quality criteria (output parameter) the maximum clamp force was selected. The optimization analysis were made using Design of Experiment procedure (DOE), implemented in the AMI 2013 commercial code. For each type of gas, 15 important computer calculations have been conducted, which allowed to obtain optimal injection parameters. Based on calculations, the impact of the control factors on clamp force was estimated. It was found that the melt temperature has the greatest impact on the quality criterion for each type of gas (Fig. 6.). For nitrogen and carbon dioxide the same processing parameters: the melt temperature - 310°C, mold temperature - 110°C, injection time - 1.2s were received. The range of optimum processing parameters vs. control parameters were illustrated by means of response surface method (RSM) (Fig. 7-8).

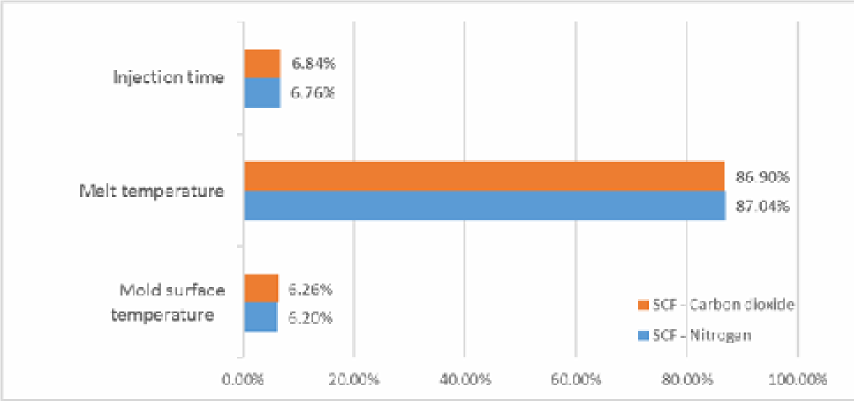


Fig. 6. Percentage impact of control factors on the value of clamp force

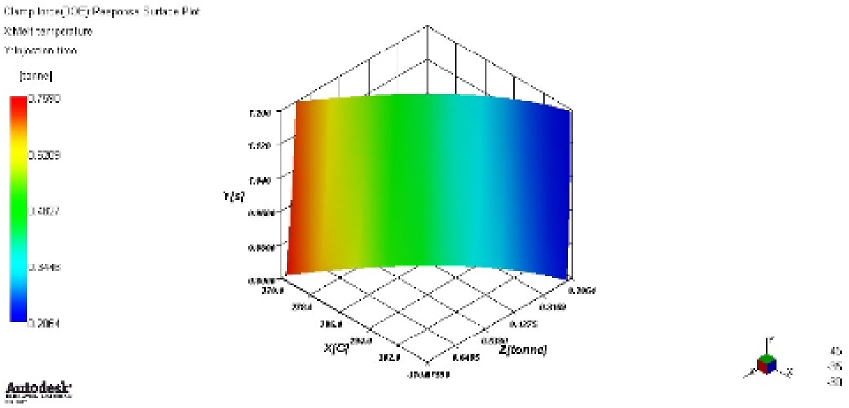


Fig. 7. RSM surface plot for clamp force depending on injection time and melt temperature (SCF - nitrogen)

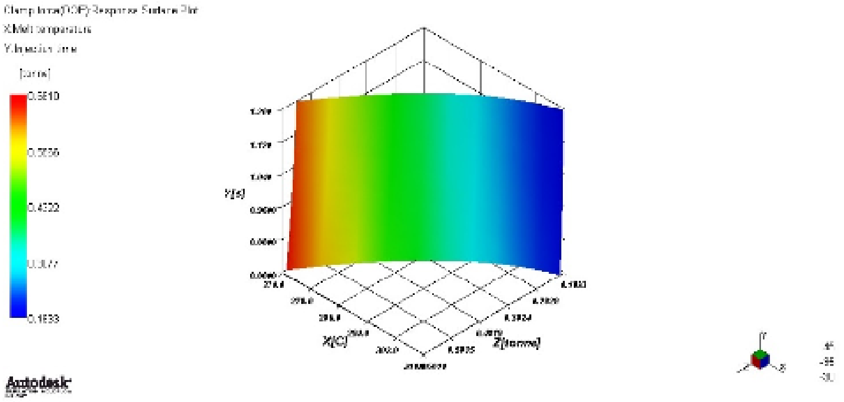


Fig. 8. RSM surface plot for clamp force depending on injection time and melt temperature (SCF - carbon dioxide)

The process parameters obtained after optimization are shown in Table 5. As a result of optimization the lower values of clamp force and maximum injection pressure were obtained. Reported earlier trend of lower clamping force value and maximum injection pressure for carbon dioxide was preserved. Furthermore, the lower weight of molded piece foaming by nitrogen was obtained.

An important issue related to the injection molding of polymer composites with fibers is their orientation [19]. In the calculations of fiber orientation the Tucker - Folgar model was applied. It was used the numerical procedure that allows to calculate the coefficient of the interaction of the fibers and the polymer matrix. Elastic properties of composites reinforced with short fibers were calculated on the base of micromechanical Halpin-Tsai model. To determine the coefficients of thermal expansion: for both longitudinal and transverse direction, the Rosen-Hashine model was selected. Analyzing the results, the difference of fibers orientation can be observed. This phenomenon is probably due to the fibers movement in polymer matrix due to enlargement of

Table 5. The results of the MuCell® numerical analysis using DOE optimization

Parameter	Unit	N_2	CO_2
Maximum injection pressure	MPa	2.18	1.93
Maximum clamp force	tonne	0.206	0.183
Total weight	g	9.35	9.60

the pores which surrounded fibers [20, 21]. As can be seen, a significant difference of fibers orientation is visible in the end region of the molded piece (Fig. 9.). The lower value of the fiber orientation tensor in the case of carbon dioxide in this area may result of lower polymer viscosity.

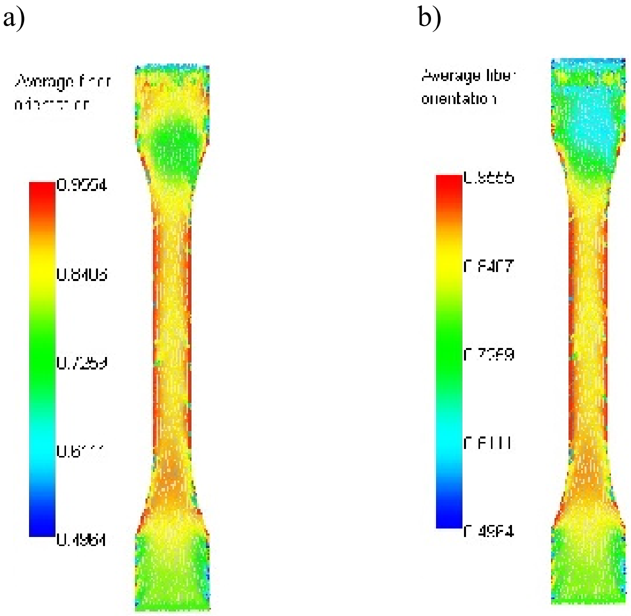


Fig. 9. The fiber orientation tensor a11 for specimen depending on the gas: a) for nitrogen, b) for carbon dioxide

However, when analyzing the area of specimen, i.e. in the neck of the dog-bone, the slight differences in the values of tensor 1-, 2-, and 3-order may be noticed. These measured values were important data needed to microstructural analysis in the next stage of presented work (Tab. 6.).

Table 6. The measured values of the fiber orientation tensor in the area of dog-bone neck

The order of the fiber orientation tensor	N_2	CO_2
a11	0.858	0.855
a22	0.127	0.130
a33	0.0149	0.015

MICROSTRUCTURAL ANALYSIS

Polymer composites are characterized by heterogeneity of structure. Problem in description of heterogeneous structure is not only the design and processing issue, but also the calculation case. One method of solving the above problem is micromechanical modeling, which gives the ability to predict the dependence of material between the micro and macro scale. The micromechanical model of heterogeneous solid is treated as a microstructure consisting of a matrix phase and a fillers which are subjected to loads defined by the boundary conditions. Numerically the problem is analyzed from the micro- (determining heterogeneity of the material) to the macro- (treated uniformly as a whole) scale. The relationship between the two scales are determined by means of a Representative Volume Element (RVE). By definition, it is considered as the smallest volume of the medium containing general information required for a complete description of the structure and properties of the analyzed material. The process of transition "micro-macro" is based on averaging operation:

$$\langle u\rangle(x)=\frac{1}{\|V_{RVE}\|}\int_{V_{RVE}} u(y)m(x-y)dV \qquad (4)$$

where:

$|V_{RVE}|$ – measure the volume of RVE,

(y) - weight function.

A Representative Volume Element is the smallest statistical parameter determining material properties. It is assumed in the macro scale, each point of the material has to be large enough to represent RVE, but also very small in relation to the considered solid [22]. Transfer from the micro to the macro scale runs in consecutively stages: determine a central point RVE for macro-defining RVE as one of the components, determine the constitutive model for each item and homogenization aimed at defining the constitutive model on the macro scale [23]. To find the macro constitutive answer to RVE, the homogenization procedures are used.

In most calculations of polymer composites the Mori-Tanaka model is used. This method is based on the problem of single inclusions in an infinite, continuous homogeneous medium. In this model, the mean values of stress and strain tensors for inclusions and matrix relate to the tensor of stresses and strains in the macro scale by strain concentration tensor:

$$B^{\varepsilon} = H^{\varepsilon}(I, C_0, C_1) \qquad (5)$$

where:

B^{ε} – the composite strain concentration tensor,

H^{ε} - the strain concentration tensor for single inclusion,

I, C_0, C_1 – the stiffness matrix of polymer and inclusions.

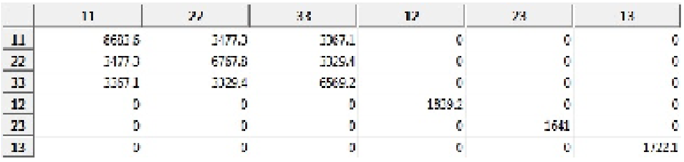
The mathematical relationship between inclusions and matrix gives an average effect of the interaction between phases [24-26].

In the present stage of work the properties prediction of composite structures for two types (carbon dioxide, nitrogen) gases was performed. For this purpose, the calculations by means Digimat MF commercial code were conducted. The material data were introduced for each phase of the composite and calculations were made using the Mori-Tanaka analytical model. The good agreement between the properties on the basis of literature data [27] and with homogenization calculations of the composite structure without porosity was received (Tab. 7.). Compliance of results was motivated to further analysis of microstructural calculations for the composite with a variable amount of pores. An important preliminary step was the introduction of the fiber orientation data (Tab 6.) from MuCell® process simulation. It was found that increasing the amount of gas deteriorates the strength properties of the material, but the type of gas in supercritical state (carbon dioxide, nitrogen), slightly determines the strength properties of molded detail. For each analyzed material was calculated stiffness matrix necessary for the structural calculation of composites (Fig. 10.). The calculated stress-strain characteristics of composites was shown in Figure 11.

Table 7. Summary results of structural analysis

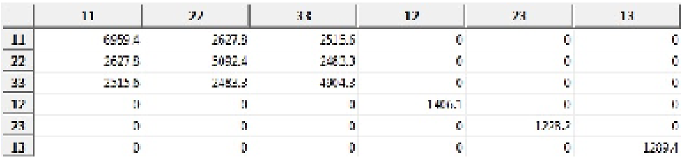
	Young Modulus [MPa]	Density [kg/m^3]
Grilon AG-25 HM [27]	6400	1170
Grilon AG-25 HM (Mori-Tanaka homogenization model)	6340.6	1160
Grilon AG-25 HM + 9% pores (SCF – N_2)	5191	1031
Grilon AG-25 HM + 9% pores (SCF –CO_2)	5136.6	1033

a)



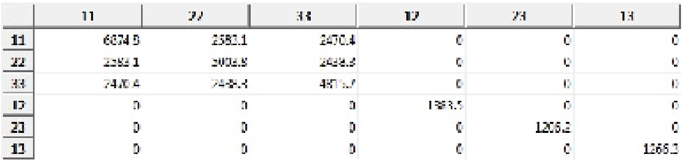
	11	22	33	12	23	13
11	8683.6	3477.3	3367.1	0	0	0
22	3477.3	6767.8	3329.4	0	0	0
33	3367.1	3329.4	6569.2	0	0	0
12	0	0	0	1809.2	0	0
23	0	0	0	0	1641	0
13	0	0	0	0	0	1722.1

b)



	11	22	33	12	23	13
11	6959.4	2627.8	2515.6	0	0	0
22	2627.8	5092.4	2483.3	0	0	0
33	2515.6	2483.3	4904.3	0	0	0
12	0	0	0	1406.7	0	0
23	0	0	0	0	1278.2	0
13	0	0	0	0	0	1289.4

c)



	11	22	33	12	23	13
11	6674.8	2583.1	2470.4	0	0	0
22	2583.1	5005.8	2438.3	0	0	0
33	2470.4	2438.3	4871.7	0	0	0
12	0	0	0	1383.5	0	0
23	0	0	0	0	1206.2	0
13	0	0	0	0	0	1266.3

Fig. 10. The calculated stiffness matrices for: a) Grilon AG-25 HM, b) Grilon AG-25 HM + 9% pores (SCF – N_2), c) Grilon AG-25 HM + 9% pores (SCF – CO_2)

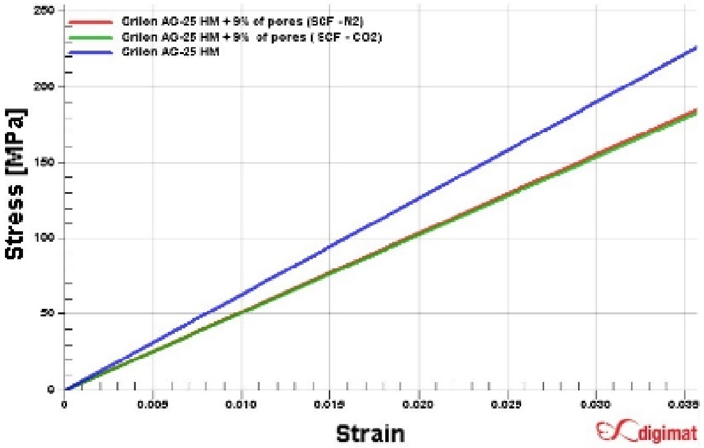


Fig. 11. The stress-strain characteristics for PA66 - GF composite without and with 9 % of pores (for two types of gas)

To calculation and also in order to visualize the fibers and pores in polymer matrix, the actual geometric data for fiber, polymer matrix and pores were used [28, 29]. Due to very small difference in values of fiber orientation tensor (Tab. 6) the generalized visualization of microstructure was developed. The visualization results for composites structure prepared in Digimat FE was shown in Figure 12.

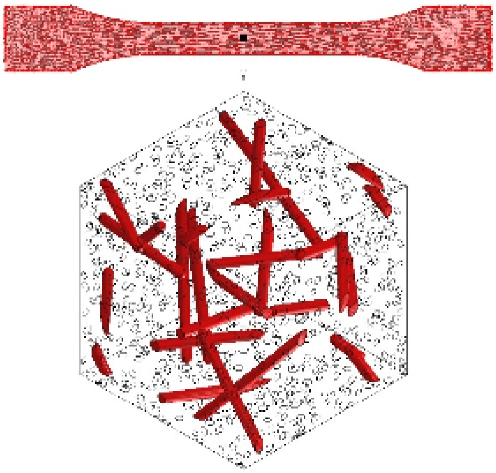


Fig. 12. Visualization of the composite microstructure with 9% of the pores

SUMMARY

In numerical analysis of MuCell® microcellular injection molding process two types of gases - carbon dioxide and nitrogen were used. The significant differences of resulting processing parameters - the lower value of the clamp force and maximum injection pressure for carbon dioxide gas - were received. This phenomenon shows the fact that the use of carbon dioxide decreases the viscosity of flowing material. On the other hand, a lower value of part weight for was received. This fact confirms that the growth of pores for nitrogen occurs intensely.

The optimization of process parameters using the Design of Experiment procedure built in AMI 2013 commercial code was made. This allowed to obtain a more efficient results. It was noted that for both carbon dioxide and nitrogen gases the same optimum processing parameters were chosen. For both types of gases the main factor affecting the clamp force was the melt temperature.

Made in the present study numerical simulations of the MuCell® injection molding process allowed to obtain data on the distribution of the fibers in the polymer matrix, depending on the gas content. A significant difference in fibers orientation were visible at the end region of molded piece (dog-bone). The lower value of the fiber orientation tensor for carbon dioxide in this area may provide a lower viscosity value of polymer flowing through the cavity. However, when analyzing the main area of molded piece, i.e. the neck in dog-bone, slight differences in tensor components of 1-,2-,3-order may notice. Measured values are important parameters needed to perform a microstructural analysis.

The use of homogenization method by means Digimat MF commercial code gives the ability to perform numerical analysis with high accuracy, taking into account the heterogeneity of the composite structure. The use of Mori-Tanaka homogenization model to composites gives good agreement of results. These results have been verified only for composites without pores, but it is assumed that results for porous composites with fiber will well correlate with experiment.

It was found that increasing the amount of gas deteriorates the strength properties of the material. However, using different supercritical fluids slightly determines the mechanical properties of products. This may be due to a slight difference in the value of the fiber orientation in the neck area of analysed dog-bone.

Acknowledgements

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A EXTRUSION PROCESS OF FOAMING PLA INTENDED FOR SUBSOIL FOR MICROORGANISMS

Abstract: *A method of preparing chemically foamed polylactide from a mixture consisting of polylactide and foaming agent was discussed in this paper. The content of foaming agent was varied in the range 1 – 10%. The extrusion of pure and foamed polymer film was carried out using the following temperature along the barrel: 180, 200, 220°C and 158°C. The influence of content of blowing agent on: density, tensile strength and structure of foamed PLA films was study. In the study was checked the viability of the microorganism in the presence of foamed PLA film and pure PLA film.*
Key words*: polylactide, foams, foaming agent, microorganisms.*

1. INTRODUCTION

Polylactide has good chemical and physical properties. It is rigid and fragile, it is often compared to poly(ethylene terephthalate) in terms of tensile strength, elastic modulus, impact resistance and barrier properties.

The disadvantages of polylactide is a high price, the possibility of partial degradation during processing, low resistance to deformation at increased temperatures, the need for drying before processing as well as adverse barrier properties, adverse plasticized state properties as well as low molecular weight [1, 2].

PLA products are used as containers, packaging and horticultural films, disposable products and equipment elements. They have also found applications in medicine, as bioresorbable implants and absorbable sutures, staples, clips, surgical masks, bandages, compresses, medical staff, pharmaceutical products and personal hygiene materials.

Biodegradable polymers (PLA, PCL) were used as drug delivery systems owing to their biocompatibility, biodegradability and lower toxicity. PLA and their copolymers in the form of nanoparticles were used in the encapsulation process of many drugs, such as psychotic, hormones and

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dermatotherapy. Biodegradable polymers were used in orthopedic applications to achieve many goals [3].

In order to improve the physicochemical and applicability properties of PLA are carried out different types of modifications. Frequently, there are prepared composites and nanocomposites or mixtures of PLA with other polymers. There are known connection with the following polymers: PHB, PCL, PMMA, polyvinyl alcohol (PVA) or starch. A disadvantage of this connection is considerable brittleness of the blend, and therefore introduces different kinds of plasticizers like glycerol. In contrast, the addition of montmorillonite (more than 5%) improves the tensile strength and barrier properties. In order to provide permanent bonding of the starch with PLA there are used engagement means, for example: maleic anhydride [4], diisocyanates [5] and acrylic acid [6]. Furthermore, such compatibilizers are used dioctyl maleate (in an amount not more than 5%) [5]. The research of Swierz-Motysia and al. [7] about receiving mixtures of thermoplastic starch and polylactide, allowed obtain material that having improved mechanical tensile properties and flexural toughness, through the use of a compatibilizer, modified polylactide reactive anhydride groups (PLAm).

Another way to modify of polylactide is a foaming process. The foaming process leads to reduction in weight of the product, increase the flexibility, reduce the cost of materials and improving damping properties (heat, noise).

In the initial stage of chemical foaming the mixture of blowing agent and polymer pellet is filled into extruder. Due to supply a heat in plasticizing system foaming agent decompose to give off gases such as nitrogen and carbon dioxide. These gases dispersed in the polymer molten. The cellular structure is foamed as a result of pressure drop through the material leaving the extruder die.

Thermoplastic materials can be foaming using chemical and physical agents (gases). Foaming of polylactide can be carried out in a continuous process (industry) or periodic (laboratory scale) [8 – 14].

Matuana and all studied influence of mass flow rate (MFR), content of foaming agent and screw rotation speed on PLA foams structure. In the study was used three types of PLA differ in value of MFR. The maximum cell fraction was equal to 45% and was obtained for sample with a content of blowing agent equal to 1.5%, a screw rotation speed of 40 rpm / min and using a PLA with melt flow rate equal to 6.5 g / 10 min [15, 16].

The physical blowing agents include water, nitrogen, carbon dioxide, which are added in the form of liquid or gas in a molten plastic polymer. Condition for real effectiveness of this method is the use of an appropriate dosing system - a gas delivery system. The final step of physical foaming process is foaming of polymer [11]. Mihai and all [17] conducted physical and chemical foaming process of PLA using twin screw extruder. Studies indicated that to obtain a foaming amorphous polylactide of low density is introduce 9% CO_2 to the material.

Production and implementation of new materials often requires research on the lack of toxicity or biocompatibility [18]. However, for new materials toxicity data are not available or show a very inconsistent results [19]. Cytotoxicity is defined as abnormalities in the structure and/or function necessary for the survival and reproduction of the cell [20]. The law relating to new substances with potential use for medical or related requires them to test for cytotoxic activity before they will be admitted for further study [21].

Using *in vitro* cultures of prokaryotic organisms it is possibility to determine the mechanism of action, minimum and maximum concentrations of toxic interactions with cells and cytotoxic effects of [22]. For testing should be selected organisms with different morphology and properties in order to reflect the diversity of possible responses *in vivo* and show the natural effects induced in the cells by the tested material [23].

The measure of the cytotoxic activity is the concentration of the test inhibitor to the cell life - EC50, that is the concentration at which the size of the evaluated parameter of activity of the cells is reduced by 50% with respect to control system [24]. Therefore, the tests used to evaluate the cytotoxicity should permit direct or indirect measurement in order to reflect of different cytotoxic activity [25]. The most frequently evaluated aspects include cell morphology, cell viability, integrity of the cell membrane, ROS production, induction of apoptosis/necrosis, the genotoxic, activity of enzymes involved in cell metabolism, changes in the content of protein or genetic material, changes in gene expression [26]. Most *in vitro* tests used for evaluating the viability of the cells based on their rate of proliferation, the activity of key enzymes or metabolic changes in the permeability and/or physiological condition of the cell membrane [27, 28].

2. MATERIALS

The polylactide was used polylactyde Ingeo 2003D NatureWorks LLC company with density equal to 1240 kg/m^3, mass flow rate (210ºC/2,16 kg) 6 g/10min.. Maxithiene BIOL7DA1000TR was used as a foaming agent (processing temperature of at least 210°C).

3. FOAMING

A foaming film of PLA was obtained using laboratory processing line consisting of a single screw extruder Plasti - Corder Brabender PLV 151 (Fig. 1), flat die and polishing rolls. The screw parameters were: working length 25D and compression ratio 3:1. Furthermore, the experimental stand was equipped with a device for measuring temperature of heating zone of the plasticizing system and the head. The temperature profile along the cylinder was: 180, 200, 220 and 158°C. Screw rotation speed was 60 rpm.

In studying of the effect of content of foaming agent was used foams prepared from a mixture of polylactide and a foaming agent. The content of foaming agent was varied between 1 and 10%.

The process for preparing of polylactide foams was divided into two phases. Before the start of the first stage polylactide was pre-dried at. 85°C in the oven type SLW 53 (POL-EKO company).

Fig. 1. A single screw extruder Plasti - Corder Brabender PLV 151

Table 1. Composition of chemically foaming PLA films

Sample	Polylactide, %	Maxithiene BIOL7DA1000TR, %
P1	100	0
P2	99	1
P3	98	2
P4	97	3
P5	96	4
P6	95	5
P7	94	6
P8	93	7
P9	92	8
P10	91	9
P11	90	10

4. TEST METHODS

Samples conditioning

Before starting the test, samples were conditioned at 23°C and 48% humidity for 16 h (according to ISO 291).

Determination of tensile properties

Tensile test of samples (5 measurements for each sample) were studied using testing machine type TIRAtest 27025. The research was performed in the machine direction (MD) according to PN-EN ISO 527-1, -3.

Total apparent density (ρ_a)

Total apparent density (ρ_a) was determined from foamed samples (dimension of samples approximately 100 mm x 100 mm - three samples for each film). Overall dimensions the samples were measured in accordance with PN-EN ISO 845, ISO 1923.

Microscopic analysis

The structure of the foams was determined by scanning electron microscopy (SEM) using a scanning electron microscope Hitachi SU8010 (Japan, 2011) with a magnification of 60 x, and voltage 1.0 kV.

Determination of the viability of the microorganisms in the presence of material PLA-MAXT

For the evaluation of viability of the microorganisms in the presence of material were used two bacterial strains. Strain of *Serratia sp.* was isolated from the environment contaminated soil characterized by a high metabolic rate, the ability to stimulate the growth of plants [29-30] and changes the microbial population in the soil comprising a plastic materials [31-32]. *Escherichia coli* strain was a laboratory strain used for example in biocidal research.

It was determined microorganism viability in the presence of PLA without foaming agent (pure PLA) and PLA with foaming agent (PLA-MAXT-P5- foaming agent content equal 4%).

It was assumed bacterial culture at 15 cm^3 of microbiological minimum liquid medium in the tubes of 50 ml (according to PN EN ISO 846). Liquid medium was inoculated with a bacterial suspension for turbidity of a 0.5 McF. The flasks were placed on three samples of material film PLA or PLA-MAXT of dimension 20 x 20 mm. The films were sterilized under UV light using a GS Gene Linker TM UV Chamber (Bio-Rad) for 90 s. The controls consisted of tubes of bacteria in a culture medium without polymeric materials.

The experiment was carried out for 5 weeks on a shaker at. 24°C and 35°C respectively for the strain of *Serratia sp.*, and *E. coli.* In order to evaluate viability of the microorganisms after the first, second, third and fifth weeks, the turbidity (McF) of the bacterial suspension and the total number of microorganisms in a culture medium by serial dilutions (OLD) were checked. In order to evaluate viability of microorganisms after incubation the bacteria on solid media (TSA containing g/L potato extract 4.0, 20.0 dextrose, agar 15.0 – for *E. coli* and R2A containing g/L: yeast extract 0.5, proteose peptone 0.5, casamino acids 0.5, glucose 0.5, soluble starch 0.5, dipotassium hydrogen phosphate 0.3, magnesium sulphate 0.05, sodium pyruvate 0.3, agar 15.0 - for a *Serratia sp*.), Petri dishes were incubated for 48 h at. 35°C and 24°C for *E. coli* and *Serratia sp.,* respectively. The result was given as colony forming units - CFU in 1cm^3 culture medium (Fig. 5). It was examined the surface of the film removed from the culture media and after washing film several times with sterile water they were analyzed using a scanning electron microscope (Hitachi SU8010, Japan).

5. RESULTS

Influence of the content blowing agent on the apparent density and strength of foams polylactide is illustrate in Fig. 1-2. Fig. 1 indicate that the highest foam density (1.13 g/cm^3) was obtained from the foam received from the composition consisting of 99% PLA and 1% blowing agent. The lowest value of density equal 0.79 g/cm^3 was obtained for a foaming film containing 96% polylactide and 4% of the blowing agent Maxithien. The increase of blowing agent caused a reduction in density to the content of the blowing agent equal to 4%, further increase of the blowing agent resulted in increase in the density foams.

From Fig. 2 indicate that tensile strength of the foam decreased with increasing foaming agent - Maxithiene. The foam of polylactide of high value tensile strength equal to 75.3 MPa was obtained from a composition containing 99% PLA and 1% of foaming agent Maxithen. The lowest value of tensile strength (24.99 MPa) was obtained for the foam prepared from the composition consisting 90% PLA and 10% of the blowing agent.

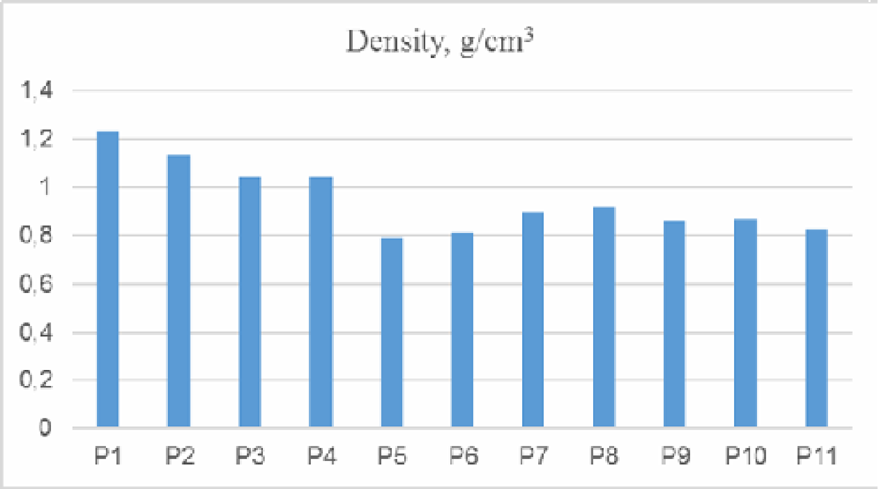


Fig. 2. Influence of the blowing agent on the density of the polylactide film

Figure 3 presents a cross-section photos of the foaming film P3, P5, P8 and P11. P3 film was characterized by a smooth surface. In the inner cross section of the sample are visible a few pores. The increase of blowing agent enhances the number of pores in internal cross-sectional. Sample P5 was characterized by elongated pores with an average size of 79 microns. When the blowing agent content is equal to 10% the cells become smaller and more spherical.

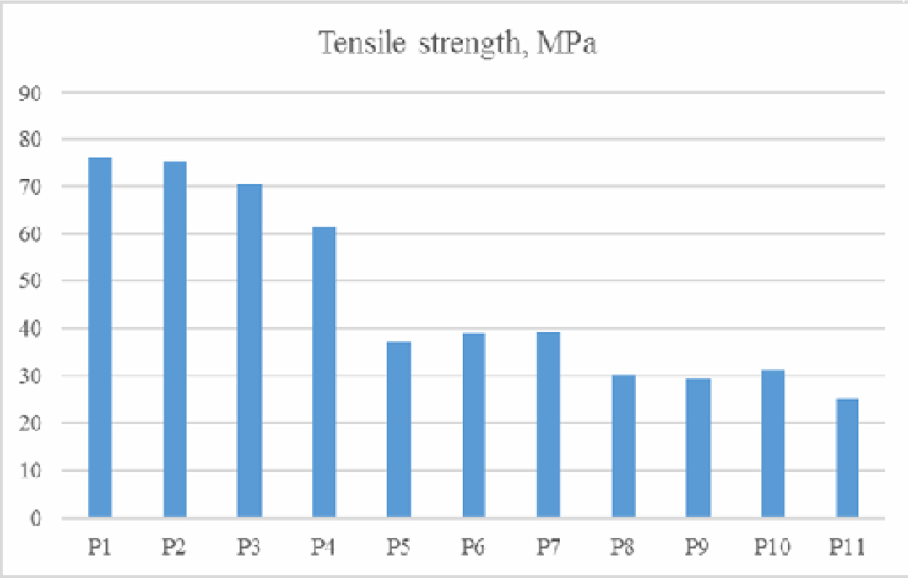


Fig. 3. Influence of the blowing agent on the tensile strength of the polylactide film

Due to the most homogeneous cellular structure and a low density film P5 was used in the tests assessing the ability of bacterial strains to growth. For comparison purposes, in microbiological testing was used a pure film of the polylactide.

Evaluation of the bacterial strains to grow in the presence of polymers *in vitro* showed better growth of microorganisms on the foaming material compared to pure PLA film. On the foaming material was observed several colonies form what are called “the grassed area”, while the pure PLA film was covered by the individual colonies (to 25% of the test surface).

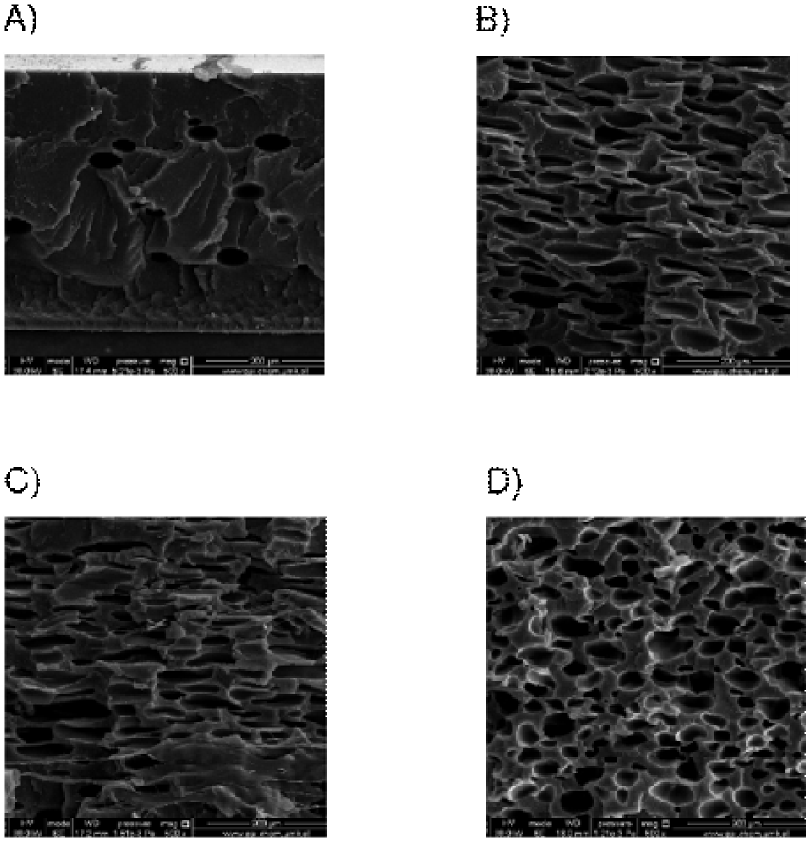
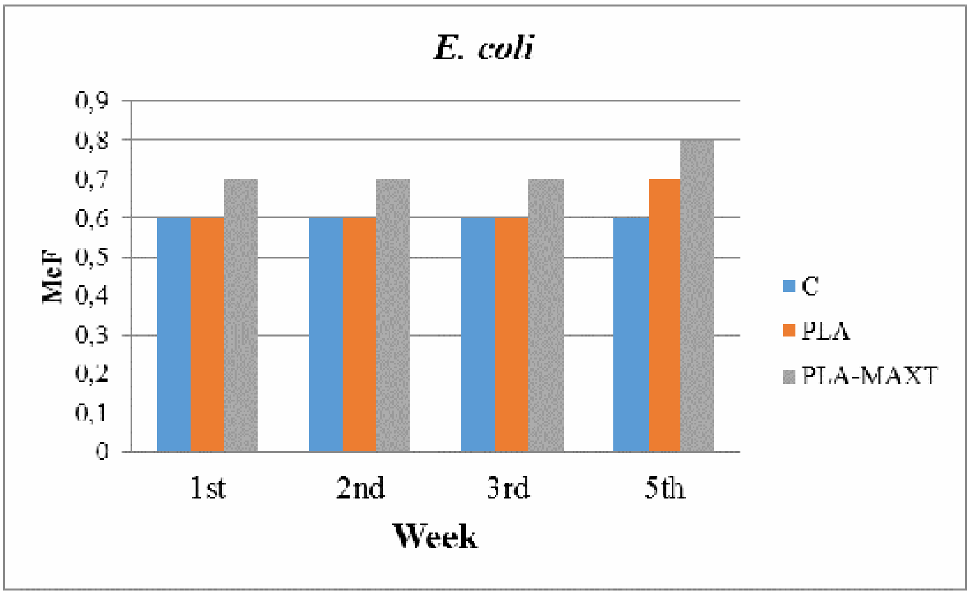


Fig. 4. SEM photos of the cell structure of PLA foams: A) 98% PLA and 2% of foaming agent, B) PLA 96% and 4% of foaming agent C) PLA 93% and 7% of foaming agent, D) 90% PLA and 10% of foaming agent

After the liquid culture the turbidity of the culture medium containing the *E. coli* increased under the influence of foaming PLA film. In the presence of the pure PLA film and foaming PLA film was observed an increase in turbidity of solutions for *Serratia sp.* after 2 weeks of incubation (Fig. 1).



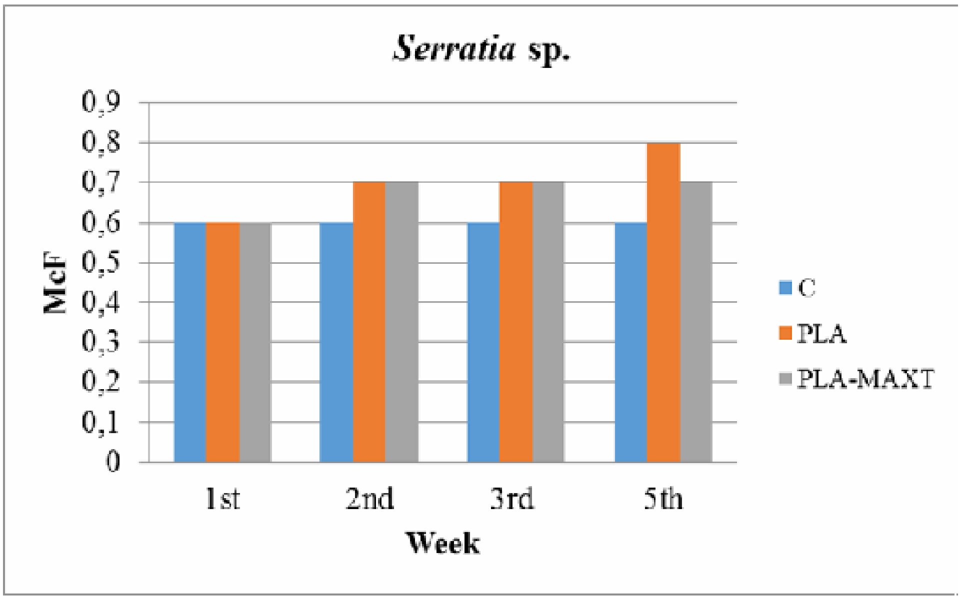
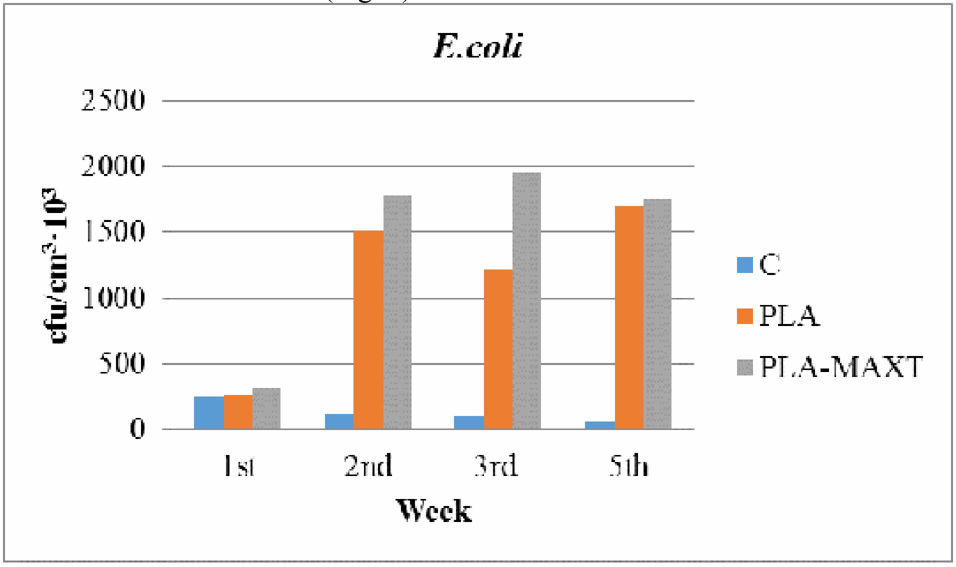


Fig. 5. The turbidity of bacterial cultures solutions of *E. coli* and *Serratia sp.* in media of the PLA and PLA-MAXT

There was a significant (more than 5-fold for *E. coli*, and more than 10-fold for *Serratia sp.*) increase in the number of living cells of both bacterial strains tested in the presence of pure PLA film and foaming PLA film after second week of incubation (Fig. 2).



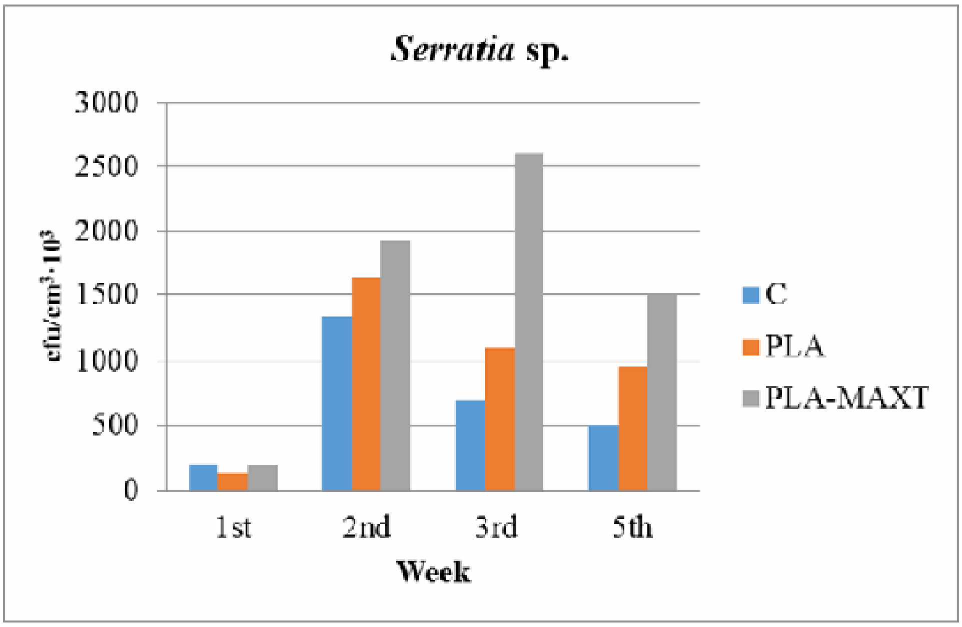
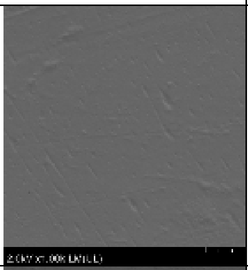
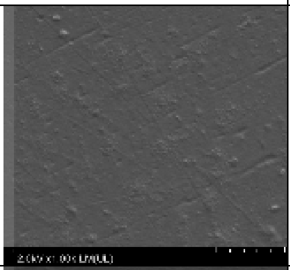
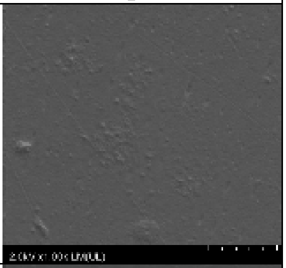
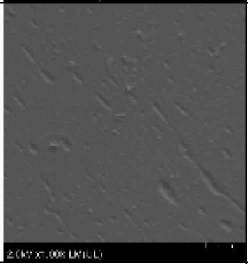
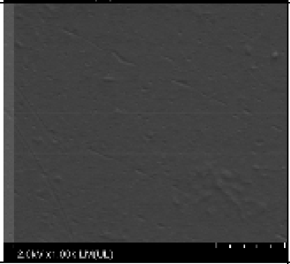
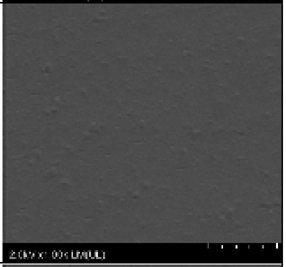
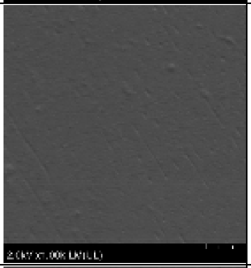
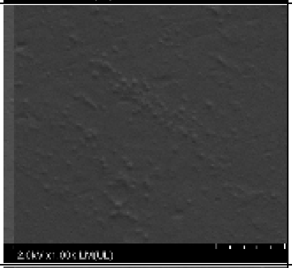
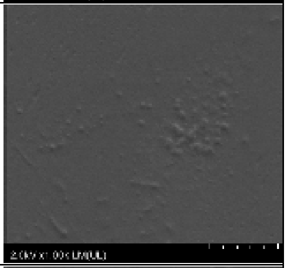
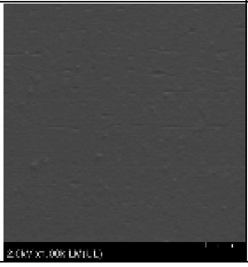
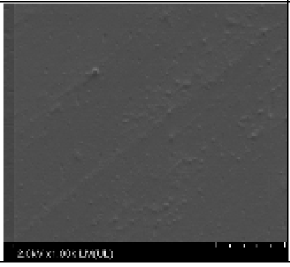
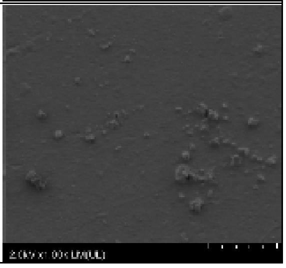


Fig. 6. The number of bacterial colonies of *E. coli* and *Serratia sp.* in a culture media that contains no materials (C) containing pure PLA film and PLA-MAXT film after an incubation period of 1-5 weeks

Using SEM it was indicated the presence of bacterial cells on the test material, especially for PLA MAXT film incubated for 3 weeks (Fig. 3).

A)

Week	PLA	PLA *E. coli*	PLA *Serratia* sp.
1st			
2nd			
3rd			
5th			

B)

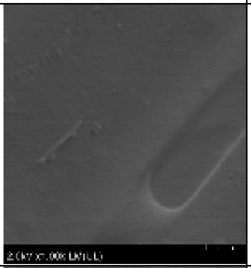
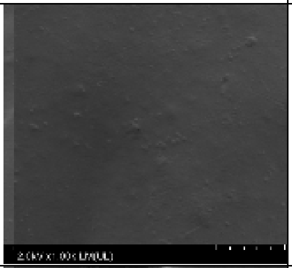
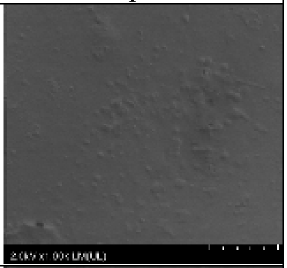
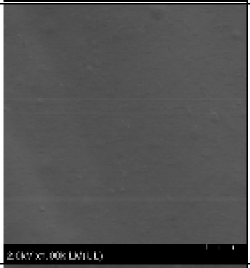
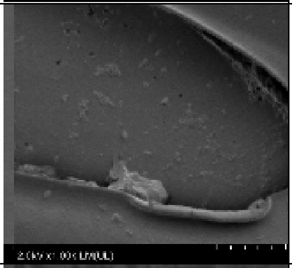
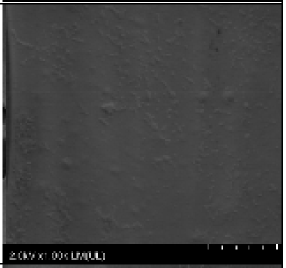
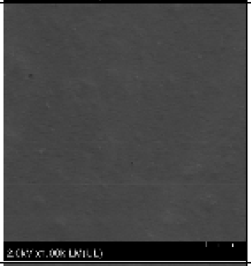
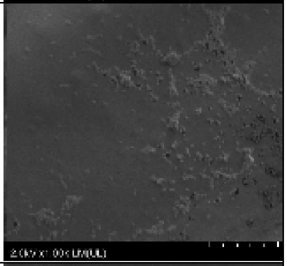
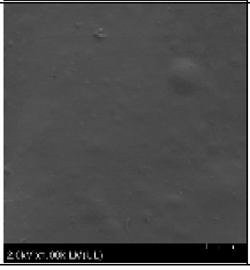
Week	MAXT	MAXT *E. coli*	MAXT *Serratia* sp.
1st			
2nd			
3rd			
5th			

Fig. 7. Microscopic analysis (SEM) of pure PLA films A) and foaming PLA B) incubated in the presence of microbiological media for E. coli and *Serratia sp.* for a period of 1 - 5 weeks

6. CONCLUSION

Polylactide foaming film are produced by continuous (industrial) or batch (laboratory scale). Compared to a batch process, a continuous process is much less expensive and capable of achieving higher efficiency at the same time.

Extruding of foaming polylactide enable possibility to significantly decrease the density of the polymer by about 30%, which gives new possibilities for the use of PLA.

Preliminary studies indicate that the new material PLA-MAXT can be used in microbiology and biotechnology, for example to conduct short-term and long-term bacterial cultures. At this stage of the study need to be continued. It seems that the modified PLA has the potential for the development of new cheaper methods of breeding microorganisms.

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Taras Skorokhoda[1)], **Galyna Lukan**[1)]

THE TECHNOLOGICAL FUNDAMENTALS OF THE OSTEOPLASTIC POROUS NANOCOMPOSITES FORMATION BASED ON PVP COPOLYMERS

Abstract: *The new porous nanocomposites on the basis of hydroxyapatite filled copolymers of methacrylic esters and polyvinylpyrrolidone which containing silver nanoparticles in the structure, were synthesized. Effect of pores forming agent nature, polyvinylpyrrolidone, hydroxyapatite and crosslinking agent amount on the composite properties was observed. Porous structure of material is formed at hydroxyapatite concentration in initial composition at least 25 weight %. Total porosity increases with increase of polyvinylpyrrolidone content. Usage of ethylene glycol dimethacrylate promotes considerable improvement of mechanical properties with slight change of porosity. In the composite structure silver nanoparticles are obtained via silver nitrate reduction by tertiary nitrogen of polyvinylpyrrolidone. The formation of silver by this reaction is confirmed by UV spectroscopy and by the chemical analysis of reaction products. The synthesized silver-containing composites possesses bactericidal properties.*

Keywords: *polyvinylpirrolidone, 2-hydroxyethylmethacrylate, porous composite, mineral filler, hydroxyapatite, cyclopentane.*

1. INTRODUCTION

Modern medicine and biotechnology pays great attention to research that focused on the development of new osteoplastic materials. These materials should provide effective regeneration of bone tissue after various kinds of operations, particularly in orthopedics and maxillofacial surgery. These applications require materials that can be produced on the basis of non-organic matrix of cattle natural bone tissue (hydroxyapatite and tricalciumphosphate) which contains chemical elements in the same form as in vital organism. The important feature of bioceramics is their low chemical reactivity, which means that such materials are almost totally inert and biocompatible [1]. Furthermore with the increasing number of human diseases nowadays, the developed countries show great interest in synthetic materials for bone-tissue engineering [2].

Hydroxyapatite (HA) is the main mineral component of bone, tooth, enamel and dentin that plays an important role in many physiological processes. As potentially the most biologically compatible and active replacement of bone tissue the hydroxyapatite attracted great attention from scientific society [3,4]. Hydroxyapatite may be stable in contact with body fluids and become essentially

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integrated with the bone [5]. However, this material is brittle and its poor mechanical properties, such as compressive strength, elastic modulus and some fracture toughness, cannot be entirely compared to unique mechanical features of cortical and cancellous human bones [2,6]. The possibly most benefitial way to overcome this disadvantage is to design porous polymer-mineral composites [7,8] synthesized from calcium-phosphate materials (which have their composition similar to bone) and biocompatible polymeric matrix, mainly on the basis of 2-hydroxyethylmethacrylate (HEMA) with polyvinylpyrrolidone (PVP) copolymers.

During staying long or even lifelong time in the human or animal body, the composites can be rejected by organisms. This process is very often accompanied by inflammation and requires the constant injections of medicines, e.g. antibiotics, into the body. As the solution of this problem the composites with micro-, nano- or colloid silver particles can be used. Silver is well-known for its antibacterial and antiseptic properties and found wide applications in medicine [9]. Therefore it is necessary to add argentum salts into the initial compositions. The salts interact with PVP polymeric matrix containing tertiary nitrogen and allow obtaining silver nanoparticles directly during composite formation without additional toxic reducing agents [10].

The aim of the present work is to develop new compositions with antiseptic and antibacterial properties based on (co)polymers of HEMA with PVP capable being applied in medicine (in osteogenesis) and to investigate the effect of composition structure on the regulations of composites formation and properties.

2. MATERIALS AND METHODS

Monomers, 2-hydroxyethylmethacrylate (HEMA, Bisomer) and ethylene glycol dimethacrylate (EDMA, Fluka) were vacuum distilled before use. Benzoyl peroxide (BPO, 97 %, SIGMA) was twice recrystallized from ethanol. Polyvinylpyrrolidone (PVP, MW=28 000, AppliChem CmbH), Polyethylene glycol (PEG-1500, Serva), Argentum nitrate (Fluka), Chloroform, Methylene chloride, Cyclopentane, Hexane, Calcium chloride, Ammonium carbonate, Sodium bicarbonate (all – SferaSim) were used as received. Hydroxyapatite (HA) $Ca_{10-x}(P0_4)_6(OH)_2$ with the particles size of 0,05-1,25 mm was synthesized at the Department of Silicates Technology of Lviv Polytechnic National University.

In a typical preparation, porous copolymers were obtained via block copolymerization [11]. PEG-1500 polyethylene glycol was used for the foam stabilization.

The average pores diameter (d_p) and polydispersivity index (PDI) were determined by size measuring of at least 200 pores using MBS-9 microscope. The structure of the composites was studied using transmission electron microscope (TEM) JEOL JEM 200 CX. The total porosity and composites density were determined using a Manehold method described in [12]. According to this method, the polymer sample is weighted in the two immiscible liquids (e.g. heptane and water). Total porosity (W, %) is calculated as:

$$W = \frac{V - V_d}{V} \cdot 100 = \frac{V - \dfrac{P_a - P_{H_2O}}{d_{H_2O}}}{V} \cdot 100; \qquad V = \frac{P_{H_2O} - P_{hept}}{d_{hept} - d_{H_2O}}$$

where: $V_{d,}$ V – volume of dry substance and sample, impregnated with water, in air respectively; $P_{a,}$ P_{H2O} i P_{hept} – weight of sample in air, in water and in heptane respectively; d_{H2O} i d_{hept} – density of water and heptane respectively.

The compression strength of the materials was determined by the standard method using universal testing machine “Kimura” type RT-601U (Japan) with effort to 10 кH. To determine the mechanical properties samples of polymer composites with a diameter of 15 mm and a height of 10 mm were used. Relative compression strength boundary of polymer composites was identified during 10 % deformation and was calculated by the following formula: $\sigma_{10}= P_{10}/S$; P_{10} – load during 10 % deformation, N; S – cross-section sample area, m^2.

UV spectroscopic studies was carried out on the Perkin-Elmer Lambda 20 UV-VIS spectrometer (light source: deuterium and halogen lamp; monochromator: holographic concave grating; detector: photodiodes; spectral bandwidth: 2 nm; software: UV WinLab v. 2.70.01).

Synthesis of silver nanoparticles was performed using the following method: A homogenous solution of 10 g PVP in 40 ml of water and solution of 1g $AgNO_3$ in 10 ml of water was added into a 250-ml round-bottom flask. The mixture was heated up to 70 °C in the dark under vigorous magnetic stirring for 2 h. The resulting reaction mixture was cooled down; the nanoparticles were isolated by centrifugation and then washed three times with deionized Q-water. Ultrapure Q-water filtered on a Milli-Q Gradient A10 system (Millipore, Molsheim, France) was used throughout the work. Bactericidal and fungicidal properties of composite samples investigated in test cultures of the bacteria Escherichia coli HB 101 (E. coli), Staphylococcus aureus (S. aureus) and the fungus Aspergillus niger (A. niger) by the standard method of diffusion of the active substance in the agar to solid nutrient medium. Microbial load was 10^9 CFU ((cells in 1 ml (colony forming unit)) in 1 ml. The bacteria incubation duration was 24 h at a temperature 35 °C, fungus – 72 h at 28 °C. The activity degree was evaluated by the size of the growth retardation zone diameter of test cultures, believing that with a diameter of 11…15 mm microorganism is insensitive to the composite, with 16…25 mm – sensitive and at greater than 25 mm – high sensitivity.

3. RESULTS AND DISCUSSION

One of the main bioplastics requirements is the presence of through porous structure with controlled micro- and macropores sizes necessary for implant composite growth by bone tissue. Therefore, at first we studied the effect of nature of potential pores forming agents on the porous structure formation and composites conditional density. The basic polymer-monomer composition was the composition [HEMA]:[PVP] = 7:3 weight parts (wt.p.) with high reactivity and without demand of high curing temperature [13]. The pores forming agents were compounds of organic and inorganic nature: chloroform, methylene chloride, cyclopentane, hexane, calcium chloride, ammonium and potassium carbonate. The organic agents form pores at evaporation, calcium chloride - after its washing by water from a ready composite, ammonium and potassium carbonates - due to the decomposition and release of carbon dioxide at composite heating. The obtained results are represented in Table 1.

Table 1. Effect of pores forming agent nature on the composites physical properties (T= 348 K, HEMA:PVP:PEG-1500=7:3:2 wt.p., [HA]=70 wt. %, [BPO]=1 wt.%)

Pores forming agent	Amount of pores forming agent, weight %	Porosity, W, %	d_p, mm	PDI	Composite conditional density, kg/m^3
Chloroform	18	42	0.79	2.69	1125
Methylene chloride	10	54	1.28	2.05	714
Cyclopentane	10	67	0.93	1.27	519
Hexane	10	Pores are not formed	–	–	–
Calcium chloride	5	66	0.29	1.71	608
Ammonium carbonate	10	67	0.37	1.76	518
Potassium carbonate	0.5	61	0.53	1.37	639

Porous material is not formed only in the case of hexane. Concerning the inorganic forming agents (calcium chloride and ammonium carbonate), the high-porous composites were obtained with fine pores, the size of which does not exceed 0.4 mm. While using organic ones: chloroform, methylene chloride and cyclopentane the materials with satisfied size of pores (0.8-1.3 mm) are formed.

The value of porosity considerably depends on the components ratio. The proportional dependence of material porosity on PVP amount is observed (Table 2).

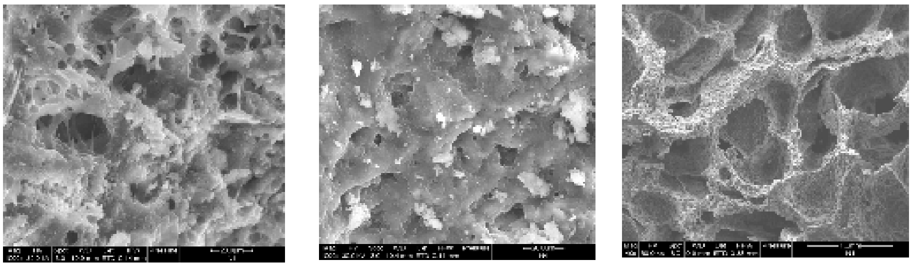
Table 2. Effect of PVP amount and crosslinking agent EDMA on the composite properties ([HA]=70 wt. %, cyclopentane is pores forming agent (10 wt. %), [BPO]=1 wt. %)

Composition of the polymer-monomer mixture, wt.p.			Porosity, W, %	d_p, mm	PDI	Relative compression strength boundary (σ), MPa
HEMA	PVP	EDMA				
10	0	–	37	1.75	1.70	10,0
9	1	–	44	1.26	1.35	9.2
8	2	–	53	1.12	1.89	9.1
7	3	–	67	0.93	1.27	10.3
7	3	1	70	1.81	1.38	15.5
7*	3	–	66	1.58	1.32	10.4
7**	3	–	67	1.50	1.45	10.4

The composition contains: *1 wt. % of $AgN0_3$; ** 1.5 wt. % of $AgNO_3$

Porosity increases from 37 % for polyHEMA to 67-70 % for copolymer HEMA-PVP with PVP content of 30 wt. %. This fact reveals that PVP positively affects not only the kinetics of composite curing but pores forming as well. The addition of crosslinking agent - ethylene glycol dimethacrylate (EDMA) - does not change the general porosity but increases compression strength by 50 %. It means that such mixtures may be effectively used because the material substituting the bone tissue undergoes considerable mechanical load. $AgN0_3$ do not affect the general porosity, though the polydispersivity index increases with the increase of their amount.

Photographs of the composites filled with HA are represented at Fig. 1. They confirm the presence of developed micro- and macroporous structure favoring the effective growth of the composite by bone tissue. Composites, which incorporates contain more PVP, have greater porosity value (Fig. 1a).



a) b) c)

Fig. 1. Photographs of micro- (a,b) and macroporous (c) structure of hydroxyapatite filled HEMA-PVP composites
[HEMA]:[PVP]:[HA], wt.p.: a,c – 6:4:7, b – 9:1:7.

The amount of the filler also affects the composite formation and its properties (Table 3). The porous composite structure is not formed without hydroxyapatite or its content not exceeding 25% even at the optimum amount of pores forming agent. To our mind, foaming takes place before the composition curing. At the same time in the investigated range the decrease of material porosity is observed with the increase of filler amount. The most homogeneous porous material with the least conditional density is formed with HA amount of 70 wt. %.

Table 3. Effect of HA amount on the composite properties (HEMA:PVP:PEG - 1500 = 7:3:2 wt.p., cyclopentane –10 wt. %)

HA amount, weight %	Porosity, W, %	d_p, mm	PDI	Composite conditional density, kg/m^3	Relative compression strength boundary (σ), MPa
0	Pores are not formed	–	–	1235	8,6
50	80	1.20	1.98	611	10.1
70	67	0.93	1.27	519	10.3
100	67	1.41	1.76	553	10.1
150	39	0.46	1.69	1106	9.4

Besides HA amount, the sizes of particles also influence the composite properties (Table 4).

Table 4. Effect of hydroxyapatite particles size on the composite properties (HEMA:PVP:PEG–1500 = 7:3:2 wt.p.; [HA] = 70 wt. %)

Size of HA particles, mm	Porosity, W, %	d_p, mm	PDI	Composite conditional density, kg/m^3
<0.10	57	1.39	1.41	770
0.10-0.20	67	0.87	1.32	678
0.32-0.40	59	1.40	1.85	738
0.63-1.00	57	1.39	1.67	750
1.00-1.18	40	1.56	2.46	941

The increase of particles size by more than 0.1 mm decreases the total porosity of compositions and increases the copolymers conditional density. Using HA with the particles less than 0.1 mm macropores of greater size are formed but the total porosity is lower. To our mind, the reason is the agglomeration of filler fine particles during the composite preparation.

In order to obtain silver nanoparticles and to provide the composites with antibacterial properties the reaction of silver recovery by interaction of its salts with tertiary nitrogen of PVP was investigated. The formation of silver by this reaction is confirmed with the presence of peak (420...430 nm) at UV spectra of products of interaction between $AgNO_3$ and PVP (Fig. 2) and with the results of the chemical analysis of reaction products, which was performed by the method of [14].

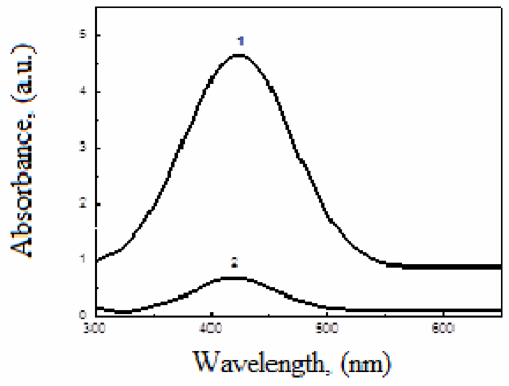
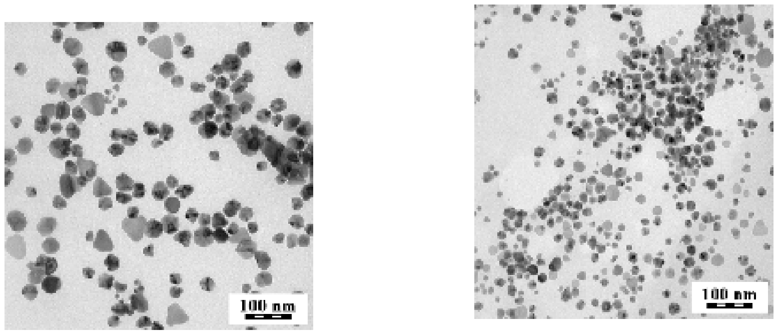


Fig. 2. UV spectra fragment of the solution of products of $AgNO_3$ interaction with PVP. M_{PVP}: $1–3\cdot10^4$; $2– 1\cdot10^4$.

The results of electron microscopy studies have shown that Argentum nitrate forms silver nanoparticles in the shape of different size polyhedrons (Fig. 3).



a) b)

Fig. 3. TEM images of silver nanoparticles after centrifugation. $[AgNO_3]$:[PVP] = 1:10 wt.p., MW PVP = 10^4, T = 348 K, re action time 1 h: Solvent: a – water, b – aqueous ethanol (50%)

The degree of completeness of the reduction reaction, under conditions that are listed in the caption to Figure 3, is 85 % after 1 h. The size of nanoparticles depends on the nature of the reaction medium. In aqueous solution there are formed silver particles with an average diameter of 40...60 nm, whereas in mixtures of water with ethanol – 10...30 nm.

Reaction of Argentum reduction by interaction of its salts with tertiary nitrogen of PVP was used to provide antibacterial properties of composites during the composite formation. Temperature conditions of composites synthesis were justified on the basis of kinetic studies of polymerization [11,13]. The polymerization was initiated by BPO (1 wt. %).

During the synthesis composites with PVP and argentums salts change their color from weak-yellow to brown. It is also the indirect confirmation of silver nanoparticles formation while interaction between argentum nitrate and PVP tertiary nitrogen. This method has irrefutable advantages over other known methods when nanoparticles and hydrogels are prepared separately or when hydrogel is saturated with argentum salts or when silver nanoparticles are obtained via its reduction by amino-containing methacrylic monomer followed by its copolymerization with other monomers [9]. Moreover, there is no necessity in toxic amino-containing reducers.

To confirm the possible practical application of the developed silver-containing composites in biomedical research industry their bactericidal and fungicidal properties were investigated [15]. The research results are presented in Table 5.

Table 5. Fungibactericidal activity of silver-containing composite (HEMA:PVP:HA:$AgNO_3$ = 7:3:7:0,6 wt.p., diameter of the composite samples 15 mm)

Diameter of the growth retardation zone, mm (%)		
E. coli	*S. aureus*	*A. niger*
24,4 (60)	26,0 (73)	20,0 (33)

As a result of comparative analysis of bactericidal and fungicidal properties of the obtained HEMA-PVP composites that contain silver nanoparticles and non-silver-containing composites on microorganisms it was found that the composites, containing silver nanoparticles, block the growth of bacteria, showing bactericidal activity.

The research results were used to develop the fundamental technological scheme of obtaining porous nanocomposites (Fig. 4). Given scheme includes the stages of preparation of raw materials and monomer-polymer composition, polymerization of the composition with simultaneous composite foaming also composite processing, checking and packaging of the product. Technological scheme provides the opportunity of composition ultrasound processing. It makes, on the one side, technological process quite difficult, but on the other makes it possible to significantly improve its productivity.

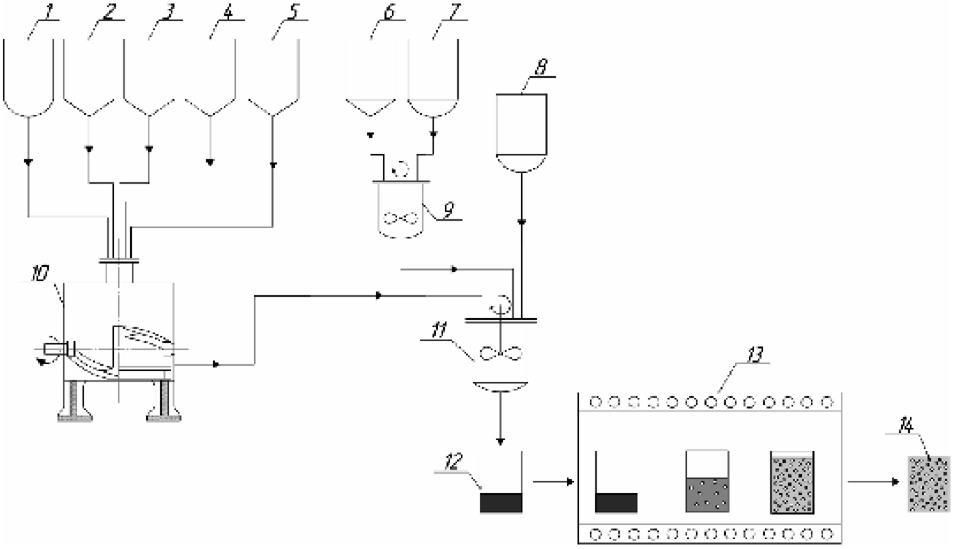


Fig. 4. The fundamental technological scheme of obtaining porous composites: 1, 7, 8 – HEMA, water and cyclopentane volumetric tanks; 2, 3, 4, 5, 6 – PB, PVP, PEG, mineral filler and $AgNO_3$ gravimetric tanks; 9, 10, 11 – mixers;12 – form; 13 – thermal furnace; 14 – product.

4. CONCLUSIONS

Thus, new porous nanocomposites on the basis of hydroxyapatite filled copolymers of methacrylic esters and polyvinylpyrrolidone were synthesized. The possibility of silver nanoparticles obtained during formation of the composite was confirmed. It is expected that these composites will possess antibacterial properties. The effect of origin and ratio of the initial components on the properties of porous filled composites was determined. These results will be used for optimization of compound ratio of the material for osteogenesis and its further investigations including medical and biological treatments.

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PARTICULARITIES OF THE COMPOSITE HYDROGEL MEMBRANES FORMING USING THERMOPLASTIC POLYAMIDE

Abstract: *The composite hydrogel membranes with reinforced selective layer based on a mixtures of PA-6/PVP were synthesized. The effectiveness of the hydrogels structure modifying on the basis of rarely structured HEMA/PVP copolymers via deposition of polyamide thin films from solution was confirmed that allows to form the hardened structured layers on their surface. Physico-mechanical properties and osmotic permeability to NaCl were defined for obtained composite membranes. It was determined that the variation of compositions of hydrogel and modifying layers and conditions of composite membranes formation allows to directly regulate their strength and permeability.*

Keywords: *composite membranes, hydrogel, polyamide-6, polyvinylpyrrolidone, solutions, dip-coating.*

1. INTRODUCTION

Among the membranology prioritz directions are the development and improvement of the principle of porous structure asymmetry and formation of polymer composite membranes. The scientific and practical interest to the synthetic, primarily polymeric, membranes became rapidly growing since the early 1960s, when Loeb and Sourirajan had received and examined the first asymmetric membranes of cellulose acetate [1]. Due to the asymmetric structure, the combination of two opposing requirements for membranes: high performance and maximum detaining power is provided.

Polymer hydrogels are crosslinked hydrophilic macromolecular systems that are capable to hold large amounts of water together with retaining of properties that are characteristic for solids (definite form, mechanical modules characterizing the properties of the material at tensile and shear deformation). This combination of properties predetermines wide range of hydrogels application – from technical areas (sorbents, gas-separating and ion-exchange membranes) to food and medicine (structure-formers of food products, drug carriers, artificial biological tissues, materials for soft contact lenses etc.) [2]. The emergence of new areas of polymeric hydrogels applications imposes new requirements for their properties. Recently, interest in polymer hydrogel materials that with the hydrophilic and diffusion-transport properties have high mechanical strength in the hydrated state, has increased. The combination of

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these properties in one material allows to create an unique polymer products, such as soft contact lenses with high oxygen permeability, carriers for water-insoluble drugs, sorbents that can absorb both hydrophilic and hydrophobic substances, new membrane materials etc. These properties can be achieved by obtaining of fundamentally new materials - composite hydrogels containing at least two components, each of which performs certain functions [3].

Formation of composite polymeric membranes is connected with two technological processes: manufacturing of the porous substrate and its coating with finely porous selective thin layer [1, 4]. Over the past decade, a wide range of composite polymer membranes suitable for desalination and purification of natural and waste water as well as various technological solutions has been created. Micro- and ultrafiltration membranes with asymmetric porous structure are applied for the purification of colloids, dissolved organic matter with a rather high molecular weight, synthetic and natural polymers etc.

However, traditional inversely-coagulation methods of composite membranes forming from concentrated polymer solutions have a number of significant drawbacks concerning both manufacturing technology of membranes and their structure and properties. Among such disadvantages are non-clearly expressed asymmetry of porous structure (which greatly reduces its separation ability) and low physico-mechanical properties of membranes.

These drawbacks will much less manifest itself in the preparation of composite membranes of asymmetric structure in which dense surface layer is deposited on a porous membrane substrate. These two layers are made of different polymeric materials. An advance in the technology of composite membranes is that each such layer can be optimized to obtain the required performance properties of the membrane. The surface layer in composite membranes can be made from a material (e.g. elastomer), which is difficult to manipulate as part of phase inversion method, for example at deposition by immersion.

This technique allows to apply the quite simple method that is widely used to create a composite membrane with a very thin but dense surface layer. Its principle is shown schematically in Fig. 1. In this case, the film substrate membrane is immersed in a special solution containing the polymer, oligomer or monomer. The concentration of the substance in the solution is very low (below 1%). When asymmetric membrane is removed from the bath containing the coating material and solvent, thin layer of solution sticks to it. This film is then placed into oven, where the solvent evaporates and a thin film fixes on a porous substrate.

Application of polymer film coating via method of pulling from solution (dip-coating) – the traditional method of solid surfaces modifying with ultrathin coatings [5, 6]. This method is particularly suitable for the application of thin polymer films with simultaneous deposition, combined with pulling-out from the solution. The scheme of this method is shown in Fig. 2.

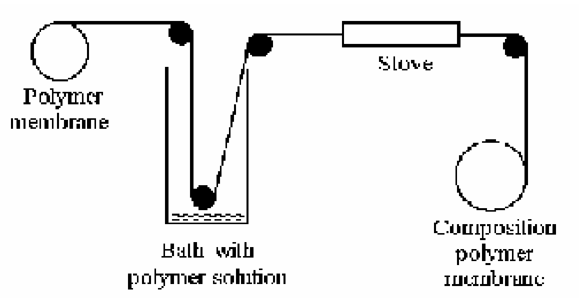

Fig. 1. The scheme of a thin layer application by immersing [4]

The substrate is removed from the polymer solution with controlled speed. Simultaneous action of surface tension of the solution and shear force at the interface along the liquid-air line (meniscus line) creates conditions for the evaporation of volatile solvent, concentrating of the solution and its uniform distribution over the surface of the substrate by gravity and surface tension. Therefore, the thickness of the polymer film is regulated by the concentration of the solution and pulling speed. For flexible polymer chains it's inversely proportional to the latter [6].

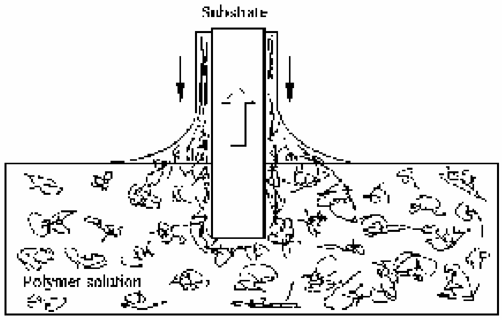

Fig. 2. Application of polymer film coating via dip-coating method

A significant advantage of the ultrathin layers deposition method by pulling from the solution is the simplicity of equipment design and low consumption of polymeric material. This method is suitable for multilayer production.

To produce hydrogel membranes of biomedical purpose, rarely structured copolymers of 2-hydroxyethyl methacrylate (HEMA) and polyvinylpyrrolidone (PVP) are commonly used [7, 8]. However, these membranes they have low mechanical strength, that significantly reduce the possibility of their use. For obtaining of the composite polymeric membranes, method of their surface modification with a thin layer of another polymer is used. The method consists of applying the polymer solution to the surface of semipermeable membrane substrate [9, 10]. The application method may vary depending on the expected result, substrate material, the thickness of the applied layer etc.

The promising for the modification of polymer hydrogels are solutions based on aliphatic polyamide. Films from them are characterized of hydrophilic properties and increased strength characteristics. The authors [11, 12] have found good compatibility of polyamide-6 (PA-6) with the PVP. This is due to the formation of hydrogen bonds between polar PVP groups and peptide groups of PA-6, that allows to obtain at a certain components ratio modifying solutions and materials based on them, that are characterized by high sorption and diffusion properties. In [12] authors have highlighted the possibility of selectively-permeable membranes obtaining, based on polymer blends of PA-6 / PVP that are characterized by considerable mechanical strength. However, their water- and salt-permeability much depends on the thickness of the film.

The aim of investigation was to obtain composite hydrogel membranes based on rarely structured HEMA/PVP copolymers, tat are strengthened with PA-6/PVP polymer nanolayers and to explore their physico-mechanical and diffusion properties.

2. MATERIALS AND METHODS

For research next components were used: HEMA (Bisomer®, USA), purified by vacuum distillation (residual pressure of 130 N/m^2, b.p.=351 K); PVP (AppliChem GmbH, Germany), highly refined with a molecular weight of $12 \cdot 10^3$ and $360 \cdot 10^3$ g/mol; potassium persulfate (PPS), pure, purified by two-time recrystallization from aqueous solution; glycerol, pure; polyamide PA-6 (Tarnamid-27, Poland); formic acid 90% solution.

To obtain hydrogel film membranes monomer-polymer compositions were dissolved in water or aqueous glycerol medium. The polymerization was performed using initiation by potassium persulfate in specially produced silica glass forms. Composition HEMA/PVP was prepared and a part of the solvent (water) was added, simultaneously solution of initiator (PPS) was prepared in the rest of the water. Both solutions were poured together and thoroughly mixed using a magnetic stirrer for 10...15 min. till the formation of a homogeneous composition. The resulting composition was purged with argon and evacuated to completely remove air bubbles. After this composition have been poured into forms so that no bubbles were formed. The forms of composition were placed in a dry-air thermostat for the polymerization. The polymerization of the compositions was performed by the following stepped mode: 55...60 °C – 2,5 hours; 75...80 °C – 2 hours (temperature control accuracy of ±1 °C). The thermostat was switched off; the forms were cooled to room temperature and placed in a water bath for 1 hour. After that the shape was revealed. The resulting hydrogel films were washed in distilled water for 24 h for complete removal of unreacted monomer and stored in a hydrated state.

To form the ultra-thin polyamide membranes solutions of polymer blends of polyamide 6 (PA-6) and PVP were used in a mixture of formic acid (HCOOH) and water. Unilateral application of thin polyamide polymer layer on the surface of hydrogel films was performed by pulling them from modifying solution (dip-coating) with subsequent evaporation of the solvent at a temperature of 75...80 °C.

The thickness of the synthesized film membranes was measured by thickness gauge indicator TR 10-60 with accuracy ±0,01 mm. Physico-mechanical properties in hydrated state were determined by film breakthrough technique with dowel indenter using a tensile machine "Kimura" 050/RT-6010 (sample deformation rate of 25 mm/min). Research methodology is described in [7].

Permeability of dialysis membrane based on PA-6/PVP mixtures for salts was investigated by the method described in [14]. The permeability of membranes for water solutions of model substance without applying external pressure was measured by osmosis. Since osmosis is a static and long-term process, as the model 4% aqueous solution of sodium chloride was selected. It allows observing a picture of permeability of synthesized composite membranes in a relatively short period of time. The amount of salt that permeated through the membrane was determined by measurements of electrical conductivity. The conductivity was measured by conductivity meter DIST-1. After definite time intervals indications of the device's scale were recorded. Pre-calibration of device was performed by salt water solutions of known concentrations and a calibration graph of resistance/salt concentration dependence was obtained (Fig. 3). By measuring the conductivity of aqueous solution and using the calibration graph, the amount of salt that has penetrated through the membrane was determined.

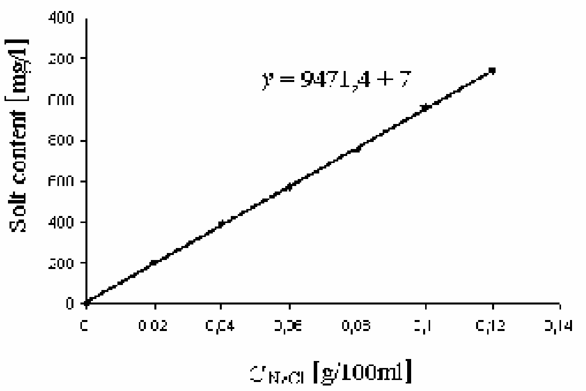

Fig. 3. Dependence of salt content from NaCl concentration (C_{NaCl}) in aqueous solution

From the data obtained, ratio G/S was calculated, where G is the number of moles of salt, that penetrated through the membrane over definite time, S – effective area of the membrane. The experimental data were used for plotting the kinetics graphs of osmotic permeability of synthesized composite membranes.

3. EXPERIMENTAL RESULTS AND DISCUSSIONS

In order to determine the relationship between strength and permeability of synthesized membranes, their compositional structure and formation conditions a number of options were changed with the sustainability of the technological regime to obtain hydrogel membrane substrates and their modification, namely:

a) Variation of HEMA/PVP ration in the hydrogel membrane substrate composition.

For the synthesis of hydrogel membranes composition (HEMA/PVP):H_2O= =60:40 wt. % were used, with varying ratios of HEMA:PVP (7:3 and 8:2 by weight).

b) Variation of solvent at hydrogel composition.

For the synthesis of hydrogel membranes compositions (HEMA:PVP):H_2O= =60:40 wt.% and (HEMA/PVP):H_2O:glycerol=60:33:7 wt. % were used.

c) Variation of PA-6/PVP content in modifying solution.

Modifying solutions were prepared by dissolving of polymeric mixtures of PA-6/PVP=95:5 wt. % in aqueous solution of HCOOH (in concentrations of 3, 5, 7 and 10 wt. %).

A relationship between compositional structure, nature of solvent and properties of hydrogel membrane substrates intended to form composite membranes was determined (Table 1).

Table 1. The dependence of the strength and permeability of hydrogel membrane substrate from a hydrogel composition and nature of the solvent

No	Hydrogel content, wt. %				Strenght of the breakout, σ, MPa	Coefficient of osmotic salt permeability, α_{Nacl}, mole/(m^2·h)
	HEMA	PVP	H_2O	glycerol		
1	42	18	40	–	0,64	5,28
2	48	12	40	–	0,68	3,40
3	48	12	33	7	0,92	4,89
4	54	6	40	–	1,02	3,85

The results showed a clear pattern: decreasing of PVP content in hydrogel membrane composition will increase its strength; addition of glycerol only enhances the effect. However, such reduction of PVP leads to a reduction of the osmotic permeability for NaCl due to consolidation of hydrogel membrane pores. In this case, the addition of glycerol to the solvent increases pores and thus increases the permeability of hydrogel membrane.

Development of the principles of technology of membrane-type thin film forming based on a new formula – a polyamide as a polymer with high strength and PVP, defines scientific and practical interest of research. To prepare the forming solutions, concentrated aqueous solutions of formic acid were used.

The peculiarity of polyamides is that their solutions can form films [1]. A flowchart of formation of such films from solution by "dry method" was developed (Fig. 4).

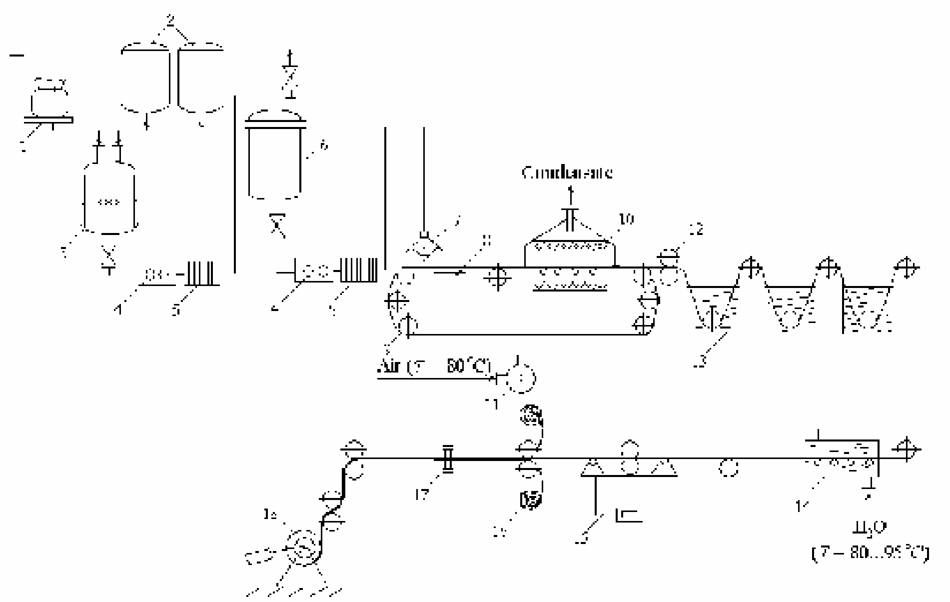

Fig. 4. The flowchart of film forming from the PA-6/PVP – based solution: 1 – gravimetric feeder; 2 – volumetric feeder for liquids; 3 – apparatus for forming solution preparation;4 – pump; 5 – filter; 6 – tank for air removal; 7 – spinneret; 8 – moving polymer tape (PTFE or PP); 9 – guide rollers; 10 – tunnel drying chamber; 11 – ventilator; 12 – refrigerator;13 – traction rollers; 14 – wash bath;15 – hydrothermal bath; 16 – device for determining the thickness and defects of films; 17 – sealing polyethylene film; 18 – welding device; 19 – winding device

Technology of films forming includes the following steps: dosage of initial components and preparation of the solution; filtration and deaeration of forming solution; irrigation of solution through the spinneret on a moving polymer tape; drying; detachment of film tape; washing and hydrothermal processing of film; flaw detection of film; packaging and winding of film. The peculiarity of the process conveyor with a movable continuous tape is that the tape is made of low-adhesive sparingly soluble polymeric materials that have heat resistance higher than 110 °C (evaporation temperature, $T_{ev.}$) like polytetrafluoroethylene or isotactic polypropylene.

From the obtained results it can be seen that with increasing of PVP content in the polymer mixture efficiency (f) is decreasing and the level (P) of physical binding of PVP in a fluctuation grid is increasing (Table 2).

Table 2. Effect of PA-6/PVP polymer blend on efficiency (f) and level (R) of physical binding of PVP (PA-6/PVP:HCOOH:H_2O=7,2:78:14,8 wt. %, C_{HCOOH} = 84 wt. %)

No	Polymer blend content, wt.%		f, %	P, %
	PA-6	PVP		
1	99	1	98,1 / 99	0,99 / 0,99
2	98	2	92,7 / 95	1,86 / 1,9
3	95	5	79,2 / 94	4,0 / 4,7
4	90	10	54,3 / 87,5	6,0 / 8,86

/ – M_{PVP}=360·10^3

PVP with a molecular weight of 360·10^3 is naturally washed out less because of more physical nodes that form a fluctuation polymer grid.

The influence of formation conditions, the amount of PVP and formic acid concentration on physic-mechanical properties of films based on PA-6/PVP blends were investigated. It was determined that the strength and relative elongation at breaking is increasing with the increasing of PVP concentration in solution to 2 wt. % (Fig. 5).

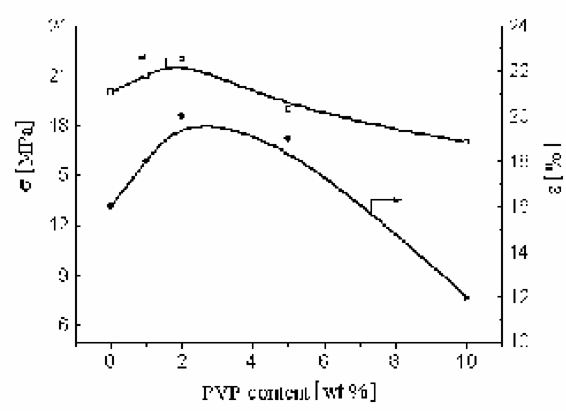

Fig. 5. Dependence of destructive stress (σ, MPa) and relative elongation (ε, %) at breaking the hydrated PA-6/PVP–based films from content of PVP. C_{HCOOH}=84 wt.%; $T_{ev.}$=80 °C; M_{PVP}=12·10^3; PA6/PVP:HCOOH:H_2O=7,2:78:14,8 wt.%

The concentration of the polymer mixture also affects the strength and deformation of the film (Fig. 6).

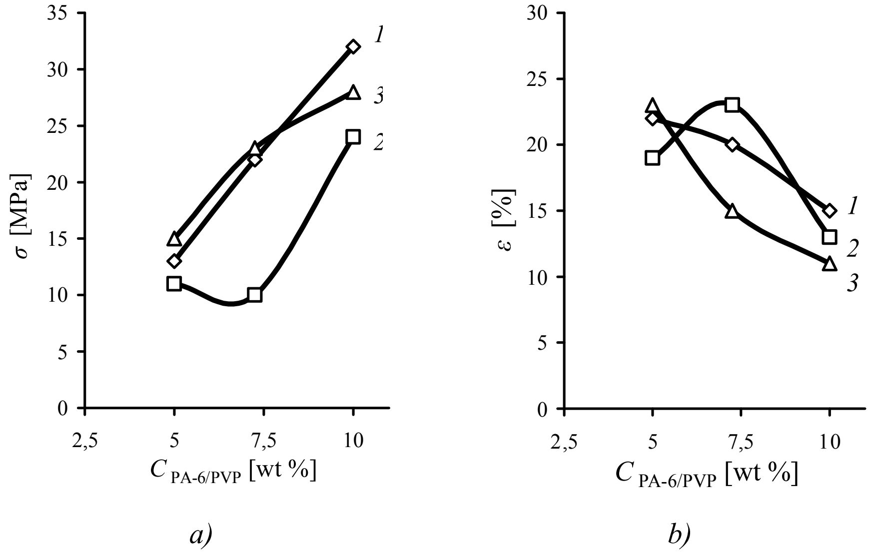

Fig. 6. Dependence of destructive tension (a) and relative elongation (b) at breaking of the PA-6/PVP–based films from concentration of the polymer mixture ($C_{PA-6/PVP}$). PA-6:PVP=98:2% wt.%,; C_{HCOOH}=84% wt.%; T_{ev}=80 °C. Films: 1 - not been processed; 2 – hydrothermally treated (95 °C); 3 – thermally treated (120 °C) in air

With increasing of the polymer blends concentration the strength of films increases and the deformation capacity decreases. However, regardless of the formation conditions obtained polyamide membranes have a much higher strength compared to the hydrogel one.

We investigated the permeability of the PA-6/PVP–based membrane during dialysis of aqueous salt solutions of different alkali metals – lithium, sodium and potassium chlorides [14]. It was found that with increasing of the cation size and increasing of its solvation ability the dialysis permeability naturally decreases (Fig. 7). This indicates intermolecular diffusion of electrolyte in a membrane [12]. At the same time the possibility of using of membranes for a dialysis process has been confirmed.

The investigation of selective-transport characteristics of the obtained membranes relative to heavy metal salts of different nature, including $CuCl_2$ and $Pb(NO_3)_2$, has been made. It was found out that membranes are highly rejection ability regarding such salts. (Fig. 8).

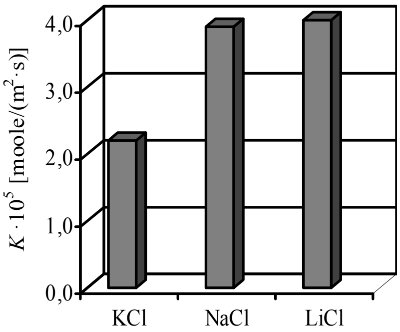

Fig. 7. Dependence of the dialysis salt permeability ($K_{[1,5\%\ NaCl]}$) of membranes based on PA-6/PVP from the nature of the electrolyte. PA-6/PVP:HCOOH:H_2O= =7,2:78:14,8 wt.%;PA-6:PVP = 98:2 wt.%; C_{HCOOH}=84 wt.%; δ=20 μm; T_{ev}=80 °C

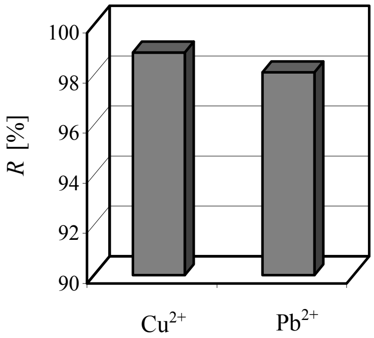

Fig. 8. Dependence of the delay (R, %) of heavy metals ions (Cu^{2+}, Pb^{2+}) of membranes based on PA-6/PVP from the nature of the electrolyte. PA-6/PVP:HCOOH:H_2O = 7,2:78:14,8 wt.%;PA-6:PVP = 98:2 wt.%; C_{HCOOH}=84 wt.%; δ=20 μm; T_{ev}=80 °C

It is known that with increasing of the radius of a heavy metal core the membrane rejection coefficient increases, but the obtained results are opposite, since ions of copper (II) are more likely to solvation, resulting in the formation of larger hydrated ionic complexes [15].

Consequently, the investigations show that the membranes synthesized from a mixture of PA-6/PVP are suitable for purification of salts of heavy metals and can be successfully used to strengthen hydrogel membranes by applying them to the surface of the hydrogel.

Based on the analysis of published data and previous studies of surface modification of hydrogel films the flowchart of the composite hydrogel membranes obtaining has been proposed (Fig. 9). The mixer 1, equipped with a paddle stirrer, was filled with pre-prepared polymer and monomer (HEMA/PVP) mixture and a part of solvent (water or a water-glycerol mixture) was added. The mixer was turned on and the prepared solution of initiator (PPS) was filled in. The composition was thoroughly stirred for 10...15 min. to the formation of a homogeneous solution. Obtained composition 3 was passed through the ceramic filter 2 and filled in the polymerization form 4. The form was covered by a glass plate so that there were no air bubbles, and was sent to the polymerization in dry-air thermostat 5, heated to a temperature of 55...60 °C for 2 hours. Then the temperature was increased to 75...80 °C. After 2,5 hours the form was cooled to the room temperature, placed in a container with deionized water 6 and disassembled. Obtained hydrogel film 7 attached on the one side of the glass plates was immersed in the container 8, into which the prepared modifying solution based on mixtures of PA-6/PVP in aqueous formic acid was poured. Modification was carried out, storing a hydrogel film in the solution during different times – 1, 3, 5 and 10 minutes. The resulting hydrogel film coated with a layer of polyamide was placed for 1 minute in the dry-air thermostat 9 at a temperature of 80...85 °C, equipped with the exhaust ventilation 10. After that obtained composite hydrogel membranes 11 were immersed in a bath of deionized water 12 and after hydration for 24 hours were moved in a container of water to be stored in a hydrated state for further research.

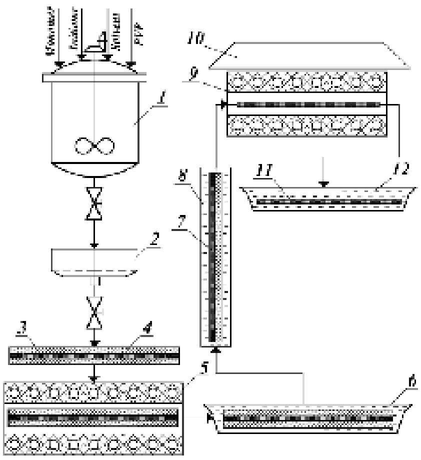

Fig. 9. The flow chart of the composite hydrogel membranes obtaining

The dependence of physico-mechanical properties of synthesized composite membranes from hydrogel membrane substrate composition and concentration of PA-6/PVP mixtures in modifying solution (Fig. 10, 11) has been investigated. It has been found the strength of composite hydrogel membranes increases with increasing of PA-6/PVP mixture concentration in modifying solution and exposure time (Fig. 10). With increasing of modifying solution concentration the strength increases for PA-6 concentration in solution up to 7 wt. %. With an increase to 10 wt. % the break strength decreases, which is caused by the critical solubility of PA-6 and its transition into a viscous state.

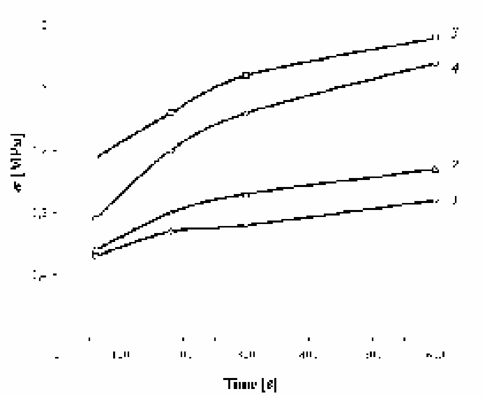

Fig. 10. The dependence of the strength of composite membranes from contact time of the hydrogel with the modifying solution and its concentration. HEMA:PVP:H_2O=42:18:40 wt.%; PA-6:PVP=95:5 wt.%; $C_{PA\text{-}6/PVP}$, wt.%:1 – 3; 2 – 5; 3 – 7; 4 – 10

The optimum concentration of PA-6 in a modifying solution is 7 wt.%, and the duration of exposure should not exceed 10 minutes for the film based on the composition of HEMA:PVP = 4:1 wt.% (Fig. 11).

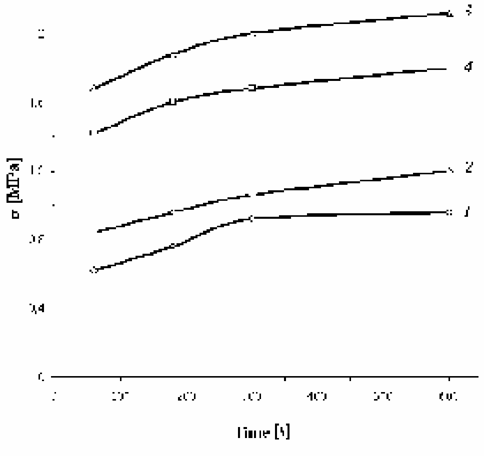

Fig. 11. The dependence of the strength of composite membranes from contact time of the hydrogel with the modifying solution and its concentration. HEMA:PVP:H_2O=42:18:40 wt.%; PA-6:PVP=95:5 wt.%; $C_{PA\text{-}6/PVP}$, wt.%: 1 – 3; 2 – 5; 3 – 7; 4 – 10

With increasing of a modifying polymer mixture concentration in a solution the permeability of composite membranes for NaCl decreases (Fig. 12, 13).

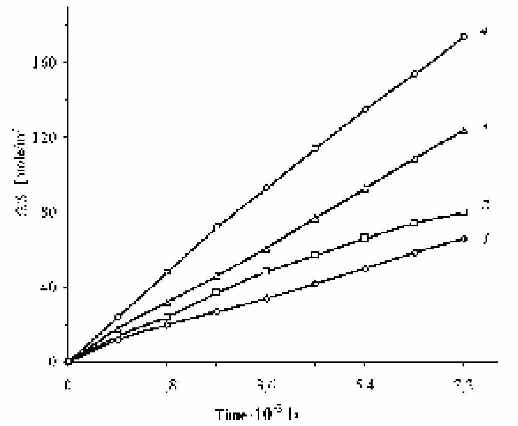

Fig. 12. The kinetic dependence of osmotic salt permeability of composite hydrogel membranes (G/S) for NaCl from the concentration of the modifying solution. HEMA:PVP:H_2O=42:18:40 wt.%; PA-6:PVP=95:5 wt.%; $C_{PA\text{-}6/PVP}$, wt.%: 1 – 0; 2 – 3; 3 – 5; 4 – 7

In the case of modification of hydrogel membranes with the HEMA:PVP=4:1 wt. % composition of the polymer matrix the maximum osmotic permeability is observed for the composite membrane modified with a mixture of PA-6/PVP with concentration of 3 wt. % in a solution of formic acid (Fig. 13).

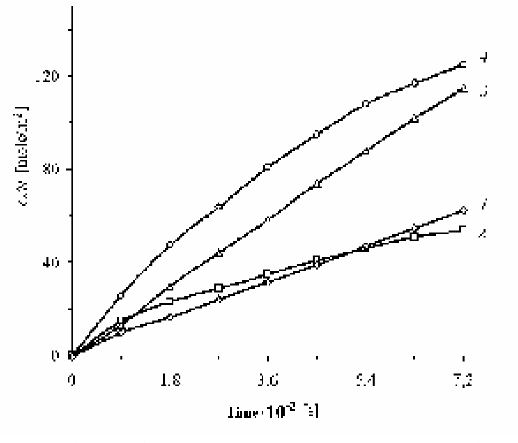

Fig. 13. The kinetic dependence of osmotic salt permeability of composite hydrogel membranes for NaCl from the concentration of the modifying solution. HEMA:PVP:H_2O=42:18:40 wt.%; PA-6:PVP=95:5 wt.%; $C_{PA\text{-}6/PVP}$, wt.%: 1 – 0; 2 – 3; 3 – 5; 4 – 7

It also has been found that for the modifying solution with the content of 7 wt. % of a PA-6/PVP mixture the osmotic permeability of composite membranes for sodium chloride in the initial stages is higher than for the mixture with the concentration of 5 wt.%.

4. CONCLUSIONS

The methodology was processed and the flowchart for forming of composite hydrogel membranes were proposed. The composite hydrogel membranes based on rarely structured copolymers of 2-hydroxyethyl methacrylate and polyvinylpyrrolidone, which are reinforced with thin films based on polymer blends of PA-6/PVP, were obtained. Physico-mechanical and diffusion properties of these membranes were studied. The methodology was processed and the hydrogel films for composite membranes forming were obtained. Using the vertical dipping method, thin layers of PA-6/PVP mixtures were applied on a hydrogel substrate and composite membranes were obtained. The strengthen effect of hydrogel films by surface modification of a PA-6/PVP mixtures was found. The ways of directed adjustment of the synthesized composite membranes permeability have been discovered, by selection of hydrogel membrane substrate, composition of modifying solution and technological parameters of modifying process.

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THE MORPHOLOGY AND PROPERTIES OF THERMOPLASTIC AND THERMOSET COMPOSITES WITH METAL CONTAINING POLYMER-SILICATE FILLERS

Abstract: *The influence of Ni-containing polymer-silicate filler modified by polyvinyl alcohol on the structural (degree of crystallinity, size of crystallites), physico-mechanical (surface hardness, strength at breaking, elastic modulus) and thermo-physical (Vicat softening point, coefficient of linear thermal expansion) properties of thermoplastic composites based on polypropylene has been found. The influence of metal-containing modified polymer-silicate filler on the features of structuring, performance and anticorrosive properties of compositions based on unsaturated polyester resin has been investigated.*

Keywords: *sodium liquid glass, polyvinyl alcohol, polypropylene, polyester resin, composite.*

1. INTRODUCTION

Today, for the development of modern technologies and their effective implementation it is necessary to use the innovative materials with specific required properties. The increased attention have thermoplastic and thermoset polymer-inorganic (nano-)composites based on inorganic fillers including silicates, which have the required for a particular application unique set of operating and technological characteristics [1].

Usually the inorganic fillers are previously modified for enhancing the technological compatibility with the polymer matrix and directional adjustment of technological and exploitation properties of polymer composites [2]. Among the methods of modifying of silicate fillers physico-chemical method, based on coprecipitation of water-soluble silicates and functionality surface-active polymers modifiers under the influence inorganic acids and (or) salts of metals is effective and ensures even distribution of the modifier on the surface and in the structure of the filler [3, 4]. The functional-active water-soluble polymer - polyvinyl alcohol (PVA), which has a high surface activity and is able to intermolecular and interfacial interactions is advisable to use for modification [5].

Polypropylene (PP) and unsaturated polyester resin occupy a special place among the wide range of polymer matrices used for development of new composite materials.

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2. MATERIALS AND EXPERIMENT

To filling polypropylene and polyester resin was used metal-containing modified silicate fillers that was obtained due to coprecipitation of sodium silicate and polymer modifier - polyvinyl alcohol under the influence of metals chlorides of different nature [6]. The developed method of coprecipitation are provided the obtaining of silicate filler with a specific active surface area of the within 60-76 m^2/g and the number of active sites on it 77-99 $\cdot 10^6$ mol/g and reduced of water absorption value by 40-60% and even distribution of the modifier on surface and in silicon-oxygen skeleton of filler.

To create a polymer composite materials as a polymer matrix of different nature were used – polypropylene Moplen HF501N («LyondellBasell» Netherlands) and polyester resin Estromal A023 ("LERG", Poland).

For polymer composites based on polypropylene with Ni-containing silicate filler, which are modified by polyvinyl alcohol (Ni-PVA-SF), was pre-mixing the bulk components in the desired ratio in the mixer drum (applying powder of silicate filler on granular of thermoplastic polymer). After receiving mechanical mixture carry out drying and homogenization of components by mixing in viscous state on extruder Cellier followed by squeezing material in the form of rods.

Production of standard samples from granular material for future research carry out in injection molding machine mark 25 KUASY 32/2. Filler content - 10% by weight.

To establish the impact of the developed Ni-containing polymer-silicate filler on supramolecular structure of polypropylene were performed using X-RAY diffraction research on diffractometer DRON-4-7 with exposure lamp with the Cu-anode and Ni-filter. Physical-mechanical properties of samples: ultimate tensile strength at breaking, border fluidity during stretching, the relative elongation during tearing was determined according to ISO 527-1, -2.

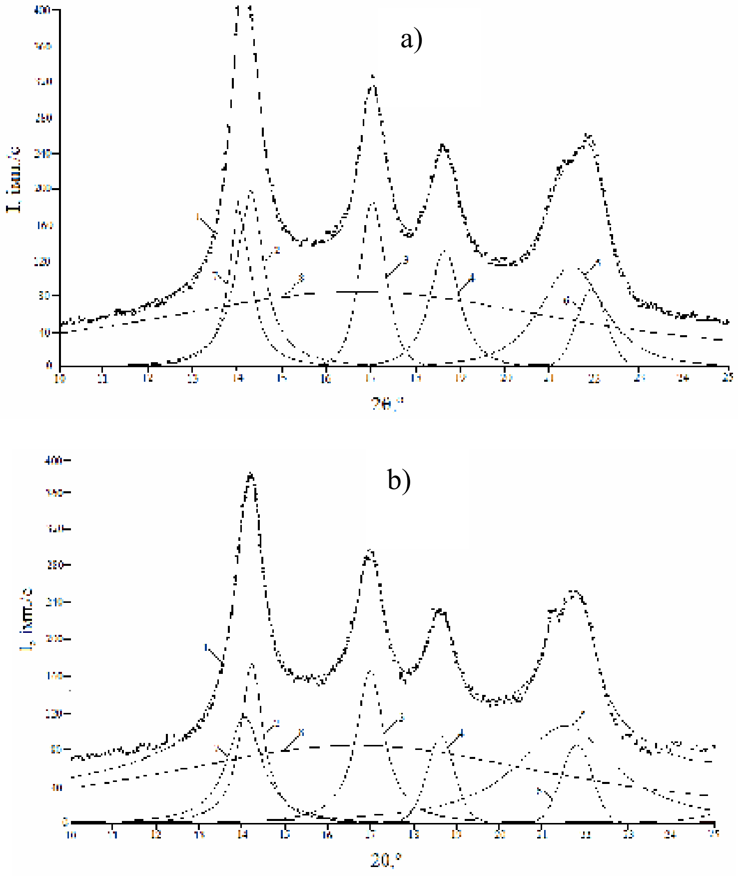
Research elastic-deformation properties of obtained materials carried on consistometers of Hepler at 293 K by indentation of conical indenter under load of 120 N and determine the characteristics of the module and deformation by calculation according to the methodology [7]. Vicat softening point of investigated materials was determined in accordance with ISO 306: 2013, loading was 50 N. The surface hardness by conical point of fluidity determined on consistometers of Hepler at 293 K indentation in the polymer sample steel cone with an angle sharpening 58^0 08' under load of 50 N for 60 s.

3. RESULTS

Supramolecular structure of polymer composites is formed by intermolecular processes at the stage of their processing under the influence of temperature and pressure, and also depends on the nature of the initial components of the composite, including the nature of Ni-containing silicate filler and parameters of mixing, interfacial interactions on the verge of filler-polymer matrix, the ability of components to crystallization and the conditions under which it occurs [8].

In this regard, the study of morphological features of developed polymer-silicate composite enable set the factors that the influence of the technological compatibility of components in polymer-silicate composites and predict their technological and exploitation properties.

The results of obtained by X-ray analysis for composites based on PP filled by Ni-PVA-SF is shown in Figure 1.



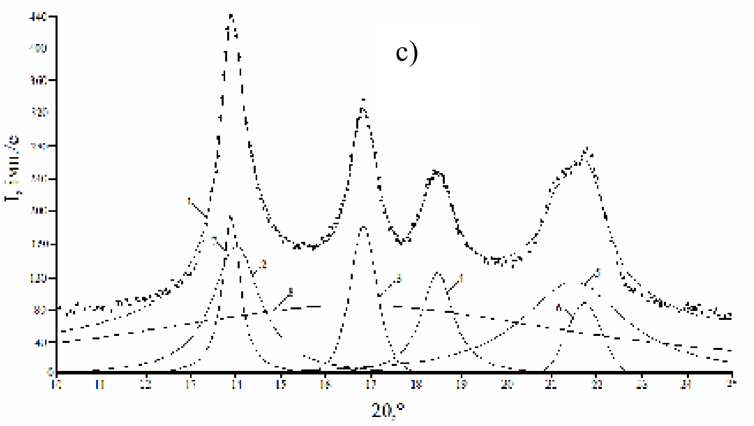


Fig. 1. Diffraction of composites based on polypropylene; Filler: a – without filler; b – Ni-SF; c – Ni-PVA-SF; 1 – diffraction approximation curve; 2, 3, 4, 5 – optimized reflex intensity curves α-phase; 6,7 – β-phase; 8 – amorphous phase

Crystal phase of filled polypropylene by metal-containing silicate filler appear in the range of diffraction angle at 2θ = 12-24°. Reflexes of crystalline phase unfilled PP appear at angles of diffraction at 2θ=14,0; 17,0; 18,6; 21,5°, and maximum of amorphous phase at 16,7°.

During the injection molding of composites based on PP are formed the polymorphic crystalline structure of monoclinic crystal lattice which dominates monoclinic α-form. In maximum orientation (so-called "shear layer") some of crystallites in hexagonal β-form coexists with α-form. In general, PP macromolecules arranged in clearly defined three-dimensional monoclinic crystal lattice. The macromolecular chains have a spiral shape and are made up of fragments with size three monomer units that are repeated.

This indicates that each successive monomer unit turned at an angle relative on 120^0. Diffraction reflexes of crystalline phase composites based on PP and Ni-containing silicate filler, especially modified by PVA, different from unfilled PP by increasing intensity reflections of planes α-phase and peak width and reducing the area of amorphous phase. Increasing the width of the peak intensity of the crystalline phase reflexes associated with reducing of size of supramolecular structures due to the increasing rate of crystallization.

These features of influence of metal-containing modified silicate filler associated with redistribution of intermolecular interactions of macromolecules PP, enhancement of physicochemical interactions between the hydrophobic nature between filler and macrochains of PP due to the presence of PVA macromolecules in polymer-silicate fillers and changes in topology of stacking polymer chains.

Confirmation of these considerations is determined using the software package WAXSFIT [9] structural parameters of developed composites: the degree of crystallinity (S_c), crystallite size (L^1_{hkl}, L^2_{hkl}), interplanar distance (d_{hkl}) at the corner of crystalline diffraction peak (2θ), height and width of the peak. The results are shown in table 1.

Table. 1. Structural parameters of composites based on PP

No	Filler	S_c, %	Plane	2θ, °	Height	Width	L^1_{hkl}, Å	L^2_{hkl}, Å	d_{hkl}, Å
1	Without filler	46,1	(110)β	14,0	190,6	0,6	159,9	102,6	6,3
			(110)α	14,3	199,1	0,7	121,5	78,2	6,2
			(040)α	17,0	186,0	0,7	130,0	110,6	5,2
			(130)α	18,6	131,1	0,8	111,5	84,1	4,8
			(111)α	21,5	113,8	1,7	53,0	40,9	4,1
			(131)β	21,9	87,6	0,8	113,6	104,4	4,2
			amorphous phase	16,7	85,3	12,3	7,3	0	5,3
2	Ni-SF	49,9	(110)β	14,1	116,3	1,0	89,2	57,6	6,3
			(110)α	14,2	173,1	0,6	141,8	91,1	6,2
			(040)α	17,0	166,3	0,8	114,4	73,6	5,2
			(130)α	18,6	95,6	0,8	118,3	105,5	4,8
			(111)α	21,5	106,3	2,8	31,9	21,0	4,1
			(131)β	21,8	85,9	0,9	104,7	98,2	4,1
			amorphous phase	16,7	85,3	12,3	7,2	0	5,3
3	Ni-PVA-SF	52,5	(110)β	13,9	195,9	0,5	190,4	122,0	6,4
			(110)α	14,0	159,0	1,3	70,2	45,5	6,3
			(040)α	16,8	182,8	0,7	128,1	108,5	5,3
			(130)α	18,5	125,8	0,9	105,3	67,7	4,8
			(111)α	21,5	113,8	2,8	31,9	21,0	4,1
			(131)β	21,7	87,6	0,9	99,9	93,7	4,1
			amorphous phase	16,7	85,3	12,3	7,2	0	5,3

The most value of degree of crystallinity S_c = 52,5% observed for the composite containing Ni-containing silicate filler modified by PVA. The particles of metal-containing silicate filler act as additional nucleation centers of crystalline phase, which leads to increased crystallization rate and degree of crystallinity. Active groups of silicon-oxygen frame of filler and functional groups of the polymer modifier in the interaction, both with separate groups CH_3 of PP polymer chain and with macromolecules in general during the viscous flow and subsequent cooling of the melt, heavily influencing the crystallization process and become additional crystallization centers. Thus, the introduction of modified Ni-containing polymer-silicate filler reduces the average size of crystallites at 10% and interplanar distance of almost not changing. Reducing the size of the crystallites and constant of interplanar distances are shows a reproducibility sequence of packaging macromolecules of filled PP compared to unfilled, which reduces defects in the crystal phase.

Based on the effects of modified Ni-containing polymer-silicate fillers on morphological characteristics of polypropylene composites, it is expedient to establish their technological and performance properties.

The performance properties of composite materials based on thermoplastic polymers, including polypropylene differ significantly from unfilled thermoplastics. For polymeric composition materials these properties over a wide range can be adjusted by physical condition and nature of the initial components, the nature of the distribution of the ingredients in the bulk material, heat treatment, technological parameters of processing and more. In this regard, considerable interest is the study of basic physical, mechanical and thermophysical properties of materials based on PP filled with modified Ni-containing silicate filler.

Physicomechanical properties of the composites are one of the most important performance properties and largely determine the field and terms of the products in their basis. Mechanical testing under static loads by using stress-elongation curve can determine the key indicators of strength during stretching. The strength of polymer composites depends not only on the size of macromolecules, their configuration and location, and the availability of intermolecular interactions, and in composite materials from nature and compatibility of components. Thus, it is important information about fracture material and its physical state in the conditions of the test. Stretching curves obtained for composites based on PP and Ni-containing polymer-silicate filler shown in fig. 2.

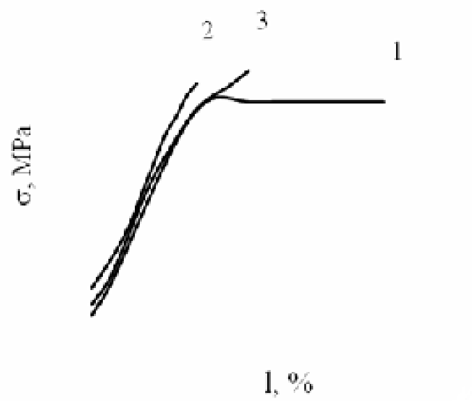


Fig. 2. Curves of stretching composites based on PP; Filler: 1 – without filler; 2 – Ni-SF; 3 – Ni-PVA-SF;

Stretching curves of developed polymer composites are typical for crystalline polymers. In particular, there are areas that meet certain state of supramolecular structure of the material under the applied load. Because the elastic deformation, which is fully reversible, meaning tension in the material initially is proportional elongation that is similar to a crystalline solid bodies and significant restructuring of the crystallites happens [10]. When the load reaches a value at which stress commensurate with the magnitude of intermolecular interactions, starts moving segments of macromolecules and destruction of supramolecular structures that promotes plastic deformation of crystallites with partial destruction of the crystal lattice and increased elongation. The basis of curves defined border tension strength (σ_b) and relative elongation (ε_b). These characteristics and surface hardness values before (F) and after (F_T) heat treatment shown in table 2.

Table 2. Physicomechanical properties of composites based on PP

No.	Filler	σ_b, MPa	ε_b, %	F, MPa	F_T, MPa
1	Without filler	41,2	66	195,7	213,4
2	Ni-SF	43,4	30	190,2	228,7
3	Ni-PVA-SF	45,6	40	231,7	240,94

The composites based on filled PP the ultimate tensile strength values is higher compared to unfilled materials, which is obviously due to the higher degree of crystallinity due to ordering of macromolecules, smaller crystallites and formation denser of fluctuation of network by participation of Ni-containing polymer-silicate filler. Thus, the largest value σ_b is observed during use as Ni-PVA-SF – 45,6 MPa. This feature is associated with the creation of more favorable conditions for crystallization of PP with the direct participation of the modified filler.

As a result of intermolecular interactions (mostly hydrophobic character) filler with macromolecules of PP occur changes in interphase layers that lead to some relative orientation of macromolecules to form denser supramolecular structures, resulting is increases a surface hardness of the composites [11].

For polymer composite of constructive and thermotechnical appointment along with strength characteristics are important resilient, highly elastic and plastic properties. These figures were determined under the strain of module-deformation principle of calculation. The study of deformation properties of composites based on PP are essential for understanding the behavior of a material under load different types (static or dynamic, short or long, etc.) and the correct choice of the application. The research results of elastic-deformation properties for composites based on PP and Ni-containing polymer-silicate filler are shown in table 3.

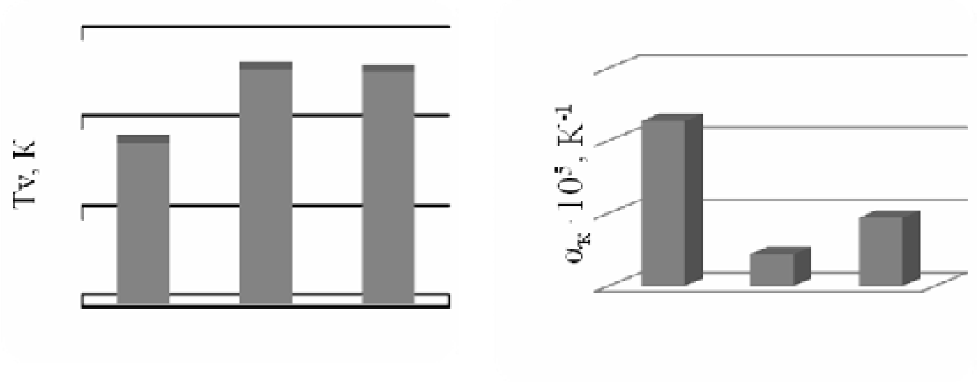
Table 3. Elastic-deformation properties of composites based on PP

No.	Parameter	Filler		
		–	Ni-SF	Ni-PVA-SF
1	Module strain E_g, MPa	512	614	677
2	The equilibrium modulus E_m, MPa	1248	1568	1677
3	Conditionally instantaneous modulus E_0, MPa	1727	2169	2165
4	Highelasticity module E_h, MPa	4496	5662	7446
5	Proportion of the elastic component in the overall deformation ε_e,	0,296	0,283	0,313
6	Proportion of the highelasticity component in the overall deformation ε_h	0,113	0,108	0,09
7	Proportion of the plastic component in the overall deformation ε_p	0,589	0,608	0,596
8	Coefficient of plasticity K_p	0,092	0,089	0,085
9	Coefficient of structure K_s	5,66	5,7	5,71

Modulus (E_m) that defined by a small displacement of atoms, changing the interatomic and intermolecular distances and bond angles of the investigated PP material increases with the introduction of Ni-containing silicate filler, modified by polyvinyl alcohol. That demonstrates the reinforcing effect of polymer-modified silicate filler because of orienting influence of active centers filler and modifier on macromolecule PP, which results in limiting their mobility and the formation in a force field around fine particles of adsorbed layers of ordered supramolecular structures. This effect of filler involves a reduction in the number of possible conformations of macromolecules in these layers, the growth medium of relaxation times, increased relaxation spectra and density packing of macromolecules. High elastic deformation (E_h) that associated with conformational changes of macromolecules somewhat reduced due to the using of modified filler, that is associated by additional intermolecular interactions filler-modifier-polymer matrix. The increase in the overall deformation proportion of plastic deformation (ε_p) that was caused irreversible movement of macromolecules for filled materials, also reflects the influence of the filler on the formation of tighter structure of the polymer, which is unable to inverse deformation.

The established of module strain shows that derived materials can be attributed to low deformability materials, which are characterized mainly strong inverse deformation and elastic aftereffect. At the same time, the introduction of filler leads to increase of the coefficient of structure, which is characteristic of spatial fluctuation network.

Described patterns also confirmed the influence of filler on Vicat softening point (T_V) and coefficient of linear thermal expansion of developed composites ($\alpha_к$) (fig. 3).



a) b)

Fig. 3. Vicat softening point (T_V) (a) and coefficient of linear thermal expansion ($\alpha_к$) of developed composites based on PP;
Filler: 1 - without filler; 2 – Ni-SF; 3 – Ni-PVA-SF.

Introduction the filler in PP promotes increases of Vicat softening point. The highest value for the heat resistance of composites based on PP discovered during use unmodified filler, and the least – for unfilled polymers. One of the significant drawbacks of polymers is a high coefficient of thermal expansion [12] that causes unacceptably large parts of resizing them with significant temperature fluctuations. The introduction of Ni-SF reduces the coefficient of thermal expansion of developed composites. These patterns obviously due to the fact that silicate particles slightly deformed under the influence of temperature and prevent thermal expansion of the composite [13]. The lowest value $\alpha_к$ are specific to composites with unmodified fillers. These features, primarily due to changes in the boundary layer at the interface between filler-thermoplastic matrix.

Due to the ability to obtain a wide range of materials, availability and relatively low cost the unsaturated polyesters find wide application in the form of fibers, composites and coatings, as well as for coherent composite materials, reinforced plastics, impregnating resins, adhesives and film-forming.

They are significantly different from other termoset plastic that have a low viscosity and can harden at room temperature without releasing by-products. Actual is the development of new organic coatings based on polyester resins which contain inhibiting components and are able to operate in areas of through damage of coverage and further protect the metal from corrosion. In this context, perspective can be used in the coatings inert fillers, including fine modified metal-containing polymer-silicate filler. Hardening of the polyester composites were carried out in the presence of cobalt naphthenate accelerator and initiator - peroxide methyl ethyl ketone at room temperature. The introduction of metal-containing polymer-silicate fillers on polyester composition will regulate the process of structuring a resin, morphology and properties of polyester composites. For all compositions regardless of the nature of the components observed rapid rise of viscosity and heat after 70-120 minutes of curing [14]. At the same time, the nature of silicate filler largely affects of the process of structuring oligomeric compositions. Based on viscometric research and thermometry found that the introduction of Zn-containing silicate filler in the amount of 2 wt%. leads to slower curing speed, and the introduction of Ni-containing silicate filler accelerates the process of curing oligomers. This is due a different activity metals relatively to influence the individual stages of the process of curing resins, especially at the stage of activation and the different nature of functional surface - active groups of fine metal-containing silicate fillers [6]. Introduction of fillers also affects the performance properties of polyester composites. Filling the polyester compositions Ni-, Co-, Ba-, and Cu-containing silicate fillers allows increase the surface hardness of composites on 10-50 MPa. However, the introduction of Zn-containing silicate filler somewhat reduces the value of surface hardness [15].

The materials based on unsaturated polyester resins are widely used as flood and impregnating resins, adhesives and film-forming and is expedient determine the strength of the adhesive compounds modified polyester compositions with metallic surface. The introduction of metal-containing polymer-silicate fillers increases the value of adhesive strength of adhesive compounds based on polyester resin by 20-30% [16]. For filled polyester compositions coated on the metal substrate while in hostile environments the capacity of coatings after a slight increase, which shows the swelling of the coating in an environment stabilizes at a certain level. Surface retain their protective effect and function primarily as a barrier to water molecules and corrodent ions. It should be noted that among of the polyester material filled of metal-containing silicate filler 2 wt%. the largest corrosion protection characterized Ni-silicate fillers, and the lowest - Zn-silicate (capacitance value are $15{,}7\cdot10^{-12}$–$16{,}9\cdot10^{-12}$ pF/cm^2 and $17{,}7\cdot10^{-12}$–$37{,}5\cdot10^{-12}$ pF/cm^2 respectively). This is due to the different nature of electrode processes that take place with the participation of metal ions and components aggressive environment. The resistance of some polyester compositions being high in the early days of research, and further reduced to a level approaching $1{,}5 \cdot 10^6$ Om·cm^2, which indicates that the penetration of aggressive environment for steel substrate and coating the loss of protective properties. Especially, it concerns compositions comprising Zn - silicate and Co - silicate filler. After the decrease in resistance on samples can observe the emergence of the first points of corrosion.

4. CONCLUSIONS

Composites based on polypropylene and metal-containing polymer-silicate filler due to equitable distribution of modifier, directed influence on the surface properties of the filler and high technological compatibility between components have increased crystallinity by 4-7% and reduced average crystallites size. This is obviously due to the fact that the filler's particles act as nucleation centers with additional crystalline phase.

The value of ultimate tensile strength at breaking of composites is increased by 5-10%, modulus - by 20-30%, heat resistance - by 10-20 K, surface hardness by 10-15% and the coefficient of linear thermal expansion is decreased by 3-5 times. These features are caused by changes in the boundary layer at the interface between filler-thermoplast matrix.

Increased mechanical, elastic-deformational, thermal and technological properties of developed composites provide their effectiveness for use in the production of materials for constructional purposes.

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IMPROVED METHOD OF CENTRIFUGAL FORMATION OF METAL-FILLED HYDROGEL FILMS WITH INCREASED STRENGTH

Abstract: *We processed the method of centrifugal forming of high-quality composite hydrogel films based on metal-filled copolymers of polyvinylpyrrolidone (PVP) with 2-hydroxyethylmethacrylate (HEMA). We developed the technological regime, stepwise formation process technological scheme. There are made improvements of the structure of the machinery and equipment that enhance productivity, efficiency and versatility of the centrifugal method of forming metal-filled hydrogels. It is determined the influence of the content and nature of metal powder filler, technological parameters of processing and formulation of initial polymer-monomer composition on the surface quality and physical-mechanical properties of the obtained composition film materials.*

Keywords: *centrifugal molding, composite materials, composite hydrogels*

1. INTRODUCTION

Composite hydrogel metal-filled materials in many cases during the operation are used in the form of films, in medicine these are membrane different kind, of transdermal drugs, implants, elements of medical equipment intended for installation of a reliable contact with the human body, the instrument making-elements of different sensors (humidity, temperature, pressure, concentration of gaseous and liquid products), etc.

One of the branches of medicine where is a particularly urgent need to develop metal-filled hydrogel materials and low-tonnage technologies of production on the basis of their film products that can be implemented directly in an outpatient or clinical environment, is metallo-therapy and magneto-therapy. In particular, the hydrogel film, filled with metals and alloys of different nature are promising in the manufacture of magnetophors and metal film applicators. Sorption capacity of metal-filled hydrogels based on HEMA-PVP copolymers gives the ability to simultaneously conduct magnetic and electrophoresis of drugs with the magneto-therapy.

However, during the production of composite film materials, two important issues come up – search and choice of the method of obtaining the predicted film thickness and the method of their filling with metals.

At present, the most common methods of obtaining hydrogel films is the

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formation from solutions of polymers and polymerization in a solvent. For the production of films, using the methods of forming between the two glass plates [1, 2], are using the glaze on glass surface using the molding knife [3] and dipping [4]. The simplest, from a technological point of view, is watering and dipping, however, the formation by watering is difficult to obtain films of predetermined and same thickness with a quality surface. It is possible to obtain ultrathin coatings by dipping, but there is a problem in obtaining of coating with the same thickness. Films made in the forms, are characterized by high quality surfaces and no thickness variation. In this case, however, there are difficulties in filling the molding cavity mold composition without air inclusions, which becomes more complicated with increasing size of the form, a decrease in film thickness and also with increase in viscosity of the composition. These problems are significantly compounded in the manufacture of filled, reinforced and multilayer films.

Also HEMA-PVP compositions are characterized by high adhesion to forming of glass surfaces. The solution of this problem requires to use of the antiadhesive substances, which are not always wanted, because they affect the purity of the films and require further processing. Therefore, it is important to develop new, simple, productive and technological methods of hydrogel film materials including metal-filled ones.

By the previous works [5] it was established regularities of the (co)polymerization of PVP-(meth)acrylate filled with the finely dispersed powders of metal compositions, which reflect the influence of the composition, nature and content of the filler metal, the reaction conditions on the process speed, yield of the polymer, structure and properties of the copolymers. The using as the initiating system of the complex PVP-Me^{n+} allowed the synthesis of copolymers with high speed (time of curing of compositions – from 10s to 30 min.) at room temperature in air. High reactivity and workability of such compositions creates the preconditions for the use of film materials on the basis of the method of centrifugal forming.

Centrifugal forming is one of the methods of producing of products from plastics in the form of bodies of rotation of the pouring material, which is in viscous condition in the mold, which rotates in the same plane. Under the action of centrifugal forces the material is distributed evenly over the inner surface of the mold in a continuous layer, getting the necessary configuration when it solidifies. Used mainly for the manufacturing of pipes, bushings, sliding bearings, gears and various billets.

The centrifugal molding is used to recycle compounds on the basis of polyester, epoxy and other cohesives, such as: caprolactam, polyacrylates, low density polyethylene, polyamides, and forming pasty compositions (plastisol) based on polyvinyl chloride. Fine granular polymeric materials in the form of powders and granules can be processed.

Analysis of the process of the centrifugal formation showed the possibility of using this method for processing compositions of HEMA-PVP in the presence of ions of metals of variable oxidation and production of film composites based on them [6]. In addition, this contributes to the high reactivity of metal-filled HEMA-PVP compositions and the ability to vary the residence time of the original composition in the liquid state. During the research, we have produced prototypes of metal-filled hydrogel films based on copolymers of HEMA with PVP, which are characterized by a set of unique characteristics – equal thickness, sorption capacity, improved physical and mechanical properties, anisotropic electrical conductivity of the surfaces, which provide a perspective of the studied materials. However, to obtain high-quality metal-filled films with predetermined characteristics and implementation of a fundamentally new method of obtaining them, it is necessary to develop the technology of the process of formation and establishing the influence of technological parameters of centrifugal method on the properties and quality of composite hydrogels.

2. PURPOSE AND OBJECTIVES

The purpose of this work was to develop the technology of centrifugal formation of metal-filled hydrogel film materials based on copolymers HEMA-PVP and to establish the influence of technological parameters of recycling, on their quality and properties.

To achieve this goal the following tasks were solved:

- development of a stepwise technological scheme of the centrifugal formation of the composite hydrogel films;
- improvement of equipment and tooling;
- determination of the influence of technological parameters of processing, the content and nature of the metal, the composition of the initial polymer-monomer, on the quality and properties of composite film materials.

3. EXPERIMENTAL

Using the results of previous researches [7], for the synthesis of filled hydrogels selected polymerization in block composition of the HEMA:PVP = 80:20 (Xw) in the presence of 0,05% $FeSO_4$.

The composition selected experimentally based on the velocity of polymerization of PVP content and $FeSO_4$, as well as the analysis of viscosity, based on the conditions of the filler particles sedimentation and the need for high performance process. For synthesis using 2-hydroxyethyl methacrylate (ρ_{20}=1079kh/m^3, n_D^{20}=1,4520), purified and distilled under vacuum (residual pressure of 14 N/m^2, Boiling point = 351 K), the content of residual ethylene dimethacrylates not more than 0,15 %; PVP with MW 12 000 and 28 000 high purification before use dried under vacuum at 338K for 2-3 h., fine powders of metals Zn, Co, Ni, Fe, Cu, Ag and FeCo alloy with particle size within 0,05-50 μm, the polymerization was carried out at 293K, outdoors, in daylight.

The bursting strength (σ_b, MPa) and percentage elongation at bursting (ε_b, %) was determined according to the method described in [8], tensile strength during the break (σ_{br}, MPa) and elongation during break (ε_{br}, %) – according to the methods described in [9].

4. RESULTS AND DISCUSSION

4.1. The development of the technological scheme of the centrifugal formation of films filled with metal powders

The basis for the development of fundamental technological scheme of the process of producing hydrogel films were based on research of kinetic regularities of copolymerization compositions based on HEMA with PVP in the presence of $FeSO_4$ [7] and in the presence of finely dispersed powders of metals [5], the structure and properties of unfilled and filled hydrogel materials and typical technological scheme of the centrifugal formation.

The high reactivity of HEMA-PVP compositions, as well as the essence of the process of forming centrifugal enable the creation of compact processing line, that will produce films of different composition (unfilled, filled, reinforced, laminated) and purpose.

The technological process consists of the following stages:

- preparation of substances and materials;
- preparation of the reaction composition;
- formation of the hydrogel film;
- washing the obtained film;
- additional processing and drying the film;
- inspection and packaging.

1. Preparation of substances and materials.

Includes HEMA purifying, drying PVP, the preparation of fillers and reinforcing materials.

2. Preparation of polymer-monomer composition.

The composition includes a monomer – HEMA, a polymer – PVP, a solvent and a polymerization catalyst is iron sulfate (II). To do this, You should prepare two solutions: No. 1 – PVP in HEMA and No.2 – $FeSO_4$ in the solvent. Before the formation of the solutions No. 1 and No. 2 they should be mixed. Loading of the components must be implemented strictly according to a chosen recipe, as their ratio has a significant action on the viscosity of the composition, structure and properties of the films.

Additionally, you must obtain a homogeneous composition, that it is important to select the mixing mode and the loading order of the composition components. For the production of films from composite hydrogels composition the filler is added to the original composition.

3. Filtration of the composition.

The filtering of composition is a necessary operation that removes undissolved agglomerates of PVP and mineral inclusions.

Ceramic, non-woven polymeric materials and filters are using for the filtration. The use of metal filters is undesirable because polymerization will occur on the metal surface of HEMA-PVP compositions that will result to the clogging of filter cells.

4. The formation of the hydrogel film.

The obtained composition is poured into a cylindrical mold. Due to the high reactivity the initial composition the formation of the film occurs at room temperature in air. The film thickness depends on the amount of loaded composition, overall size – on mold dimensions. For the production of reinforced products, it is necessary to insert a reinforcing material into the polymeric inset of the mold before the assembly of the unit. In the result of forming, obtained tubular film has to be removed from the form and sent to washing.

5. Washing the film

Washing the films is necessary to remove unreacted monomer and non-graft PVP. Duration of washing depends on the formulation of the original composition and film thickness.

6. Additional treatment and drying the film

Before drying, to prevent shrinkage of the film, it can be processed with non volatile liquids such as glycerin, diethyleneglycol or aqueous solutions. Later the film needs to be dried. The water evaporates and the glycerin or diethyleneglycol remains in the pores of the film. Drying of the films is carried out with hot air. To prevent deformation of the film during drying, it is fixed in the mesh polymer frame. The drying time depends on temperature, composition of the copolymer and the film thickness.

7. Defectoscopy and packaging

The final stage of obtaining hydrogel films is their defectoscopy – checking for defects, trimming the edges, dosing and packaging. Cutting into pieces of the desired width is possible. After these operations, the film is packaged in a plastic container.

The technological scheme of production of hydrogel films is shown in Fig.1. Depending on the task, the technology and equipment enable to produce nonfilled films (method 1) filled with powder-fillers of different nature (organic, mineral, metal) (method 2) and reinforced (method 3).

According to the method 1, process is as follows. From the volumetric measuring tank 3 and the weighter 4 into the mixer 7 are feeding, respectively HEMA and PVP, solvent and catalyst accordingly from the volumetric measuring device 1 and the weight of the dispenser 2 and the mixer 6. The obtained solutions are mixed in the mixer 8 and then are feeding on the filter 10. After filtration, the produced composition is loaded into a mold of centrifugal setting 11. The formed film supplies to the washing by solvent from the residue of unreacted monomer, for additional treatment and packaging.

According to the method 2, obtained by the method 1 polymer-monomer composition feeding into to the mixer 9 for mixing with the filler, which is supplied to the mixer 9 from the weighter of the dispenser 5. Next, the obtained mixture is processed into a finished product similar to method 1.

Method 3 allows to obtain the reinforced hydrogel film. For this purpose, fiber-reinforced material passes the stage of preparation on the table 12, by the roller 13 is placed in to polymer insert that is inserted into the cylindrical centrifugal installation 11. After that, loading of the filtered polymer-monomer composition takes place from the mixer 8 (similar to method 1).

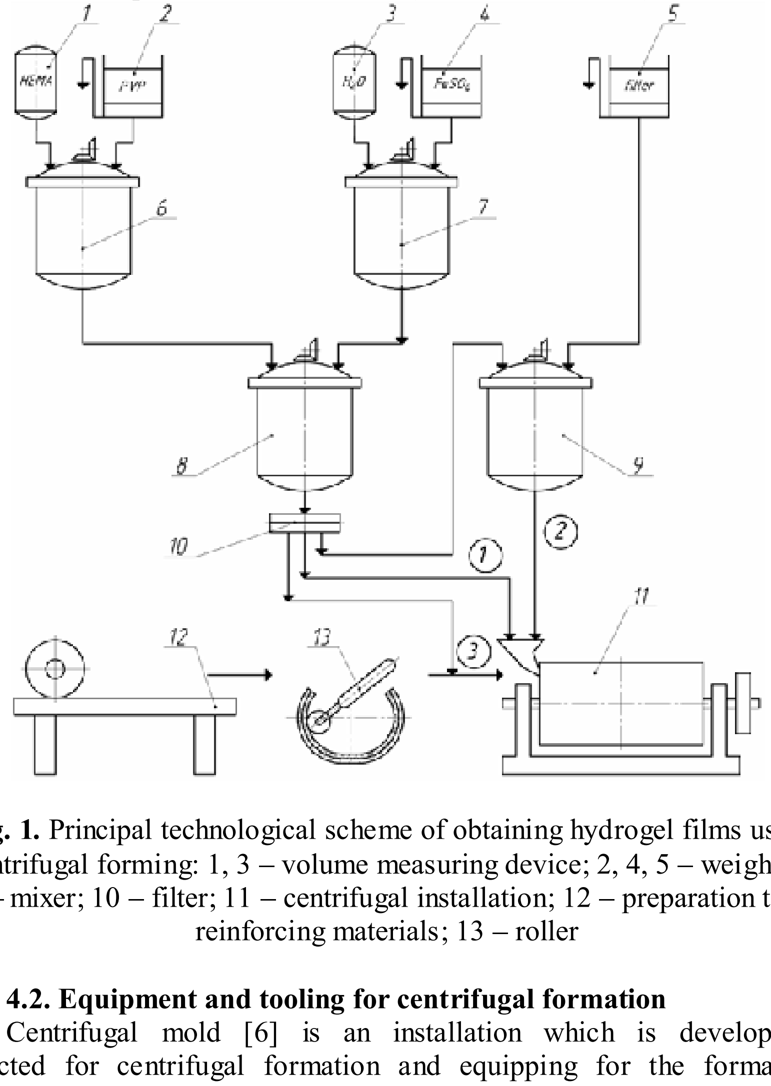


Fig. 1. Principal technological scheme of obtaining hydrogel films using centrifugal forming: 1, 3 – volume measuring device; 2, 4, 5 – weighter; 6 to 9 – mixer; 10 – filter; 11 – centrifugal installation; 12 – preparation table for reinforcing materials; 13 – roller

4.2. Equipment and tooling for centrifugal formation

Centrifugal mold [6] is an installation which is developed and constructed for centrifugal formation and equipping for the formation of composite films. Bilocular mold design (Fig. 2.) was developed with the purpose of improving the performance of the process of formation. If necessary, the quantity of sockets may increase. Such implementation of cylindrical mold enhances its performance because it can simultaneously produce multiple products (possibly from compositions of different composition) in one technological cycle.

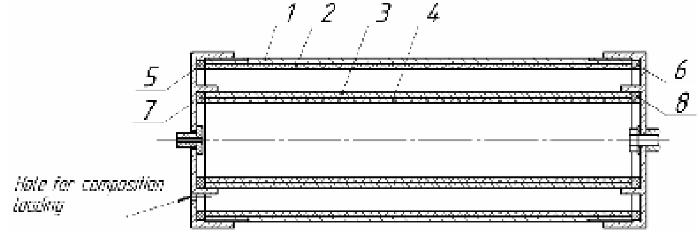


Fig. 2. Design of bilocular centrifugal mold: 1, 3 – cylindrical mold; 2, 4 – polymer inset; 5 to 8 – gaskets

In some cases it is necessary to conduct the polymerization process at elevated temperatures. A heating chamber (Fig. 3.) is provided for heating centrifugal molds. Heating chamber consists of two parts. At the bottom fixed part 2 heaters 4 are located. The inertia in the transfer of heat through a polymeric inset, and a constant mixing of air due to the rotation of the mold of the heating chamber provides it with a great thermostatic conditions. Installation of centrifugal molds occurs when folding top 1 into the heating chamber. After the mold is closed, the upper portion of the camera, the motor is activated and heaters, which operate in automatic mode.

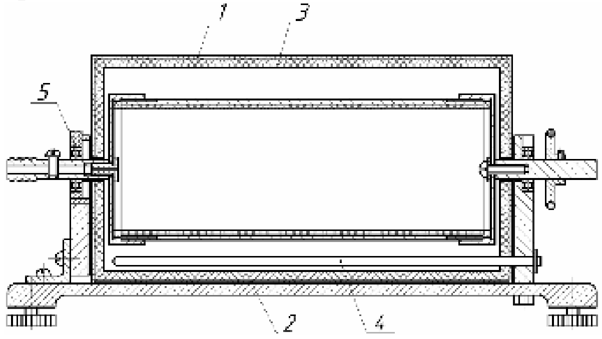


Fig. 3. The centrifugal form with a heating chamber: 1 – upper part of the chamber; 2 – bottom part of the chamber; 3 – thermal insulation material; 4 – heaters; 5 – compensator of thermal expansion of the form

Equipment heating chamber centrifugal installation reduces its performance through the additional axial forces that occur through thermal expansion of the mold length. This will be especially noticeable for larger mold sizes. Due to the mold heating, the thermal elongation of the body, which causes additional axial forces, which through the cover and shafts are transmitted to the supports and the nodes of rotation of the installation, which leads to distortions and overload nodes of rotation and, consequently, to defective of the hydrogel film. To eliminate this drawback in the design of the molds, it is provided by the thermal expansion compensation joint (Fig. 4.). The compensator consists of a metal cylindrical sleeve 1 in which is mounted a teflon insert 2. Joints - clearance fit. Landing clearance shall provide the free forward motion of the insert 2 in the sleeve 1. To prevent rotation of the insert 2 in its construction provides a rectangular ledge, which gap is installed in a rectangular groove of the sleeve 1. The length of the groove of the sleeve 1 is 2/3 of its width.

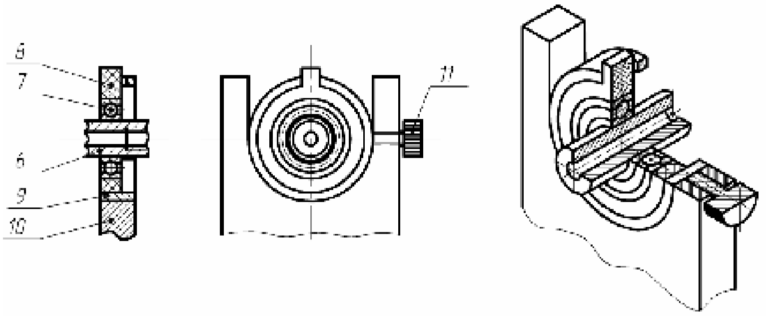


Fig. 4. The structure of the compensator of thermal expansion of the cylindrical form: 1– metal sleeve; 2 – teflon inset; 3 – ball bearing; 4 – cylindrical mold shaft; 5 – support; 6 – mounting screw

In the inset 2 with an interference fit mounted ball bearing 3 which is mounted on the shaft 4. Fixed connection sleeve 1 with a support 5 is provided a mounting screw 6. During heating and longitudinal extension forms the shaft 4 with the bearing 3 and the inset 2 can move in the sleeve 1 of a support 5 without creating axial forces.

After the process of forming the heaters and the motor are turned off. During cooling, the mold is reducing in size by length and displacement of the inset 2 in the sleeve 1 in the opposite direction.

Thus, the shafts with bearings, mounted in the supports with the use of compensators of thermal expansion, do not feel alternating radial loads, which reduces the availability of the set and does not degrade the properties of the hydrogel films.

4.3. The properties of the composite hydrogel films obtained by centrifugal molding

4.3.1. The study of the process of filler segregation

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

The phenomenon of segregation is a major factor during centrifugal molding of HEMA-PVP compositions filled with powders of metals, which will influence the anisotropy of properties of thin film materials. It is obvious that the filling material particles under the action of centrifugal force will migrate in viscous composition to the inner surface of the mold, i.e. in the outer layers of the film. The magnitude of centrifugal force depends mainly on the frequency of rotation of the cylindrical form, mold diameter and density of the composition [6]. The intensity of stratification may be observed in the current structure of the composite film. In Fig. 5. presents the distribution of the metal powder filler, depending on the frequency of rotation of the centrifugal mold.

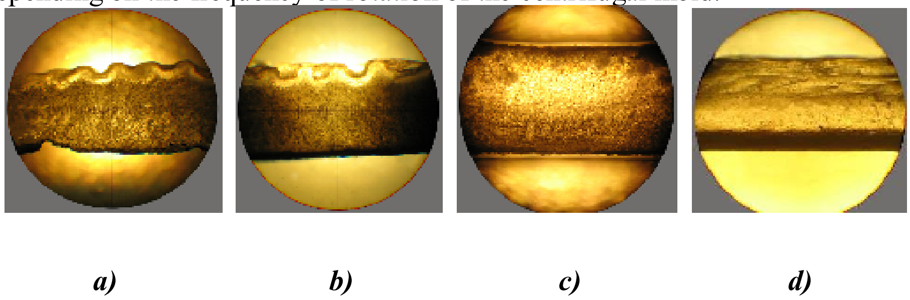
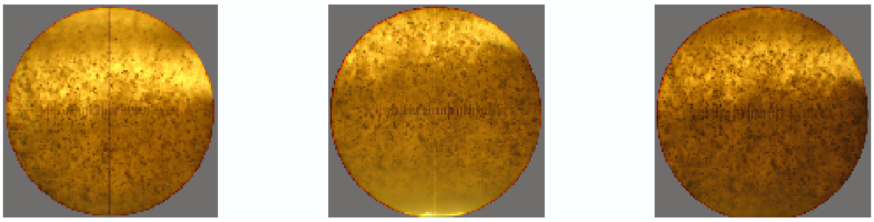


Fig. 5. The influence of frequency of rotation of the cylindrical mold (ω, rev/min) on the filler segregation (HEMA:PVP:H_2O=70:30:50 Xw, [Zn]=40 wt%.): a – 250, b – 700, c – 1350; d – 2000

As you can see, most of the filler is evenly distributed across the film thickness in the case of the lowest rotation speeds (Fig. 5., a). And, quite naturally, that the stratification composition is enhanced with increasing speed, the cylindrical mold.

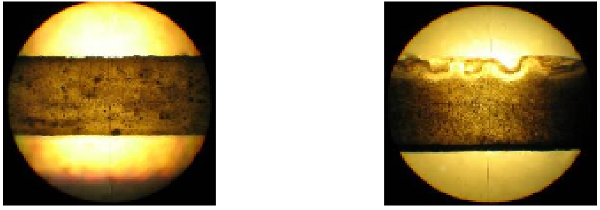
In addition to these kinematic and physical factors on the structure of the metal-filled film will affect the viscosity of the composition and the rate of polymerization, which depends on the composition and content of solvent. The intensity of growth in viscosity affects the rate of polymerization, which increases with the increase in the composition of the PVP content and decreases in case of dilution of the composition with a solvent [10]. Changes in the formulation of the composition are transformed on the structure of the obtained materials. The increase in viscosity due to the introduction of a greater number of PVP affects the nature of segregation of the filler (Fig. 6.), however, this effect is much smaller than the effect of the presence in the composition of the solvent (Fig. 7.).



a) *b)* *c)*

Fig. 6. The effect of the composition (HEMA:PVP, Xw) the nature of the filling of the films by thickness (composition:solvent (water)=2:1, ω=700 rev/min): a – 90:10; b – 80:20; 70:30

The sample obtained without solvent is characterized by the most uniform distribution of the filler through the thickness (Fig. 7., a). With the dilution of the composition with solvent, there occurs a stratification of the composition and the redistribution of a greater amount of filler in the outer layers.



a) **b)**

Fig. 7. The influence of the content of solvent (Xw) the nature of the filling of the films by thickness (HEMA:PVP=70:30 Xw; [Zn]=20wt%.; ω=700 rev/min): a – 0; b – 50

4.3.2. The quality of the composite films surface

The investigation of filler distribution in thickness of the composite films is interesting, given their specific purpose. For example, to improve conductivity or usage as materials for magnetic therapy and metallotherapy, it is desirable to form the film with the most pronounced phenomenon of segregation. At the same time, to use metal-filled films as antirust or sorbents required materials with a uniform distribution of the filler in volume. From a technological point of view more important is the quality of the film surface. To analyze the characteristics of film materials, especially surface quality, we introduce the concept of "external film surface" – a surface that is in contact with the inner surface of a centrifugal mold, and "inner film surface", is directed to a mold cavity. Obtained by centrifugal formation of the hydrogel film samples of materials such as unfilled and filled has attracted the attention by their equal thickness that does not exceed 1% and high surface quality. For comparison, it is represented the surface of the filled powder of zinc hydrogel sample, obtained in the mold between the two plastic plates (Fig. 8., a) and by centrifugal molding (outer surface) (Fig. 8., b).

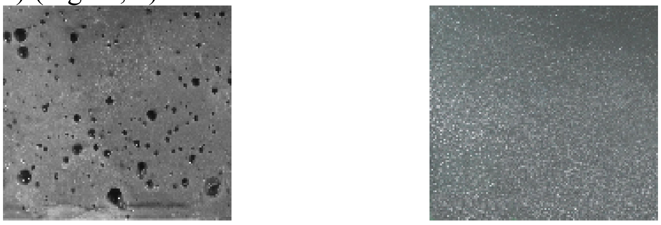

a) *b)*

Fig. 8. Effect of forming method on the surface quality of composite metal-filled hydrogel film materials (HEMA:PVP:H_2O=70:30:50 Xw, [Zn]=20wt%): a – casting into mold, b – centrifugal molding

High reactivity and viscosity of metal-filled HEMA-PVP composition is the cause of poor filling of the molding cavity and the complicated removal of air bubbles from the composition (Fig. 8., a). These problems are eliminated through the composition by the centrifugal method – high revolutions and molds centrifugal force are the main factors that result in formation of quality film surface and remove air bubbles from the volume of the composition (Fig. 8, b).

To compare the action of different factors on the quality of external and internal surfaces of a film formed of the same thickness is 1,2±0,1 mm. Surface quality of the film, especially the internal, which is not in contact with the centrifugal form, much depends on the speed of its rotation (Fig. 9.). The product made with the frequency of rotation of the form, close to critical (the critical frequency for the used mold is 198 rev/min) is characterized by worst quality film with varying thickness, with visible dents and protrusions (Fig. 9., a). For speed 700 rev/min the film surface has a certain waviness in the direction of rotation (Fig. 9., b). The products obtained with a rotational speed of 1350 rev/min and higher characterized by the best quality of the inner surface.

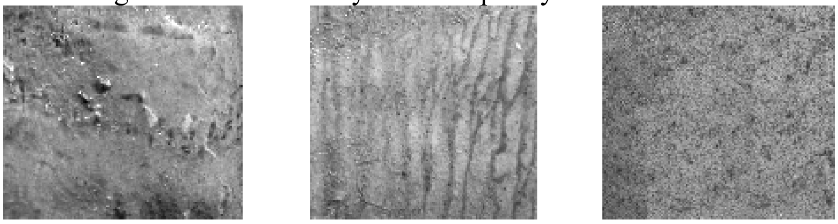

a) *b)* *c)*

Fig. 9. Effect of centrifugal mold rotation frequency (ω, rev/min) on films surface quality, that doesn't contact with forming surface (HEMA:PVP:H_2O=70:30:10 Xw): a – 250; b – 700; c – 1350

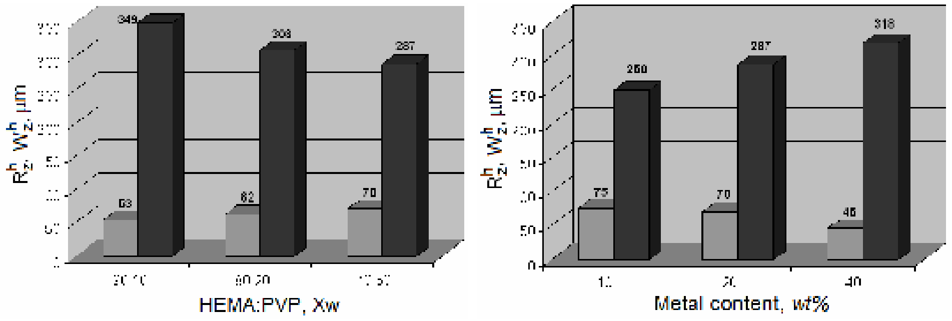
In addition to the speed of rotation of the forms a tangible impact on the formation of the inner surface has had a presence in the original composition of the solvent (Fig. 10.).

a) b)

Fig. 10. The dependence of the quality of the inner surface metal-filled hydrogel films from the content of the solvent (HEMA:PVP=70:30 Xw, [Zn]=20wt%.; ω=700rev/min): a) H_2O content – 50Xw, b) H_2O content – 25Xw

For the purpose of comparative quality characteristics of obtained films was investigated roughness (R_z^h, μm) and waviness (W_z^h, μm) of the outer and inner surfaces, respectively. Analysis of the results obtained showed the diverse influence of kinetic and physical factors on the formation of the outer and inner surface of metal-filled film materials. It is determined that the quality of the finished product will primarily depend on the composition of the molding composition – the ratio of HEMA:PVP, the content of the solvent, the content and nature of metal powder filler. The composition of the polymer-monomer mixture provides the appropriate viscosity of the system and the duration of such technological parameters as pot life and the time of formation. It is proved that with increasing the content of PVP in the composition of the internal surface increases, is some worse (Fig. 11.). One reason for this influence may be different intensity of migration of the filler in the outer layers due to the difference in the viscosity of the system which increases with PVP content. Composition HEMA:PVP=90:10Xw has the highest fluidity, and therefore the particles of filler are more focused in the outer layers. The metal surface of the filler is simultaneously the catalyst for the formation of polymers therefore, the speed of approval of composition in the external and internal layers through a different number of active centers, will be different.

Different content of the filler will affect the structure of the copolymer [11]. Due to the formation of more cross-linked structure of the polymer network and the growth of internal stresses in the volume of films that contribute to the uneven orientation of binder and growth of roughness on the inner surface of the films. With the increasing of PVP content in the composition increases its viscosity increasing intermolecular interactions, decreasing the delamination of the filler, especially the fine fraction and even the rate of polymerization of the height of the sample and, consequently, reducing the roughness of the inner surface. The proof of this assumption can be the difference in the quality of the inner surface for films of various thicknesses (Fig. 12).



a) *b)*

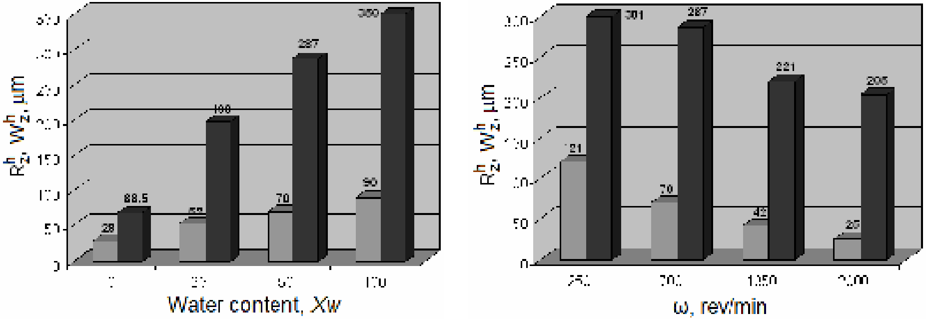
Fig. 11. The influence of formulation of polymer-monomer composition (a) and the content in the composition of the metal filler (b) on the quality surfaces of composite films (▨ – R_z^h outer surface; ■ – W_z^h inner surface): a – H_2O content – 50Xw, [Zn]=20wt%.; ω=700rev/min; b – HEMA:PVP:H_2O=70:30:50Xw, ω=700rev/min

a) *b)*

Fig. 12. The effect of film thickness on the quality of the inner surface (HEMA:PVP: H_2O=70:30:100Xw, [Zn]=20 wt%.; ω=700rev/min): a –1 mm, b – 4mm

At the same time, it was found that with increasing content of PVP in the composition it is observed the certain deterioration in the quality of the outer surface. The increase of roughness in this case occurs through the increase of the energy of cohesion and the deterioration of wettability of the surface composition of cylindrical mold. The opposite dependence is observed in the case of different content in the composition of the filler metal. The quality of the surface that is in contact with the forming surface of cylindrical mold, while increasing filler content increases slightly and is noticeable after the content of the metal powder more than 20 wt% of the masses (Fig. 11.). Growth of roughness of the inner surface is due to segregation of the filler, a decrease in active centers in the inner layers of the hydrogel film and an increase in the external. With the increase of the metal concentration, increases the rate of polymerization in the outer layers, resulting in increased viscosity of the composition, its heterogeneity and, as a consequence, the internal orientational stress.

The dilution of the composition with the solvent (water), in addition to increasing its fluidity, reduce the concentration of the monomer, thereby increasing the curing time of the inner layers and contributing to the formation of a rare structure of HEMA-PVP copolymers [10]. In addition, increased migration of filler in the outer layers of the compositions, diluted with large quantities of solvent, is the cause of obtaining a film materials with worse quality (Fig. 12., b, Fig. 13., a). During processing by the method of centrifugal molding materials of different nature on the quality of finished products the most influenced by the frequency of rotation of the form. Metal-filled hydrogel materials based on HEMA-PVP copolymers are not exception. Purity of the surface of the film in contact with the inner surface forming a cylindrical mold, depends on the power of contact of the film with the mold surface (Fig. 13., b). This interaction is proportional to the frequency of rotation of the mold and, consequently, pressure on the composition that arises. Actually, the amount of migration of the filler will depend mainly on the intensity of the centrifugal force. However, there has been some improvement and the inner surface of the film materials. It is obvious that the dominant influence on its formation in this case is the kinetic factor centrifugal force, which, with increasing revolutions frequency too increases and pressure on the composition, which is a consequence of the centrifugal force.



a) *b)*

Fig. 13. The dependence of the surface quality of the composite film from the content of the solvent (a) and frequency of the rotation of the form (b) (▩ – R_z^h outer surface; ■ – W_z^h inner surface): a – HEMA:PVP=70:30Xw, [Zn]=20wt%.; ω=700rev/min; b – HEMA:PVP:H_2O=70:30:50Xw, [Zn]=20 wt%

Among the metals that have been used in the work, the surface of the zinc is most active during the copolymerization of HEMA with PVP [5] so zinc-filled composition characterized by the lowest pot life and time of formation. It is also established that the catalytic activity of metals in relation to the polymerization of HEMA-PVP compositions increases in the set of Ag – Cu –Ni – Co – Fe – Zn. To obtain hydrogel films filled with other metals and to reduce in this case, the time of viability and formation have been obtained compositions based on mixtures of metal powders with zinc (Fig. 14.). As show results of researches, the best quality, both external and internal surfaces are characterized by the film material filled with copper powder (10 wt%.) and zinc powder (10 wt%.). For this material the value of the parameter waviness W_z^h is close to the value of surface roughness R_z^h.

Analyzing the received results it is established that the distribution of the metal filler on the film thickness in addition to the kinetic parameters sufficiently depends on the reactivity of the molding compositions and the rate of change of its viscosity characteristics. Considering these factors, the best results in surface quality metal-filled films at elevated speeds of rotation of the mold was achieved by two methods. The first is the introduction of a technological mode stage forpolimerization, which consists in maintaining the molding compositions beyond mold during the period of forpolimerization (τ_{fp}), which was established with the calculation time that is less than the duration of gelation.

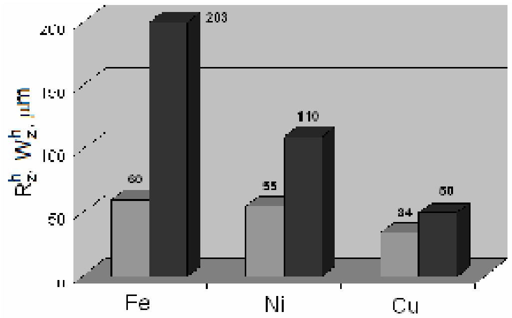


Fig. 14. The dependence of the quality of the surface composite films by nature of the combined filler. HEMA:PVP:H_2O=70:30:50Xw, ω=700rev/min, filler – 10 wt% Me+10 wt% Zn (▨ – R_z^h outer surface; ■ – W_z^h inner surface)

Experienced method, the dependence between the period of forpolimerization and pot life of the composition [6]:

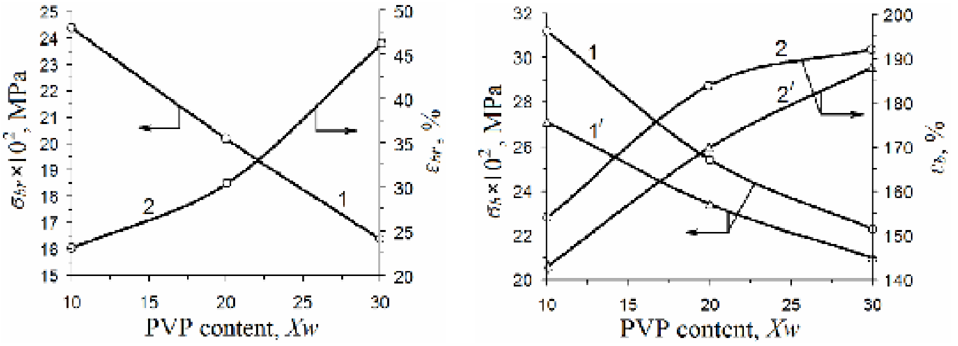
$$\tau_{fp} \le \tau_p - 0{,}2 \div 0{,}3 \text{min}$$

The second method includes the forming of composite film in two stages with different speeds of form rotation. At the first stage the form with composition is rotated with a frequency that is less than critical during a time period which equals τ_p. An additional mixing of composition is provided due to the low speed of form rotation. Speed of form rotation is increased after reaching τ_p.

4.3.3. Physical-mechanical characteristics of metal-filled hydrogels

The strength properties of the investigated films was characterized by tensile strength during the break (σ_{br}, MPa), elastic – elongation during break (ε_{br}, %). First by interesting is research of the effect on the properties of composite films such factors as the composition of the polymer-monomer composition, filler content and solvent rotational speed of the form. The data obtained showed that with increasing the content of PVP in the composition is from 10 to 30 Xw strength decreases significantly during break (Fig. 15., a). This is due to a decrease in the number of chains of macromolecules in the unit volume of the swollen polymer, which resist destruction because with the increase of PVP in the original composition decreases the effectiveness of its grafting [10]. A significant increase (twice) the relative elongation during break with increasing PVP content up to 30Xw due to the simultaneous action of two factors:

1) the influence of PVP on the composition and structure of the copolymer due to the injection due to the grafting with polyHEMA, macromolecules, PVP in the polymer forms a network with an increased size of the fragments of the chains between nodes of cross-linking [10]. Also, the part washed during the hydration of PVP, which did not participate in the reaction of grafting, improves the porosity of the polymer network.



a) b)

Fig. 15. The effect of PVP content in the composition on the physical-mechanical properties of metal-filled hydrogel films in break (a) and bursting (b) (composition : solvent (water) = 2:1, [Zn] = 20wt.%, [$FeSO_4$] = 0,01wt.%, ω = 700rev/min). **a:** 1 – tensile strength during the break (σ_{br}, MPa); 2 – elongation during break (ε_{br}, %). **b:** 1, $1'$ – bursting strength (σ_b, MPa); 2, $2'$ – percentage elongation at bursting (ε_b, %). (1, 2 – the inner surface, $1'$, $2'$ – is the outer surface)

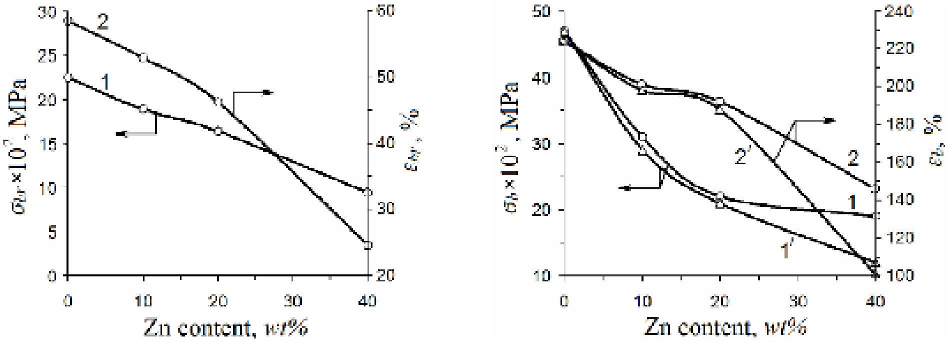
In the case of tensile forces long stretches of the chains between nodes of cross-linking capable to be straightened to a greater extent than short, and contributes to ε_{br} increasing.

2) Effect of PVP content on the initial viscosity of the composition which depends on the intensity of segregation of the filler and the heterogeneity of the

film thickness. With the increase of the homogeneity of the film material, increasing its strength and elasticity.

However, research on stretching do not allow to account in full the impact strength of the films, the phenomenon of segregation of the filler and to detect the anisotropy of physical and mechanical properties. With this aim, additionally, investigated the stability of the films for a bursting, which is characterized by bursting strength (σ_b, MPa) and percentage elongation at bursting (ε_b, %). Research on bursting provide an opportunity to establish the strength and elastic characteristics of the hydrogel films depending on the surface of the force application. With this aim, we measured by applying a force to the outer surface and the inner and determined the bursting strength and percentage elongation at bursting, respectively, external (σ^{e}_{b}, ε^{e}_{b}) and internal (σ^{i}_{b}, ε^{i}_{b}) surfaces. As evidenced by the data in Fig. 15., b the character of dependences of parameters σ_b, ε_b for a bursting from the content in the molding compositions of PVP is the same change σ^{e}_{br}, ε^{e}_{br}. However, as stipulated by the amount σ_b and ε_b affects the type of surface to which force is applied. It is determined that the parameters σ^{i}_{br}, ε^{i}_{br} in their values are dominated by values σ^{e}_{br}, ε^{e}_{br} (Fig. 15., b). This difference depends on the homogeneity of the material and the intensity of stratification of the filler on the film thickness (Fig. 6).

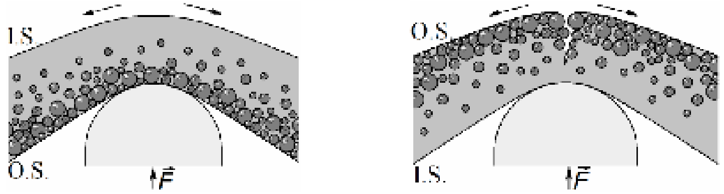
The introduction into polymer powders of metals increases the surface hardness of filled with HEMA-PVP copolymers in the solid state [10]. However, in the case of swollen samples, the increase in the metal content of the initial composition leads to a decrease in strength and elongation of the material in relation to non-filled, during the bursting and during the break (Fig. 16).



a) *b)*

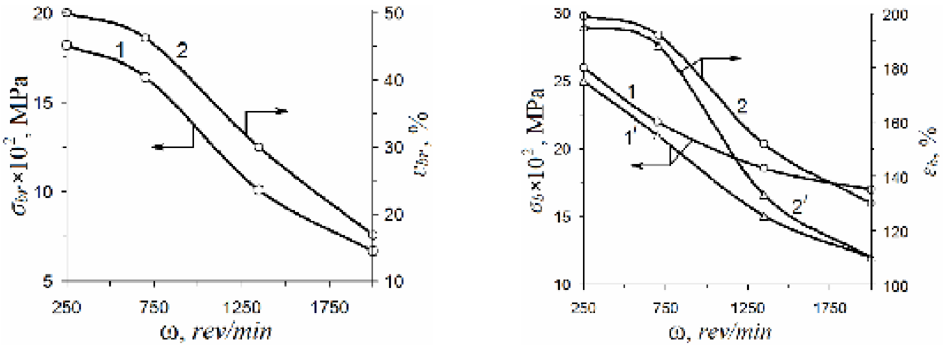
Fig. 16. The dependence of physical-mechanical properties metal-filled hydrogel films in break (a) and bursting (b) content of metal (HEMA:PVP:H_2O=70:30:50 Xw, [$FeSO_4$] = 0,01 wt.%, n =700rev/min). **a:** 1 – tensile strength during the break (σ_{br}, MPa); 2 – elongation during break (ε_{br}, %). **b:** 1, 1′ – bursting strength (σ_b, MPa); 2, 2′ – percentage elongation at bursting (ε_b, %). (1, 2 – the inner surface, 1′, 2′ – is the outer surface)

The data obtained is an additional confirmation of physical interaction between metal surface and polymer. Therefore, particles of metals, and especially their agglomerates, which are formed in the outer layer of the film, playing the role of stress concentrators and are the centers of development of cracks during the application of load, the consequence of which is the destruction of the sample (Fig. 17.). With increasing of rotation frequency of centrifugal mold increases the intensity of migration of the filler to the outer surface of the film (Fig. 5.). With the increase in filler content in the outer layers increases the number of stress concentrators, increasing the size of agglomerates and decreases between the thickness of the contact, resulting in reduced strength and elastic properties of the composite films (Fig. 18., a, b) and enhanced anisotropy of their properties (Fig. 18., b).



a) *b)*

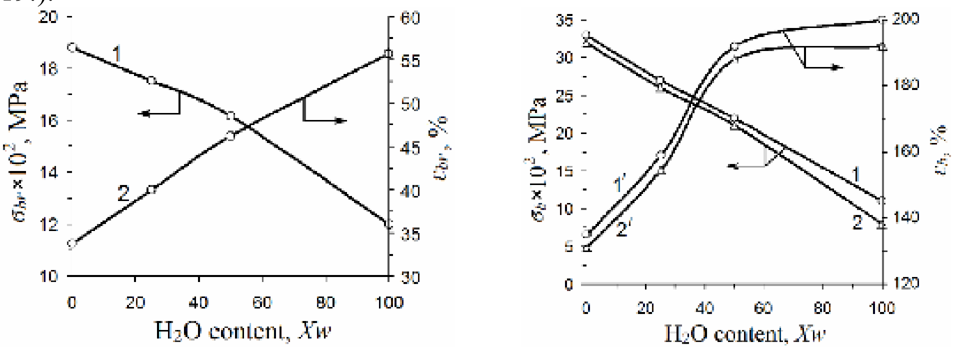
Fig. 17. The behavior of the composite film during the bursting the inner (a) and outer (b) surfaces of (IS – internal surface, OS – outer surface)



a) *b)*

Fig. 18. The dependence of physical-mechanical properties metal-filled hydrogel films in break (a) and bursting (b) of the rotational frequency of the form (n, rpm) (HEMA:PVP:H_2O=70:30:50 Xw, [Zn]=20wt.%, [$FeSO_4$] = 0,01 wt.%). **a:** 1 – tensile strength during the break (σ_{br}, MPa); 2 – elongation during break (ε_{br}, %). **b:** 1, $1^{/}$ – bursting strength (σ_b, MPa); 2, $2^{/}$ – percentage elongation at bursting (ε_b, %). (1, 2 – the inner surface, $1^{/}$, $2^{/}$ – is the outer surface)

The mechanism of reduction of strength characteristics of composite film materials due to segregation of the filler due to loss of film strength (decreasing as σ_{br} and σ^{e}_{br} with σ^{i}_{br}) due to dilution of the composition with a solvent (Fig. 19.).



a) *b)*

Fig. 19. The dependence of physical-mechanical properties metal-filled hydrogel films in break (a) and bursting (b) the content of the solvent (HEMA:PVP=70:30 Xw, [Zn]=20wt.%, [$FeSO_4$] = 0,01wt.%, n =700rev/min). **a:** 1 – tensile strength during the break (σ_{br}, MPa); 2 – elongation during break (ε_{br}, %). **b:** 1, $1'$ – bursting strength (σ_b, MPa); 2, $2'$ – percentage elongation at bursting (ε_b, %). (1, 2 – the inner surface; $1'$, $2'$ – is the outer surface)

At the same time there is an increase in elasticity of films. ε_{br} growth is due to increase elasticity of hydrogel matrix due to a significant decrease of efficiency of grafting PVP [10] and the reduction of crosslinking density of polymer network [11]. Confirmation of the contribution of the characteristics of the matrix on the properties of films the results of the study σ^{e}_{b}, ε^{e}_{b} and σ^{i}_{b} ε^{i}_{b}. As evidenced by the data in Fig. 19., if the internal layer of the film prevails over strength and elasticity properties external. This factor is a consequence of the influence on the total elasticity of the film, which is characterized by the parameter of elongation for rupture.

5. CONCLUSIONS

The developed technological scheme for obtaining hydrogel films based on copolymers of polyvinylpyrrolidone with 2-hydroxiethyl methacrylate by centrifugal formation, in which it is possible to obtain non-filled films, reinforced and filled with finely dispersed powders of metals. With the aim of increasing the productivity and efficiency of the method suggested the use of multiple cavity centrifugal molds. Centrifugal equipment installation chamber heating gives you the opportunity to carry out the polymerization at different temperatures.

It was determined that obtained metal-filled films are characterized by the anisotropy of the surface quality and physical-mechanical properties. The difference in the properties of surfaces is a consequence of the segregation of the filler, which mainly depends on the viscosity of the composition and speed of the form. On the viscosity of the polymer-monomer composition affects the content of PVP, solvent, presence in the technological process stage of forpolimerization.

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